東京帝國大學紀要

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JOURNAL OF THE COLLEGE OF SCIENCE, IMPERIAL UNIVERSITY,
TŌKYŌ, JAPAN.
VOL. XXV., ARTICLE 1.

On the Inversion of Cane Sugar.

By

Yukichi Osaka, *Rigakuhakushi.*

Hill (Journ. Chem. Soc. 73, 634; 1898.) has shown that the hydrolysis of maltose by the catalytic action of an enzyme is incomplete and that the less the degree of hydrolysis, the more concentrated is the solution. As to the inversion of cane sugar by the catalytic action of an acid, it has been studied extensively from several points of view and it is well known that the hydrolysis is complete. It is not, however, improbable, that the hydrolysis of cane sugar may also be in some measure incomplete when the solution is highly concentrated. In this respect I have undertaken the investigation of the inversion of cane sugar and obtained the results expected, as shown in the following communication.

Pure commercial cane sugar was purified by precipitation from the cold saturated aqueous solution with absolute alcohol and washing it with ether. The experiments and the calculation of the results were carried out as follows:

I. *80 grams of cane sugar in 100 c.c. of the solution.*

20 grams of cane sugar were introduced into a weighed measuring flask of 25 c.c. capacity and dissolved in a small

quantity of water by warming. When it was cold, 5 c.c. of 2.5 normal hydrochloric acid were added and the solution was diluted nearly to the mark. A small piece of camphor was then added to the solution and the flask left in a thermostat at 25° over night. On the next day water at 25° was added to the mark and weighed. The two solutions thus prepared weighed :

(*a*) 32.787, (*b*) 32.799 ; mean : 32.793.

About 5 c.c. of the solution were taken out from each of the solution into two weighed measuring flasks of 25 c.c. capacity and weighed. About 4 c.c. of 2.5 norm. hydrochloric acid were added to each of them and the solutions were diluted to about 20 c.c. The four diluted solutions thus prepared, together with the two original solutions, were again left in the thermostat over night.

On the next day about 5 c.c. of the two original solutions were taken out, each into two weighed measuring flasks of 25 c.c. capacity, and weighed. In order to prevent its further inversion on dilution, 3.4 grams of sodium acetate were added to the solutions taken out, which were then diluted to the mark. The same amount of the salt was also introduced into each of the solutions diluted the day previous to make them as nearly as possible similar to those newly prepared and then the solutions were further diluted to the mark. It was ascertained by experiments that a small difference in the concentrations of hydrochloric acid exerts no remarkable influence on the optical rotation of sugar solutions.

The eight dilute solutions thus prepared were then subjected to polarimetric observations, a polarisation apparatus after LANDOLT being used with a LIPPICH's polariser.

		Solution taken out in grams.	Rotation of the solution diluted to 25 c.c.
		Inverted in the original solution.	
(*a*)	(1)	6.3341	−6.282°
	(2)	6.3398	−6.270°
(*b*)	(3)	6.3391	−6.272°
	(4)	6.3565	−6.290°
		Inverted in the dilute solution.	
(*a*)	(5)	6.4350	−6.646°
	(6)	6.3612	−6.608°
(*b*)	(7)	6.4488	−6.660°
	(8)	6.4067	−6.608°

In order to obtain the mean value of the rotations of the solutions of the same treatment and to be able to compare those of the solutions of different treatments with each other, it was assumed that within narrow limits of concentrations, as in the case in hand, the rotations are proportional to the concentrations of the solutions. The average amount of the solutions taken out in eight instances was 6.3776 grams and the rotation of it diluted to 25 c.c. was calculated from the above data as follows:

(*a*)	(1)	−6.325°	(*a*)	(5)	−6.587°
	(2)	−6.307°		(6)	−6.625°
(*b*)	(3)	−6.310°	(*b*)	(7)	−6.586°
	(4)	−6.311°		(8)	−6.578°
Mean :		−6.313°	Mean :		−6.594°

25 c.c. of the original solution weighed 32.793 grams and contained 20 grams of sugar, so that 6.3776 grams of the solution contained 3.8896 grams. The same amount of sugar was dissolved in water with the addition of sodium acetate and hydrochloric

acid so as to make the solution similar to those in the other cases, diluted to 25 c.c. and polarised :

(9) 20.094°, (10) 20.104° ; mean : 20.099.°

Thus we find the degree of the inversion in the original solution in percentage as follows :

$$\frac{20.099+6.313}{20.099+6.594}\times 100=98.9.$$

With solution of other concentrations, the experiments and calculation were carried out quite similarly, so that merely the results will be reported.

II. *70 grams of cane sugar in 100 c.c. of the solution.*

25 c.c. of the solution weighed :

(*a*) 31.872, (*b*) 31.872 ; mean : 31.872.

		Solution taken out in grams.	Rotation of the solution diluted to 25 c.c.	Rotation calculated for the mean dilute solution.
			Inverted in the original solution.	
(*a*)	(1)	6.1883	−5.659°	−5.663°
	(2)	6.2090	−5.662°	−5.647°
(*b*)	(3)	6.1627	−5.628°	−5.656°
	(4)	6.1826	−5.638°	−5.647°
			Mean :	−5.653°
			Inverted in the dilute solution.	
(*a*)	(5)	6.2103	−5.798°	−5.782°
	(6)	6.2014	−5.778°	−5.771°
(*b*)	(7)	6.1988	−5.770°	−5.764°
	(8)	6.1884	−5.756°	−5.760°
			Mean :	−5.769°

The optical rotation of the sugar solution, not inverted, corresponding to the mean dilute solution was:

(9) 17.592°, (10) 17.572°; mean: 17.582°

Thus the degree of the inversion in the original solution in percentage is as follows:

$$\frac{17.582+5.653}{17.582+5.769}\times 100=99.5.$$

III. *60 grams of cane sugar in 100 c.c. of the solution.*

25 c.c. of the solution weighed:

(*a*) 30.967, (*b*) 30.963; mean: 30.965.

		Solution taken out in grams.	Rotation of the solution diluted to 25 c.c.	Rotation calculated for the mean dilute solution.
			Inverted in the original solution.	
(*a*)	(1)	6.0483	−4.916°	−4.917°
	(2)	6.0710	−4.950°	−4.933°
(*b*)	(3)	6.0287	−4.896°	−4.913°
	(4)	6.0503	−4.944°	−4.943°
			Mean:	−4.926°
			Inverted in the dilute solution.	
(*a*)	(5)	6.0255	−4.976°	−4.996°
	(6)	6.0683	−5.014°	−4.999°
(*b*)	(7)	6.0342	−5.006°	−5.019°
	(8)	6.0721	−4.994°	−4.976°
			Mean:	−4.998°

The optical rotation of the sugar solution, not inverted, corresponding to the mean dilute solution was :

(9) 15.126°, (10) 15.138° ; mean : 15.132.°

Thus the degree of the inversion in the original solution in percentage is as follows :

$$\frac{15.132+4.926}{15.132+4.998}\times 100=99.6.$$

IV. ***50 grams of cane sugar in 100 c.c. of the solution.***

25 c.c. of the solution weighed :

(*a*) 30.016, (*b*) 30.020 ; mean : 30.018.

		Solution taken out in grams.	Rotation of the solution diluted to 25 c.c.	Rotation calculated for the mean dilute solution.
			Inverted in the original solution.	
(*a*)	(1)	5.8721	−4.140°	−4.142°
	(2)	5.8818	−4.140°	−4.136°
(*b*)	(3)	5.8721	−4.132°	−4.135°
	(4)	5.8674	−4.141°	−4.147°
			Mean :	−4.140°
			Inverted in the dilute solution.	
(*a*)	(5)	5.8767	−4.180°	−4.179°
	(6)	5.8770	−4.183°	−4.182°
(*b*)	(7)	5.8803	−4.170°	−4.167°
	(8)	5.8764	−4.178°	−4.177°
			Mean :	−4.176°

The optical rotation of the sugar solution, not inverted, corresponding to the mean dilute solution was:

(9) 12.682°, (10) 12.669°; mean: 12.675°

Thus the degree of the inversion in the original solution in percentage is as follows:

$$\frac{12.675+4.140}{12.675+4.176}\times 100=99.8.$$

V. The *reverse reaction* was next studied. The experiments were carried out as follows:

About 20 grams of cane sugar were dissolved in a flask of 50 c.c. capacity and hydrochloric acid was added to a concentration of 0.5 normal, when the solution was diluted to 50 c.c.

When the inversion was complete, about 5 c.c. of the solution were taken out into a weighed flask of 25 c.c. capacity and weighed. After the addition of sodium acetate, it was diluted to 25 c.c. and polarised.

Solution taken out in grams.	Rotation of the solution diluted to 25 c.c.
5.7507	−3.83°
5.7478	−3.82°

About 5 c.c. of the same original solution were taken out into a weighed flask of 25 c.c. capacity and weighed. Air was passed over its surface by means of a powerful water pump and when the volume of the solution was reduced to about one-half, the flask was weighed again. Sodium acetate was then added, diluted to the mark and polarised.

Solution taken out in grams.	Solution after evaporation.	Loss by evaporation.	Rotation of the solution diluted to 25 c.c.
5.7505	3.0629	2.6876	−3.30°
5.7582	3.3187	2.4395	−3.36°
5.7576	3.4573	2.3003	−3.43°
5.7582	3.5686	2.1896	−3.53°

From these results it is very probable that in a concentrated solution a reversion of cane sugar from its hydrolytic products takes place. The reversion product may not be maltose or isomaltose; as I have found it, the reversion of maltose (or isomaltose) from d-glucose in a concentrated solution by the catalytic action of an acid did not take place in any remarkable degree at a temperature of 25° during a period of two months.

Thus the inversion of cane sugar by an acid seems to be a reversible reaction. In dilute solution the inversion may be regarded as practically complete and its incompleteness becomes remarkable first when the concentrations are very high; and the more incomplete, the more concentrated the solutions are, as expected from the theory.

Chemical Institute, Kyōto Imperial University.
June, 1907.

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JOURNAL OF THE COLLEGE OF SCIENCE, IMPERIAL UNIVERSITY,
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VOL. XXV., ARTICLE 2.

The Complex Ferri-malonates.

By

M. Matsui, *Rigakushi.*

In the course of an experiment it was observed that an acetate, when mixed with a malonate, does not react with ferric chloride so as to form the red ferric acetate. The solution turns green on the addition of ferric chloride, and the green solution thus formed seems to contain no ferric ion, as potassium thiocyanate does not give the red colouration characteristic of ferric thiocyanate. An oxalate produces a similar result. In this latter case it has been proved that the green colouration produced by ferric chloride is due to the formation of the salts of the general composition $Fe(OOC.COOM)_3$, which were first prepared by RAMMELSBERG[1] and subsequently investigated by many others.[2] From the analogy of the two acids—malonic and oxalic—it may naturally be concluded that the ferric ion will combine with the malonic acid ion to form some complex ion, as in the case of chromium and cobalt, whose complex malonates have already been much studied.[3] The author has isolated a few of the complex ferri-malonates and

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[1] Pogg. Ann. **46**, 283 (1838); **68**, 276 (1846).
[2] BUSSY: Jour. pr. Chem. **16**, 395 (1839).
KISTIAKOWSKI: Zeit. physik. Chem. **6**, 100 (1890).
ROSENHEIM: Zeit. anorg. Chem. **11**, 214 (1896).
[3] E. A. WERNER: Jour. Chem. Soc., Trans. **85**, 1444 (1904).
L. HOWE: Jour. Am. Chem. Soc. **25**, 445 (1903).
R. C. LORD: Jour. Phys. Chem. **11**, 173 (1907).

found them all to have a composition corresponding to the formula $Fe\,(OOC\,.\,CH_2\,.\,COO\,M)_3$.

Sodium ferri-malonate.

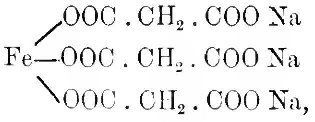
To a solution of sodium malonate, ferric chloride was added drop by drop as long as a portion of the mixed solution did not give a red colour to potassium thiocyanate. The solution was then concentrated on a water-bath and cooled, when greenish sandy crystals separated out. The crystals were quickly washed with water and dried between folds of filter-paper.

To ascertain whether it contained any water of crystallization a portion of the salt was heated in an air-bath at 140° for 4 hours; no loss of weight having been observed, the temperature of the bath was raised first to 160° and then to 200°, at which temperature the substance began to decompose, but the weight was found still constant. The iron was weighed as ferric oxide, and the sodium as sodium carbonate. The results were as follows:

I.	0·5476	gram	substance	gave	0·10037	gram ferric oxide.
II.	0·4020	,,	,,	,,	0·07527	,, ,, ,,
III.	0·4310	,,	,,	,,	0·1605	,, sodium carbonate.

	Calculated for $Fe\,(OOC\,.\,CH_2\,.\,COO\,Na)_3$.	Found. I.	II.	III.
Iron	12·97	12·82	13·10	—
Sodium	16·04	—	—	16·19.

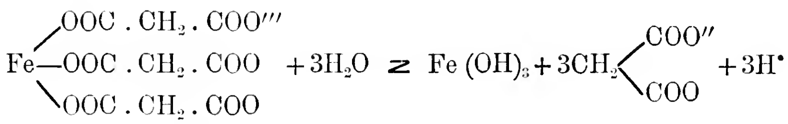
The salt may be formulated as



$$Fe\begin{cases} OOC\,.\,CH_2\,.\,COO\,Na \\ OOC\,.\,CH_2\,.\,COO\,Na \\ OOC\,.\,CH_2\,.\,COO\,Na, \end{cases}$$

which in the aqueous solution dissociates into sodium ion and ferri-malonic acid ion.

The salt is soluble in water, insoluble in alcohol. Its aqueous solution is unstable, the green colour soon changing into brown even at an ordinary temperature. The change is, however, by no means complete, as the brown solution, when evaporated spontaneously, leaves the green crystals mixed with a brown amorphous substance. Judging from the fact that the solution becomes very stable on addition of sodium malonate, the instability of the salt in an aqueous solution may be ascribed to the hydrolysis which all ferric salts are liable to undergo. Thus—



$$\mathrm{Fe}\begin{cases}\mathrm{OOC\,.\,CH_2\,.\,COO'''}\\ \mathrm{OOC\,.\,CH_2\,.\,COO}\\ \mathrm{OOC\,.\,CH_2\,.\,COO}\end{cases} + 3H_2O \rightleftharpoons \mathrm{Fe\,(OH)_3} + 3\mathrm{CH_2}\begin{cases}\mathrm{COO''}\\ \mathrm{COO}\end{cases} + 3\mathrm{H^{\bullet}}$$

It is unstable towards acids and alkalies. The former convert the iron into the simple ionic state, and the latter, when slightly in excess, precipitate it as ferric hydroxide.

Potassium ferri-malonate.

This was prepared from potassium malonate and ferric chloride in a manner quite analogous to that in the case of the sodium salt. The analytical results were as follows:

I. 0·2267 gram substance gave 0·0287 gram water (by loss).
II. 0·3004 ,, ,, ,, 0·04257 ,, ferric oxide.
III. 0·4065 ,, ,, ,, 0·05917 ,, ,, ,,
IV. 0·3418 ,, ,, ,, 0·1440 ,, potassium chloride.
V. 0·3660 ,, ,, ,, 0·1529 ,, ,, ,,

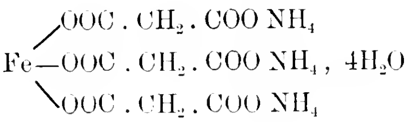
	Calculated for $\mathrm{Fe\,(OOC\,.\,CH_2\,.\,COO\,K)_3,\,4H_2O}$.	Found I.	II.	III.	IV.	V.
Water	13·07	12·66	—	—	—	—
Iron	10·14	—	9·95	10·07	—	—
Potassium	21·30	—	—	—	22·24	21·92

The water was nearly all expelled by heating the salt at 160° for 5 hours, beyond which no appreciable loss of weight was perceived, though the temperature was raised to 200°, at which temperature the salt was again heated for 4 hours. The potassium was first converted into the carbonate and weighed as the chloride. The above data show that its composition is exactly like that of the sodium salt, except that it contains four molecules of the water of crystallization.

The potassium salt forms green prismatic crystals, and its properties, both chemical and physical, are similar to those of the sodium salt.

Ammonium ferri-malonate.

Ammonium ferri-malonate, prepared from ammonium malonate and ferric chloride, closely resembles the potassium salt in colour and crystalline form. Its composition may be formulated as



$$Fe\begin{cases} OOC . CH_2 . COO\,NH_4 \\ OOC . CH_2 . COO\,NH_4 ,\ 4H_2O \\ OOC . CH_2 . COO\,NH_4 \end{cases}$$

from the following analytical data :

I. 0·1630 gram substance gave 0·0234 gram water on 8 hours' heating at 160°.

II. 0·1228 gram substance gave 0·0193 gram ferric oxide.

	Calculated for $Fe(OOC . CH_2 . COO\,NH_4)_3,\ 4H_2O$.	Found I.	Found II.
Water	14·76	14·36	—
Iron	11·27	—	10·94

Barium and calcium salts have been obtained but not analysed.

The complex acid corresponding to these salts has not yet been isolated, but its existence in the aqueous solution is certain, as a green solution is produced by dissolving moist ferric hydroxide to saturation in a warm solution of malonic acid, and this green solution gives the above mentioned salts on neutralization.

It should here be mentioned that ferrous iron also forms the complex malonates, which are precipitated as yellowish crystals from a mixed solution of a malonate and ferrous sulphate on the addition of absolute alcohol. They are all very unstable, changing immediately in open air into the corresponding ferri-malonate.

Chemical Institute, Kyoto Imperial University,
June, 1907.

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VOL. XXV., ARTICLE 3.

On the Constitution of the so-called Elæomargaric Acid.

By

Tokuhei Kametaka, *Rigakushi.*

I showed three years ago (Jour. of the College of Science, Imperial University of Tokyo, Vol. XIX., Article 12; Jour. Chem. Soc., 1903, **83**, 1042–1045) that the composition of the so-called elæomargaric acid is neither $C_{17}H_{30}O_2$, as given by its discoverer CLOËZ (Compt. rend., 1876, **83**, 943.) nor $C_{18}H_{30}O_2$, as asserted by L. MAQUENNE (Compt. rend., 1902, **135**, 696–698); but that it must be $C_{18}H_{32}O_2$, isomeric with linolic acid. Since then I have continued the work with the object of determining, if possible, the constitution of the acid. Unfortunately, no definite conclusion on this point has yet been reached; but in view of the fact that circumstances will prevent me from continuing the work for some time, I propose to describe some of the results thus far obtained.

With regard to the constitution of elæomargaric acid, CLOËZ's own words are as follows:—

„L'acide élæomargarique est un homologue supérieur des acides sorbique, linoléique et palmitolique; il se place entre ce dernier et l'acide stéarolique, obtenu artificiellement par l'action de la potasse sur l'acide oléique bromé." (*loc. cit.*).

L. MAQUENNE, who, as above stated, regards the composition of the acid as $C_{18}H_{30}O_2$, observes that azelaic acid ($C_9H_{16}O_4$) and n-valerianic acid are formed by the oxidation of the acid as well as its stereoisomer elæostearic acid, and states :—

„Le reste de la molécule, qui comprend encore 4^{at} de carbone, est entièrement détruit, ce qui laisse indecise la question de savoir si l'acide élæostéarique renferme deux ou trois liaisons multiples ; en d'autres termes, s'il est éthylénique et acétylénique ou triethylenique.

Le seul fait certain qui découle des résultats précédants c'est que l'acide élæostéarique possède deux lacunes dans les positions 5 et 9." (*loc. cit.*).

Now, according to O. DOEBNER (Ber., 1890, **23**, 2374), sorbic acid $CH_3-CH=CH-CH=CH-CO_2H$ and other acids containing the group $-CH=CH-CH=CH-CO_2H$ when oxidised with potassium permanganate in a slightly alkaline solution give tartaric acid among other products ; but on oxidising elæomargaric acid in the same manner, it was found that no tartaric acid was produced. It appears, therefore, that the statement by CLOËZ that elæomargaric acid is a homologue of sorbic acid is not founded upon fact. Moreover, elæomargaric acid, unlike stearolic acid, and behenolic acid, does not give a definite product with conc. sulphuric acid. CLOËZ's idea that elæomargaric acid is a homologue of stearolic acid and contains a triple bond is, therefore, also rendered improbable.

Further, on repeating MAQUENNE's oxidation process, a large quantity of azelaic acid was indeed obtained, but the presence of n-valerianic acid could not be established with certainty. There seems, therefore, to be no doubt that one double bond out of the two, which elæomargaric acid doubtless contains, is in the middle of the chain of 18 carbon atoms. As to the position of the other double bond no definite conclusion can be drawn at present; but in view of the fact that many unsaturated acids, which give azelaic acid $CO_2H(CH_2)_7CO_2H$, on oxidation, such for example as oleic acid and stearolic acid, contain the group $=CH(CH_2)_7CO_2H$ or $\equiv C(CH_2)_7CO_2H$, it appears probable that it is on that side of the middle double bond which is further removed from the carboxyl group. The result of the action of aniline upon elæomargaric acid, as described further on, favours this view.

Experimental.

Oxidation of elæomargaric acid with potassium permanganate.

Following the method of oxidation described by DOEBNER (*loc. cit.*), 10 gr. of elæomargaric acid was dissolved in caustic potash sufficient for its neutralisation, diluted with water to 2 litres, and cooled to 2–3°. To this solution, 18 gr. of potassium permanganate dissolved in 2 litres of water and cooled to 2–3° was gradually added. After standing for 3 hours the precipitate of manganese dioxide was filtered off, and the filtrate concentrated to ¼ litre and acidified with hydrochloric acid, when a brown percipitate was formed, which was collected and recrystallised several times from alcohol. In this manner, a white crystalline substance of m. p. 130° was obtained, which, from the determination of the acid equivalent by means of standard baryta water, proved to be dihydroxystearic acid.

The filtrate from the impure dihydroxystearic acid was rendered slightly alkaline with ammonia, and calcium chloride added, when a white precipitate was formed. This apparently consisted of calcium oxalate, and no tartaric acid could be detected.

The oxidation process was repeated, not, however, at low temperatures as before, but at an ordinary temperature (about 12°). In this case, azelaic acid (m. p. 105°) was formed, besides dihydroxystearic acid, but again no tartaric acid was obtained.

As the formation of dihydroxystearic acid $C_{18}H_{34}(OH)_2O_2$ by the oxidising action of potassium permanganate upon elæomargaric acid $C_{18}H_{32}O_2$, i. e. by a mere addition of $2H_2O$, appeared somewhat strange, I next tried HAZURA's method of oxidation, the elæomargaric acid used having been carefully recrystallised from alcohol and made free from accompanying oleic acid. Here again dihydroxystearic acid was obtained, besides azelaic acid and an unknown substance of a white crystalline nature, m. p. 123–125°, soluble in water and alcohol, but insoluble in ether. Sativic acid was not formed. This was probably due to the high temperature employed and the decomposition of sativic acid once formed into azelaic acid. Lastly, elæomargaric acid was oxidised by MAQUENNE's method (Bull. soc. chim., 1899, 3^e série, **21**, 1061) on a water-bath ; a large quantity of azelaic acid was obtained, but no n-valerianic acid could be detected in the mother liquor.

Action of concentrated sulphuric acid upon elæomargaric acid.

Following the method, by which the constitutions of behenolic and stearolic acids were determined (J. BARUCH, Ber., 1893, **26**, 839 ; 1894, **27**, 172), elæomargaric acid was mixed with 5 times its weight of pure conc. sulphuric acid ; heat was evolved and the smell of sulphur dioxide perceived, the crystals of elæomargaric acid melting into a dark liquid. After standing for

3 4 hours, the liquid was poured into a large quantity of water, when a greenish-blue resinous mass was obtained, which could not be crystallised either from alcohol, acetic acid, acetic ester, or other solvents. This negative result may perhaps be taken as showing that elæomargaric acid differs from behenolic and stearolic acids in not containing a triple bond.

Fusion of elæomargaric acid with caustic potash.

Crystallised elæomargaric acid was fused with about four times its weight of solid caustic potash, in a nickel or iron crucible, at about 400° for 3–4 hours. A part of the acid floated on the surface of the fused mass and did not quite dissolve. The dark coloured mass obtained on cooling was extracted with water, filtered, and acidified with hydrochloric acid, when a small quantity of a brown substance separated, which, after repeated recrystallisation from alcohol, gave a white crystalline substance, whose melting point was 95–96°. Its acid equivalent was found to be about 515, so that it was not azelaic acid, although its melting point almost exactly agreed with that of the latter. The quantity of the substance was too minute to admit of an elementary analysis.

In another fusion experiment a small quantity of a white crystalline substance, melting at about 58°, was obtained, whose acid equivalent was found to be about 255. It was probably *palmitic acid* ($C_{16}H_{32}O_2 = 256$).

Reaction between elæomargaric acid and aniline.

According to W. AUTENRIETH and C. PRETZELL (Ber., 1903, 36, 1262) unsaturated monobasic acids of the olefine series, in which the double bond is between the $\alpha\beta$ or $\beta\gamma$ carbon atoms, react with aniline and form not only anilides but also aniline addition products.

Following their method and with the object of seeing whether elæomargaric acid gives analogous compounds, about 10 grammes of the pure acid and an equal weight of freshly distilled aniline (about 3 mol.) were heated together in a small flask on an oil-bath to 180–190° for 3–4 hours. After cooling, water and dilute acetic acid were added and well shaken in order to remove free aniline; the residual crystalline mass was twice recrystallised from alcohol. White lustrous scaly crystals were thus obtained, which melted at about 80°.

Nitrogen determinations gave the following results:—

0.075 gr. of the substance gave 3 c.c. nitrogen at 6°, 764.4 m.m.

$\therefore$ N=4.90%,

0.2445 gr. of the substance gave 8.3 c.c. nitrogen at 3°, 765.4 m.m.

$\therefore$ N=4.22%.

Calculated for the anilide $C_{18}H_{31}O \cdot NH\,C_6H_5$ N=3.94%.

On keeping these crystals (m. p. 80°) in a desiccator, they became sticky and turned yellow, owing probably to their being not quite pure.

In other experiments, white scaly crystals of m. p. 67° were obtained. These crystals do not change on keeping. Nitrogen determinations gave the following results:—

0.2352 gr. of the substance gave 6.8 c.c. at 10°, 764.7 m.m.

$\therefore$ N=3.48%,

0.3298 gr. of the substance gave 10.0 c.c. at 10°, 769 m.m.

$\therefore$ N=3.67%.

Mean 3.58%.

The anilide of elæomargaric acid $C_{18}H_{31}O \cdot NH\,C_6H_5$ requires $N=3.94\%$, while the addition product of the anilide with one molecule of aniline requires $N=6.25\%$.

The product above obtained must therefore be the anilide of elæomargaric acid and is still unsaturated. To the glacial acetic acid solution of the anilide of m. p. 80°, bromine was added drop by drop until the red colour of bromine no longer disappeared; on cooling with ice, a white precipitate was obtained, whose m. p. was found to be about 95°.

The non-formation of aniline addition product may be taken as an indication that the double bonds in elæomargaric acid are not near the carboxyl group.

Esters of elæomargaric acid.

Methyl and ethyl esters of elæomargaric acid were prepared by the usual method. The methyl ester decomposed on warming, becoming dark coloured and giving off a disagreeable odour. But the ethyl ester was stable and of a transparent yellow colour, distilling at 230–240° under a pressure of 25 m.m.

From the ethyl ester, a bromine addition-product was prepared by the usual method, which was at first a colourless, transparent liquid, but on standing it gradually became dark coloured.

Since my first paper on elæomargaric acid appeared in 1903, the only literature on this subject which I have been able to find, is a paper by Moritz Kitt (Chem. Rev. Fett- u. Harz-Ind., **II**, 190-191), which, however, I have only seen in abstract

(Chem. Central-Blatt, 1904, II, 949). He seems not to have seen my paper, nor that of L. MAQUENNE (Comp. rend., 1902, **135**, 696), as no reference to these papers is made. It also appears that he had obtained no definite results as to the composition or constitution of this acid.

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VOL. XXV., ARTICLE 4.

Notes on Japanese Vegetable Oils.

By

Tokuhei Kametaka, *Rigakushi.*

1. Japanese Wood Oil (*Kiri-abura*).

(*a*) The iodine value.

Whereas Japanese wood oil dries more rapidly than linseed oil, the iodine value of the former is lower than that of the latter. The iodine value of this oil is, however, variously stated by different observers. Thus, it is 169.02 according to K. Higuchi, 159–161 according to De Negri and Suburlati, 167 (Hübl's method) and 169.5 (Wijis' method) according to Ingle, 149.7–165.7 according to Jenkins, and 155.4–165.6 according to Williams. Even the highest value 169.5, given by Ingle, is lower than that (170–188 according to different observers) for linseed oil. H. Ingle (J. S. C. I., 1902, 187) is of the opinion that the lowness of the iodine value of Japanese wood oil may be due to its previous oxidation, stating at the same time that "there are reasons for supposing that wood oil has a different constitution from the other drying oils."

In order to examine the fresh oil I procured the seeds of *Elæococca vernicia* from Echizen and pressed them myself in the cold, taking care to expose the oil as little as possible to the air. The oil pressed out was slightly turbid, so it was passed through a filter paper by the aid of a water-pump. The clear oil thus obtained was directly used for the following determination of the iodine value.

0.1489 gr. of the oil was dissolved in 10 c.c. of chloroform, and 25 c.c. of Hübl's solution was added. After standing for about 24 hours in the dark, the excess of iodine was titrated back with standard thiosulphate solution (1 c.c. = 0.01231 gr. iodine), of which 29.3 c.c. was required, whilst in a blank experiment 48.7 c.c. of the thiosulphate solution was required. The iodine value is, therefore,

$$\frac{(48.7-29.3)\times 0.01231\times 100}{0.1489}=160.3$$

Two other such experimints gave 160.8 and 162.8, so that the mean of the three experiments was 161.3.

After storing the cold-drawn oil in an ordinary stoppered bottle in the dark for eleven months, its iodine value was redetermined according to Hübl's method. The results were 149.3 and 150.6, mean 150.0, so that during the eleven months the iodine value of the oil had decreased by 161.3−150.0=11.3. Meanwhile, the iodine value of the oil was also determined according to Wijis' method. Wijis' solution was prepared as follows:—

12.7 gr. of iodine was dissolved in one litre of glacial acetic acid; to this solution dried chlorine gas was passed until a sudden change in colour occurred. The solution was warmed on a water-bath, and the excess of chlorine changed into chloracetic acid. Using this solution the iodine value was determined in the same manner as in Hübl's method, but the time of standing was only 3–4 hours. The results of two experiments made with the cold-drawn oil, which has been stored in an ordinary stoppered bottle in the dark for three months, were 155.7 and 156.8, mean 156.3.

By WIJIS' method we usually obtain an iodine value which is a little higher than that obtained by HÜBL's method. But owing to the oxidation, which has taken place during the three months, the iodine value obtained by WIJIS' method was found to be lower than the value obtained by HÜBL's method with the original oil. Determination with WIJIS' method was also repeated with the eleven months oil, which gave the values 153.6, 151.6 and 154.3, mean 153.2, so that during the eight months the decrease of iodine value amounted to 156.3−153.2=3.1.

These experiments show that the fact that the iodine value of Japanese wood oil, which, as above found, is 161.3, or lower than that of linseed oil, can not be ascribed to previous oxidation, as has been believed by many, and that on oxidation the value is much diminished.

The lowness of the iodine value is also apparent from a consideration of the composition of the oil. This oil, unlike linseed oil, contains none of the highly unsaturated acids, such as linolenic acid $C_{18}H_{30}O_2$, but consists of the glyceride of elæomargaric acid and olein, in the proportion, according to CLOËZ, of 75% of the former to 25% of the latter. The theoretical iodine value of the former glyceride being 173.6 and that of the latter 86.2, the calculated iodine value of the oil, assuming the above proportion to be correct, is 151.8. Or, taking the above found iodine value, 161.3, the proportion of the two constituents may be calculated thus,

$$173.6\,x + 86.2\,(1-x) = 161.3, \qquad \therefore \quad x = 0.8592\,;$$

that is, the oil consists of about 86% elæomargarin and 14% olein. This proportion, rather than the one given by CLOËZ, seems to be justified by the yield of elæomargaric acid from the oil.

The iodine value of pure elæomargaric acid itself was determined and found to be 180.2 (HÜBL's method), and 183.1 (WIJIS' method); the iodine value calculated from the formula $C_{18}H_{32}O_2$ is 181.4, with which both of the above values are in fair agreement.

(*b*) Some other constants of Japanese wood oil were determined with the following results:—

Acid value 3.81.

Specific gravity $\left(\frac{24^\circ}{24^\circ}\right)$ 0.9307.

Saponification value 196.0.

(*c*) Existence of an enzyme in the seeds of *Elæococca vernicia.*

The seeds of *Elæococca vernicia,* after removing the outer husk were crushed in a mortar and extracted with water, and at other times with glycerin, and the precipitate obtained on the addition of alcohol was filtered, washed with alcohol, dried at low heat and powdered. The greyish brown substance thus obtained was added to a mixture of ethyl acetic ester or the Japanese wood oil itself and water, and the mixture titrated from time to time with baryta-water along with a blank mixture, phenolphthalein being used in both cases as the indicator. Though the saponifying action of the enzyme was not remarkable, its effect was apparent from the greater quantity of baryta-water required in each case to neutralize the liquid than in the blank experiment.

It is possible that this enzyme, being present in a small quantity in the oil itself, plays some part in the rapid drying of this oil.

2. **Camellia Oil or Oil of *Thea japonica (L.) Nois***
(*Tsubaki-abura*).

The sample used was commercially pure.

Specific gravity $\left(\frac{15°}{4°}\right)$ 0.9138.

Iodine value (Hübl's method) 79.47; the oil, therefore, belongs to the class of non-drying oils.

The mixed acids obtained by saponifying this oil were oxidised by potassium permanganate according to Hazura's method, but at an ordinary temperature. A large quantity of white lustrous crystals of m. p. 128–130° was obtained. The acid equivalent was found to agree with that of dihydroxystearic acid. No sativic acid or linusic acid was obtained. From these facts it is evident that the principal acid in this oil is oleic acid.

No solid bromine addition product was obtained.

3. **Oil of *Terreya nucifera S. et Z.***
(*Kayano-abura*).

This sample I made myself by pressing the seeds in the cold.

The iodine value (Hübl's method) was found to be 137.3.

The mixed acids obtained by saponifying the oil with alcoholic potash were recrystallized from acetic acid or from alcohol. White scaly crystals of m. p. 57.5° were obtained. This substance does not change in the air, nor absorbs bromine in acetic acid solution. The figures obtained for its acid equivalent were 270.3, 280 and 281; it therefore appears likely that the acid is stearic acid $C_{18}H_{36}O_2=284$, or possibly a mixture of stearic and palmitic acids.

A bromine addition product of the mixed acids was obtained in the usual manner, its melting point, 114°, agreeing with that of tetrabromostearic acid $C_{18}H_{32}Br_4O_2$. This oil therefore contains linolic acid $C_{18}H_{32}O_2$ or its isomers besides stearic acid.

4. **Soja bean Oil or Oil of *Glycine hispida Maxim.***
(*Daidzu-abura*).

The sample used was pure oil obtained from Tokushima.

A bromine addition product of the mixed acids was obtained melting at 110°. This appears to be tetrabromostearic acid $C_{18}H_{32}Br_4O_2$.

Oxidation of the mixed acids by HAZURA's method gave dihydroxystearic acid and sativic acid, the yield being about 27.5 parts of the former and 10 parts of the latter from 100 parts of the oil.

From these experiments it can be seen that the unsaturated acids in this oil are principally oleic acid and linolic acid, or its isomer.

5. **Oil of *Perilla ocymoides L.***
(*Eno-abura*).

A commercially pure sample was employed.

The bromine addition product of the mixed acids prepared in the usual manner separated out from hot glacial acetic acid as a white voluminous precipitate, which under the microscope showed no crystalline structure but consisted of fine oily drops, m. p. 181°. A bromine determination gave the following result :—

From 0.2235 gr. substance 0.3160 gr. AgBr was obtained, $\therefore$ Br = 62.61%. Calculated for the formula $C_{18}H_{30}Br_6O_2$, Br = 63.32%.

It appears therefore that linolenic acid or its isomer is contained in this oil.

The mixed acids were heated with aniline as in the preparation of the anilide of elæomargaric acid; a white non-crystalline substance of m. p. 60–62° was thus obtained. The acetic acid solution of this anilide absorbs bromine, so that it is still an unsaturated compound.

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On the Viscosity of dilute Alcoholic Solutions.

By

Toshio Hirata, *Rigakushi.*

ARRHENIUS[1] has shown first that the viscosity of an aqueous

Errata.

Page	7,	19th line, for Fig. 1 read Fig. 7.
„	10,	8th line, for Fig. 37, b read Fig. 37, a.
„	32,	footnote, for geschl. read geschl.
„	„	footnote, for geschl. read geschl.
„	42,	23rd line, for Fig. 1 read Fig. 19.
„	53,	16th line, for Fig. 35 read Fig. 53.

ARRHENIUS has further shown that the formula can be applied to aqueous solutions of electrolytes and non-electrolytes up to 1.5 normal and 10 vol. per cent. solutions respectively, in which the resulting error rarely exceeds one per cent.

The correctness of the above results in the case of aqueous solutions has since been confirmed by the works of REYHER,[2] WAGNER[3] and others.

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[1] Zeit. physik. Chem., 1887, I, 285.
[2] „ „ „ 1888, II, 744.
[3] „ „ „ 1890, V, 40.

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On the Viscosity of dilute Alcoholic Solutions.

By

Toshio Hirata, *Rigakushi.*

ARRHENIUS[1] has shown first that the viscosity of an aqueous solution containing any two indifferent dissolved substances can be expressed with good results by the following exponential formula,

$$z = A^x B^y, \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where A and B are two constants characteristic of the substances dissolved at a constant temperature, x and y being their respective volume percentages. Since $z=1$, when $x=y=0$, the viscosity thus expressed is the specific viscosity of the solution, where the viscosity of the solvent is made unity. When only one substance is dissolved the formula reduces to the simpler one,

$$z = A^x. \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

ARRHENIUS has further shown that the formula can be applied to aqueous solutions of electrolytes and non-electrolytes up to 1.5 normal and 10 vol. per cent. solutions respectively, in which the resulting error rarely exceeds one per cent.

The correctness of the above results in the case of aqueous solutions has since been confirmed by the works of REYHER,[2] WAGNER[3] and others.

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3) „ „ „ 1890, V, 40.

Believing it to be of some interest to determine whether such regularities exist in other solvents than water, I undertook some experiments on the viscosities of alcoholic solutions.

The following experiments were made using ethyl alcohol as the solvent, which was obtained by dehydrating commercial "absolute alcohol" with freshly burnt lime; all the dissolved substances used, were tested for the impurities frequently contained in them and freed from these; their densities, boiling points and, when easily observable, their melting points, were compared with those given for the pure substances and found quite satisfactory.

The experimental method was as follows:—A glass tube, like an ordinary test tube closed at one end, and furnished with a glass stopper at the other, was taken. The tube was graduated in cubic centimeter from the bottom up to 20 c.c. Into this tube the required volume of the liquid to be dissolved was poured and the solvent alcohol gradually added, with frequent shakings, until it filled 20 c.c. The dissolved substance and the solvent, before mixing, were kept in a thermostat whose temperature was 25°C. The solution thus made was kept in the thermostat for a sufficient length of time before it viscosity was measured.

Solutions containing only one dissolved substance were made as follows, and the measurements made on each: At first, 5 c.c. of the substance to be dissolved was taken and diluted to 20 c.c. with the alcohol; then the half, i. e. 10 c.c., of the solution, was taken and diluted again to 20 c.c.; in this way, 25, 12.5. 6.25, 3.125, 1.5625 and 0.7813 vol. per cent. solutions were made.

The viscosimeter used in the experiment was that of OSTWALD (Fig. 1) and had the following dimensions: Length of the

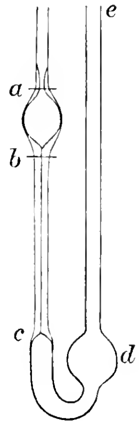

Fig. 1.

capillary tube *bc*, 12 cm.; diameter of the capillary, 0.0544 cm.; volume of the upper bulb between the marks *a* and *b*, 6.51 c.c. The total volume of liquid used was 9 c.c.

After the fixed volume (=9 c.c.) of the solution had been poured in at *e* by means of a pipette, the apparatus was sunk vertically under the water of the thermostat until the mark *a* was a sufficient distance below the surface. The liquid in the bulb *d* was pushed up, by pressing in some dry air at *e*, and when its head reached the mark *a*, the pressure was removed and the liquid was left to flow down the capillary by its own weight. The time required to flow down from *a* to *b* was then read.

The time was measured by means of a watch, capable of being read to one fifth of a second.

As is well known, when t and t' are the times of flow from a to b, and s and s' are the densities of any two liquids respectively, then the ratio of their absolute viscosities η and η' is,

$$\frac{\eta'}{\eta}=\frac{s'.t'}{s.t}.$$

Hence if we know the time of flow and the density of a liquid we can readily calculate the specific viscosity of that liquid. I measured the specific gravity of a liquid with a SPRENGEL's U-shaped pyknometer whose capacity was about 3 c.c.

At first, I made the determinations with solutions having only one dissolved substance.

I found that the formula (2) gives good results, in a wide range of concentrations, with the dissolved substances I had taken, except in the case of water; the following table gives the constant A and the specific viscosities z (the viscosity of ethyl alcohol at 25°C. being unity) of the substances dissolved and the upper limits of concentrations expressed in vol. %, below which the calculation from (2) gives differences less than one per cent from the direct observations.

Dissolved substance.	A	z	Limit.
Acetone	0.9786	0.2946	12.5
Ethyl ether	0.9840	0.2292	25
Ethyl acetate	0.9865	0.4189	25
Carbon bisulphide	0.9888	0.3583	25
Ethyl bromide	0.9888	0.3815	25
Ethyl iodide	0.9918	0.5611	25
Methyl alcohol	0.9922	0.5270	25
Benzene	0.9924	0.5608	25
Chlorobenzene	0.9970	0.6989	25
Nitrobenzene	1.001	1.687	25
Ethyl benzoate	1.001	1.7918	25
Propyl alcohol	1.0053	1.841	25
Aniline	1.007	4.306	25
Amyl alcohol	1.0085	3.455	12.5
Glycerine	1.055	—	12.5

In the above table the dissolved substances are arranged according to their constants A. We see from the table that, *in general*, the substances of greater viscosity give greater constants and we can not find the remarkable fact that ARRHENIUS observed in aqueous solutions, viz., that the constant A of glycerine is less than that of ether.

We further noticed, when compared with aqueous solutions at 25°C., that while in the aqueous solutions the constants A of all non-electrolytes are greater than unity, many of the constants found in the alcoholic solutions are less than unity.

The following tables show the differences between the observed viscosities and those calculated from the above constants.

Acetone.

$A = 0.9786.$

x	z	A^x	Diff.
25	0.6137	0.5823	−0.0314
12.5	0.7653	0.7631	−0.0022
6.25	0.8695	0.8735	+0.0040
3.125	0.9355	0.9346	−0.0009
1.5625	0.9689	0.9668	−0.0021
0.78125	0.9905	0.9832	−0.0073

Ethyl ether.

$A = 0.9840.$

x	z	A^x	Diff.
25	0.6620	0.6682	+0.0062
12.5	0.8187	0.8174	−0.0013
6.25	0.9069	0.9041	−0.0028
3.125	0.9575	0.9508	−0.0067
1.5625	0.9823	0.9751	−0.0072
0.78125	0.9949	0.9875	−0.0074

Ethyl acetate.

$A = 0.9865.$

x	z	A^x	Diff.
25	0.7163	0.7119	−0.0044
12.5	0.8424	0.8438	+0.0014
6.25	0.9137	0.9186	+0.0049
3.125	0.9614	0.9584	−0.0030
1.5625	0.9845	0.9790	−0.0055
0.78125	0.9963	0.9894	−0.0069

Carbon bisulphide.

$A=0.9888.$

x	z	A^x	Diff.
25	0.7491	0.7546	−0.0055
12.5	0.8656	0.8687	+0.0031
6.25	0.9326	0.9320	−0.0006
3.125	0.9666	0.9654	−0.0012
1.5625	0.9910	0.9826	−0.0084
0.78125	0.9971	0.9912	−0.0059

Ethyl bromide.

$A=0.9888.$

x	z	A^x	Diff.
25	0.7488	0.7546	+0.0058
12.5	0.8687	0.8687	± 0
6.25	0.9324	0.9320	−0.0004
3.125	0.9682	0.9654	−0.0028
1.5625	0.9857	0.9826	−0.0031
0.78125	0.9940	0.9912	−0.0028

Ethyl iodide.

$A=0.9918.$

x	z	A^x	Diff.
25	0.8078	0.8140	+0.0062
12.5	0.9029	0.9022	−0.0007
6.25	0.9514	0.9498	−0.0016
3.125	0.9815	0.9746	−0.0069
1.5625	0.9912	0.9872	−0.0040
0.78125	0.9950	0.9936	−0.0014

Methyl alcohol.

$A = 0.9922.$

x	z	A^x	Diff.
25	0.8218	0.8222	+0.0004
12.5	0.9062	0.9068	+0.0006
6.25	0.9500	0.9522	+0.0022
3.125	0.9744	0.9758	+0.0014
1.5625	0.9870	0.9878	+0.0008

Benzene.

$A = 0.9924.$

x	z	A^x	Diff.
25	0.8267	0.8264	−0.0003
12.5	0.9090	0.9090	± 0
6.25	0.9548	0.9534	−0.0014
3.125	0.9827	0.9764	−0.0063
1.5625	0.9955	0.9882	−0.0073
0.78125	0.9959	0.9941	−0.0018

Chlorobenzene.

$A = 0.9970.$

x	z	A^x	Diff.
25	0.9189	0.9276	+0.0087
12.5	0.9674	0.9631	−0.0043
6.25	0.9894	0.9814	−0.0080
3.125	0.9972	0.9907	−0.0065
1.5625	1.0012	0.9953	−0.0059
0.78125	1.0029	0.9977	−0.0052

Nitrobenzene.

$A=1.001.$

x	z	A^x	Diff.
25	1.0230	1.0253	+0.0023
12.5	1.0078	1.0126	+0.0048
6.25	1.0062	1.0063	+0.0001
3.125	1.0074	1.0031	−0.0043
1.5625	1.0058	1.0016	−0.0042
0.78125	1.0074	1.0008	−0.0066

Ethyl benzoate.

$A=1.001.$

x	z	A^x	Diff.
25	1.0324	1.0253	−0.0071
12.5	1.0126	1.0126	± 0
6.25	1.0066	1.0063	−0.0003
3.125	1.0080	1.0031	−0.0049
1.5625	1.0075	1.0016	−0.0059
0.78125	1.0079	1.0008	−0.0071

Propyl alcohol (normal).

$A=1.0053.$

x	z	A^x	Diff.
25	1.1406	1.1413	+0.0007
12.5	1.0684	1.0683	−0.0001
6.25	1.0353	1.0336	−0.0017
3.125	1.0185	1.0167	−0.0018
1.5625	1.0088	1.0083	−0.0005
0.78125	1.0045	1.0041	−0.0004

Aniline.

$A=1.007.$

x	z	A^x	Diff.
25	1.2081	1.1905	−0.0176
12.5	1.0864	1.0911	+0.0047
6.25	1.0439	1.0446	+0.0007
3.125	1.0279	1.0220	−0.0059
1.5625	1.0176	1.0110	−0.0066
0.78125	1.0103	1.0055	−0.0048

Amyl alcohol (isobutyl carbinol).

$A=1.0085.$

x	z	A^x	Diff.
25	1.2401	1.2357	−0.0044
12.5	1.1074	1.1116	+0.0042
6.25	1.0508	1.0543	+0.0035
3.125	1.0258	1.0268	+0.0010
1.5625	1.0127	1.0133	+0.0006

Glycerine.

$A=1.055.$

x	z	A^x	Diff.
25	4.1224	3.8134	−0.3090
12.5	1.9600	1.9528	−0.0072
6.25	1.3958	1.3974	+0.0016
3.125	1.1746	1.1821	+0.0075
1.5625	1.0814	1.0873	+0.0059
0.78125	1.0492	1.0427	−0.0065

As is seen from the tables, most of the dissolved substances above mentioned are calculable with the formula (2) with differences less than one per cent up to 25 vol. % solutions and a few, i. e. three out of the fifteen, up to 12.5 vol. % solutions. But when water is the dissolved substance the formula does not apply in the same manner unless the concentrations of the solutions are less than 3 vol. % as the following tables show:

Water.

x	z	A^x ($A=1.032$)	Diff.	A^x ($A=1.040$)	Diff.	A^x ($A=1.043$)	Diff.	A^x ($A=1.045$)	Diff.
25	1.8300	2.1978	−0.3680	—	—	—	—	—	—
12.5	1.4715	1.4825	−0.0110	1.6327	−0.1612	—	—	—	—
6.25	1.2575	1.2176	+0.0399	1.2778	−0.0203	—	—	—	—
3.125	1.1407	1.1034	+0.0373	1.1304	+0.0103	1.1406	+0.0001	1.1475	−0.0068
1.5625	1.0808	1.0505	+0.0303	1.0632	+0.0176	1.0680	+0.0128	1.0712	+0.0096
0.78125	1.0412	1.0249	+0.0163	1.0311	+0.0101	1.0334	+0.0078	1.0350	+0.0062

This is also clear from the shape of the viscosity curve of the water solutions, the dotted line in the figure (Fig. 2) is that calculated from $A=1.032$.

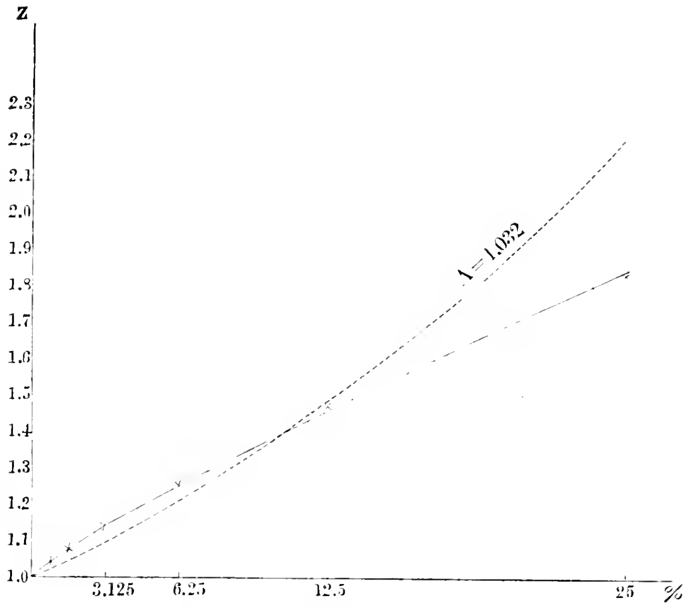

Fig. 2.

Next, I tried the application of formula (1) to solutions containing two dissolved substances. The results were that, so far as my experiment went, the formula gave good results at least to 10 vol. % solutions.

The pairs of the dissolved substances I have taken are as follows:

Dissolved substances.	Limit.
Carbon bisulphide and ethyl ether	20 vol. %
Nitrobenzene and ethyl ether	20 ,,
Acetone and nitrobenzene	20 ,,
Benzene and nitrobenzene	10 ,,
Benzene and carbon bisulphide	10 ,,
Aniline and carbon bisulphide	10 ,,
Benzene and propyl alcohol	20 ,,
Benzene and ethyl benzoate	20 ,,

I found in this case, that when the constants A and B were calculated from the observed viscosities by the formula,

$$z = A^x . B^y,$$

the values of A and B thus obtained were nearly equal to the constants which we had found when only one substance was used; and on calculating z using the latter constants, it was found that the observed and the calculated values did not differ by more than one per cent. This is shown in the following tables; the constants used are all those found before. The limits, within which the above relations hold good, and noted in the right hand column of the above table, are the maximum concentrations of the two dissolved substances taken together and expressed in volume percentage. The maximum volume percentage of each of the two dissolved substances is one-half of the above limits.

Carbon bisulphide and **Ethyl ether**.

Carbon bisulphide: $A = 0.9888$.
Ethyl ether: $B = 0.9840$.

x	y	z	$A^x . B^y$	Diff.
10	10	0.7600	0.7604	+0.0004
5	5	0.8704	0.8720	+0.0016
2.5	2.5	0.9347	0.9338	−0.0009
5	10	0.8024	0.8044	+0.0020
2.5	5	0.8976	0.8969	−0.0007
10	5	0.8255	0.8243	−0.0012

Nitrobenzene and Ethyl ether.

Nitrobenzene : $A=1.001$.
Ethyl ether : $B=0.9840$.

x	y	z	$A^x . B^y$	Diff.
10	10	0.8635	0.8596	−0.0039
5	5	0.9288	0.9271	−0.0017
2.5	2.5	0.9637	0.9629	−0.0008
5	10	0.8592	0.8553	−0.0039
2.5	5	0.9295	0.9248	−0.0047
10	5	0.9315	0.9318	+0.0003

Acetone and Nitrobenzene.

Acetone : $A=0.9786$.
Nitrobenzene : $B=1.001$.

x	y	z	$A^x . B^y$	Diff.
10	10	0.8195	0.8136	−0.0059
5	5	0.8997	0.9020	+0.0023
2.5	2.5	0.9476	0.9497	+0.0021
5	10	0.8997	0.9065	+0.0068
10	5	0.8092	0.8095	+0.0003

Benzene and Nitrobenzene.

Benzene : $A=0.9924$.
Nitrobenzene : $B=1.001$.

x	y	z	$A^x . B^y$	Diff.
10	10	0.9205	0.9359	+0.0154
5	5	0.9597	0.9674	+0.0077
2.5	2.5	0.9818	0.9836	+0.0018
5	10	0.9600	0.9722	+0.0122
2.5	5	0.9816	0.9860	+0.0044
10	5	0.9250	0.9312	+0.0062
5	2.5	0.9618	0.9650	+0.0037

Benzene and **Carbon bisulphide.**

Benzene : $A=0.9924$.

Carbon bisulphide : $B=0.9888$.

x	y	z	$A^x.B^y$	Diff.
10	10	0.8119	0.8279	+0.0160
5	5	0.9035	0.9099	+0.0064
2.5	2.5	0.9498	0.9539	+0.0041
10	5	0.8636	0.8758	+0.0122
5	2.5	0.9325	0.9359	+0.0034
5	10	0.8463	0.8600	+0.0137
2.5	5	0.9191	0.9274	+0.0083

Aniline and **Carbon bisulphide.**

Aniline : $A=1.007$.

Carbon bisulphide : $B=0.9888$.

x	y	z	$A^x.B^y$	Diff.
10	10	0.9296	0.9580	+0.0284
5	5	0.9690	0.9788	+0.0098
2.5	2.5	0.9862	0.9893	+0.0031
10	5	0.9989	1.0135	+0.0146
5	2.5	1.0061	1.0067	+0.0006
5	10	0.9078	0.9252	+0.0174
2.5	5	0.9589	0.9619	+0.0030

Benzene and **Propyl alcohol.**

Benzene : $A=0.9924$.

Propyl alcohol : $B=1.0053$.

x	y	z	$A^x.B^y$	Diff.
10	10	0.9711	0.9768	+0.0057
5	5	0.9895	0.9884	−0.0011
2.5	2.5	0.9945	0.9942	−0.0003
10	5	0.9476	0.9514	+0.0038
5	10	1.0103	1.0148	+0.0045

Benzene and **Ethyl benzoate.**

Benzene: $A=0.9924$.

Ethyl benzoate: $B=1.001$.

x	y	z	$A^x . B^y$	Diff.
10	10	0.9266	0.9359	+0.0093
5	5	0.9619	0.9674	+0.0055
2.5	2.5	0.9785	0.9836	+0.0051
5	10	0.9672	0.9722	+0.0050
10	5	0.9232	0.9312	+0.0080

SUMMARY.

1. It is shown that ARRHENIUS' formula, $z=A^x . B^y$, which gives good results in dilute aqueous solutions also holds good when ethyl alcohol is used as the solvent.

2. The formula can be applied to the solution of all the substances that I have examined with an error of less than one per cent, at least to 10 volume percentage concentration. Water forms an exception.

3. When water is the dissolved substance the formula can be applied only to very dilute solutions. When the concentration exceeds 3 volume percentage the error amounts to more than one per cent.

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Ueber den Hauptbestandteil des japanischen Lacks.

Von

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Der japanische Lack (*Kiurushi*) ist ein flüssiges Exsudat aus dem im Sommer zwecks dieser Gewinnung absichtlich verletzten Stamme eines Baumes (*Rhus vernicifera* Dc.), welche meistens in Ostasien gedeiht. Es ist wohlbekannt, dass die Flüssigkeit ein vorzügliches, gegen die gewöhnlichen Reagentien widerstandsfähiges Anstreichmittel darbietet. Daher werden besonders in Japan verschiedene Gefässe, Möbel etc. damit lackiert und zwar manchmal mit so grosser Sorgfalt und Geschicktlichkeit ausgearbeitet, dass die Lackwaren als Objekte eines der schönsten Kunstgewerbe Japans überall bewundert werden.

Die Natur dieser wichtigen Substanz aufzuklären, ist für die japanischen Chemiker ein interessanter Gegenstand, und schon früher haben sich Y. Hiraga, H. Yoshida,(1) K. Miyama(2) nach einander damit beschäftigt. Auch unter europäischen Chemikern haben Bertrand,(3) Tschirch und Stevan(4) einige Untersuchungen

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(1) Jour. Chem. Soc. 1883, p. 472.

(2) Japanischer Amtsbericht, No. 7000 (herausgegeben im 27. October, 1906).

(3) Ann. Chim. Phys. 7^s, **12**, (1897) p. 115.
Soc. Chim. d. Paris, 3^s, **11**, (1894) p. 614 et 717.

(4) Archiv. d. Pharmacie, Bd. **243**, (1905) 504.
In dieser abhandlung befindet sich eine ausführliche Beschreibung über die früheren Untersuchungen dieser Substanz. Sie zu lesen, empfehlen wir den Herrn, welche noch eingehendere Kenntnisse bekommen wollen.

darüber veröffentlicht. Die erste grundlegende Arbeit ist von YOSHIDA geliefert worden. Er hat den Lack in zwei Teile—einen in Alkohol löslichen und einen darin unlöslichen—getrennt. Den ersteren, welcher, in der alkoholischen Lösung mit Metallsalzen behandelt, die betreffenden Metalle enthaltenden Niederschläge bildet, hat er als eine Säure angenommen und ihm einen Namen, Urushinsäure, gegeben, während er den zweiten in der Hauptsache als eine Mischung eines die Oxydation einführenden Enzyms und einer Art von Gummi nachgewiesen hat. BERTRAND nannte die in Alkohol lösliche Substanz Laccol, und das Enzym Laccase, aber nur auf die Wirkung dieser Oxydase lenkte er ausschliesslich seine Aufmerksamkeit.

Urushinsäure macht 60–80% der Lackflüssigkeit aus, je nach den Pflanzenarten, der Jahreszeit und der Herkunft. Sie giebt dem Lack die vortrefflichen Eigenschaften als Anstreichmittel. Daher haben YOSHIDA, TSCHIRCH und STEVAN, und MIYAMA diese Säure mehr oder weniger eingehend untersucht. Aber die Säure ist nicht destillierbar, nicht krystallisirbar, und krystallisirbare Derivate sind nicht zu erhalten, d. h. alle gewöhnliche Reinigungsmethoden versagen. Nach der Arbeit von TSCHIRCH und STEVAN scheint dieser Körper eine Mischung entweder von verschiedenen Polymeren oder von Produkten verschiedener Oxydationsstufen zu sein, welche sich durch ihre Löslichkeit von einander unterscheiden. BERTRAND und MIYAMA haben gedacht, dass die Säure ein Phenol sei. Während TSCHIRCH und STEVAN durch die Unterschiede der Löslichkeit ihre Trennung versuchten, wollten sich YOSHIDA und MIYAMA mit der schwierigen Reinigung nicht lange aufhalten und haben sich bestrebt, durch trocken Destillation, Oxydation, Kalischmelze etc. des sicher noch nicht einheitlichen Körpers einen Einblick in seine Natur zu gewinnen.

Aber es war ihnen nicht gelungen, die schon bekannten einfacheren Körper aus den Zersetzungsprodukten zu isolieren.

Wir haben auch aus dem gleichen Grunde direkt die sogenannte Urushinsäure untersucht, immer grössere Menge davon benutzt und etwas genauer gearbeitet. So konnten wir einige wohl definierte Substanzen isolieren.

Unser Untersuchungsmaterial wurde im Sommer 1906 aus der Plantage in Hatanomura, Kanagawaken, ca. 40 Meilen westlich von Yokohama, unter passender Aufsicht gesammelt. Zur Reinigung haben wir ungefähr die gleiche Methode wie MIYAMA benutzt, d. h., die durch abs. Alkohol ausgezogene rohe Urushinsäure wurde nach Abdestillieren des Alkohols wieder mit einer grösseren Menge Petrolaethers behandelt. Der darin lösliche Teil wurde untersucht. Wir haben dabei ungefähr doppelt so viel Petrolaether als MIYAMA gebraucht. Die Säure hat folgende Zusammensetzung,(1) C 79.65%, H 9.75%, während die Säure von MIYAMA etwas weniger Kohlenstoff und Wasserstoff enthält (C 78.25%, H 9.60%). Dieser Unterschied kommt vielleicht von kleinen Verschiedenheiten im Reinigungsverfahren und vom Ausgangsmaterial und gibt uns einen weiteren Beweis für die Nichteinheitlichkeit dieser Substanz.

Die alkoholische Lösung der Urushinsäure reduciert Silberlösung, Bleiessig erzeugt einen Niederschlag, Eisenchlorid eine schwarzgrüne Färbung. Sie wird durch Alkali auch schwarzgrün gefärbt und an der Luft leicht oxydiert. Sie liefert Acetyl- und Benzoylderivate.(2) Diese Eigenschaften erinnern uns an diejenigen der mehrwertigen Phenole.

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(1) Der von TSCHIRCH und STEVAN gefundene Stickstoff (ca. 1.5%) hat sich nach MIYAMA als Kohlenoxyd erwiesen. Wir werden bis uns eine noch bessere Reinigung gelingt, und wir diese Frage endgültig entscheiden können, vorläufig nach MIYAMA diesen Körper stickstofffrei annehmen.

(2) Nach MIYAMA (l. c.).

Die Trockendestillation der Urushinsäure⁽¹⁾ geht glatt von statten und liefert uns verschiedene Kohlenwasserstoffe und mehrwertige Phenole, die Anwesenheit von Methan, Hexan, Hexylen, Heptan, Heptylen, Octan, Octylen, $C_{14}H_{28}$, $C_{14}H_{26}$ und Brenzcatechin wurde wahrgenommen. Daneben entsteht noch eine sehr geringe Menge von Kohlensäure und Fettsäuren. Es ist bemerkenswert, dass wir keinen einfachen aromatischen Kohlenwasserstoff und gewöhnliches Terpen gefunden haben.

Die Säure wird leicht durch Salpetersäure oxydiert, und aus den Oxydationsprodukten haben wir Korksäure, Bernsteinsäure und Oxalsäure isoliert. Wenn wir noch genauer gearbeitet hätten, könnten wir vielleicht noch andere, zwischen Korksäure und Oxalsäure stehende Dicarbonsäuren und vielleicht sogar auch einige Nitroverbindungen gefunden haben.

Dann haben wir zum ersten Mal die Methylierung der Urushinsäure versucht und eine Substanz bekommen, die nicht mehr die phenolartigen Reaktionen des Ausgangsmaterials zeigt, durch alkoholische Kalilauge nicht mehr leicht verseift und durch Salpetersäure auch nicht mehr leicht oxydiert wird. Die Methoxylbestimmung nach ZEISEL scheint uns zu zeigen, dass ungefähr ein Sechstel des gesammten Sauerstoffes noch nicht methoxyliert ist. Aber zur Zeit kann man noch nicht entscheiden, ob sich in diesem Falle ein Teil der vorhandenen Methoxylgruppe nach ZEISEL überhaupt nicht nachweisen lässt oder wirklich ein Teil des Sauerstoffs noch nicht methoxyliert ist.

Wir haben auch die Säure acetyliert. Es geht sehr leicht, und eine leicht gefärbte, durch alkoholische Kalilauge leicht verseifbare Substanz resultiert. Aber die Acetylbestimmung stösst

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(1) Für diesen Versuch und die Oxydation mit Salpetersäure (s. u.) haben wir das noch nicht mit Petrolaether behandelte rohe Materiel gebraucht.

auf Schwierigkeiten, da die Urushinsäure selbst durch Erhitzen mit alkoholischer Kalilauge auch eine Veränderung erleidet und flüchtige Säuren liefert. Aber es ist sicher, dass der grössere Teil des Sauerstoffs acetyliert ist.

Wir glauben, dass die oben skizzirten Resultate, obwohl sie noch in vielen Punkte zu flüchtig bearbeitet sind, folgende Schlüsse zu ziehen gestatten: (1) wenigstens der grössere Teil des Sauerstoffs in der Urushinsäure befindet sich in der Form von phenolischem Hydroxyl, (2) die Urushinsäure enthält eine grosse Kohlenwasserstoffgruppe.

Wir wollen noch andere Verfahren für ihre Reinigung versuchen, aber auch gleichzeitig die Oxydation der methylierten Säure ausführen, um damit möglichst schnell noch mehr Licht in die Zusammensetzung dieser Substanz bringen zu können. Einer von uns hat sich schon in dieser Richtung beschäftigt.(1)

EXPERIMENTELLES.

1. Die Reinigung der Urushinsäure.

Der japanische Lack, welche eine dicke Flüssigkeit bildet, wurde durch ein leinenes Tuch gepresst, das Filtrat mit ca. 10 Teilen abs. Alkohols versetzt, gut geschüttelt und durch ein Faltenfilter filtriert. Das alkoholische Filtrat wurde aus dem Wasserbade erst unter gewöhnlichem, dann unter vermindertem

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(1) Die Destillation mit Zinkstaub wurde in kleinem Maasstabe versucht, aber nicht weiter fortgesetzt, weil sie keinen grossen Unterschied zu der Trockendestillation zu haben scheint. Die Kalischmelze dieses Körpers wurde auch nicht eingehend verfolgt, weil sie nur eine geringe Menge von phenolartigen Krystallen (ca. 0.02 g. aus 50 g. Säure) lieferte, und meistenteils ohne bemerkenswerte Veränderung bleibt.

Druck eingeengt. Der Rückstand bildet die rohe Urushinsäure und wurde für die Trockendestillation und Oxydation sofort benutzt.

Für die weitere Reinigung wurde die rohe Säure in ca. 2 Teilen Petrolaethers gelöst, wiederholt mit Wasser gewaschen und mit Chlorcalcium getrocknet. Zur filtrierten Lösung wurde noch mehr Petrolaether gesetzt. Wenn die Menge der zugesetzten Flüssigkeit ca. 8 Teile der Säure überschreitet, entsteht eine Trübung, welche mit der Menge des Petrolaethers immer zunimmt. Nach der Einführung von ca. 50 Teilen des Lösungsmittels wurde das Gemisch über Nacht ruhig stehen gelassen und dann filtriert. Das Filtrat wurde erst aus dem Wasserbade unter gewöhnlichem dann aus dem Oelbade (bis 150° in Bad) unter vermindertem, Drucke abgedampft. Wir haben dabei bemerkt, dass das Filtrat sich beim Erwärmen wieder trübt, aber diese Trübung verschwindet wieder beim Erkalten. Der Rückstand hat folgende Zusammensetzung:

	Subst.	CO_2	H_2O	C	H
1.	0.1673	0.4897	0.1480	79.81	9.90
2.	0.2137	0.6234	0.1836	79.49	9.60
			Im Mittel	79.65	9.75

Wenn man ihn vorläufig als einheitlichen Körper annimmt und seine Formel berechnet, bekommt man $C_{40}H_{58}O_4$ (C 79.72%, H 9.63%).(1) Wie haben für Methylirung und Acetylierung diese Substanz gebraucht.

Der in Petrolaether unlösliche Teil bildet ungefähr den achte Teil der gesammten Säure und ist ziemlich unlöslich in den gewöhnlichen Lösungsmitteln, ausser in Aether.

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(1) Das Molekulargewicht dieses Körpers ist nach MIYAMA 509.

2. Die Trockendestillation der Urushinsäure.

In eine gläserne Retorte wurden 200 g. der Säure eingeführt und mit direkter Flamme schnell erhitzt. Gegen 280° (Thermometer in der Flüssigkeit) fängt die Zersetzung an, und nach ca. 20–30 Minuten dauerndem Schäumen siedet der Retorteninhalt ruhig. Dabei bleibt die Temperatur lange zwischen 370°–390°. Eine braun gefärbte Flüssigkeit und ein farbloses Gas sind die Hauptprodukte. Das entwickelte Gas wurde durch einen langsamen Strom des Kohlensäuregases(1) erst durch Brom und conc. Kalilauge gewaschen und dann in einem Gasometer aufgefangen. Nach der Destillation bleibt in der Retorte eine schwarze, pechartige Substanz zurück, welche ungefähr den vierten Teil der angewandten Säure beträgt. Wir haben dieses Verfahren wiederholt und aus ca. 800 g. der Säure ca. 600 g. flüssiges Destillat, ca. 18 Liter Gas und ca. 60 g. Bromverbindungen erhalten.

Wie haben das wie Kohlensäuregas riechende und etwas schwerer als Luft wiegende (sp. G. 1.14, Luft=1.) Gas mit flüssiger Luft kondensiert und dann in drei Teile fractioniert. Der flüchtigste Teil ist fast reines Methan und der Rest eine Mischung von höheren Kohlenwasserstoffen.

Die Bromverbindung wurde erst mit verdünnter Kalilauge, dann mit Wasser gewaschen, mit Chlorcalcium getrocknet und destilliert. Sie geht meistenteils zw. 80°–200° über, von 170° an aber unter Abgabe von Bromwasserstoff. Es war uns nicht gelungen, durch Fraktionierung einige bedeutend überwiegende

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(1) Die Existenz der Kohlensäure in den gasförmigen Zersetzungsprodukte ist als ganz geringfügig vorher geprüft.

Fraktionen zu erhalten. Der dem Bromaethylen (siede p. 131°) entsprechende Teil ist sehr gering.

Das flüssige Destillat, welches das Hauptzersetzungsprodukt bildet, wurde etwas eingehender untersucht. Es ist rötlich braun gefärbt und wird beim Aufbewahren an der Luft allmählich dunkler. Es wurde zuerst mit Wasser gut geschüttelt, wodurch das Wasser schwach saure Reaktion annimmt, aber schon durch ca. 15 ccm. n. Natronlauge wird es neutral. Beim Abdampfen der wässerigen Lösung bleibt eine ziemlich grosse Menge braungefärbter Krystalle zurück. Man kann sie leicht durch Destillation unter vermindertem Druck und darauf folgende Umkrystallisation aus Benzol reinigen. Sie schmelzen dann zw. 102°–104° und zeigen alle Reaktionen des Brenzcatechins. Auch stimmt die Analyse darauf,

Subst. 0.0864 g	CO_2	0.0419 g	H_2O	0.2060 g
gef.	C	65.03%	H	5.39%
als $C_6H_4(OH)_2$ ber.	,,	65.43 ,,	,,	5.49 ,,

Wir haben dann das mit Wasser gewaschene Oel der Wasserdampfdestillation unterworfen. Der mit Dampf leicht übergehende Teil beträgt ca. 120 g. Der Destillationsrückstand enthält noch etwas Brenzcatechin und daneben ca. 8 g. in Wasser löslicher, aber nicht krystallisierbarer Phenole, deren Natur aber noch nicht weiter untersucht wurde. Die gesammte Menge des gereinigten Brenzcatechins beträgt ca. 30 g.

Das mit Dampf leicht flüchtige Oel, welches schon bei 20° zu destillieren beginnt, wurde erst in drei Teile, von 20° bis 150°, 150°–200°, und über 200° fracktioniert. Der erste unterhalb 150° siedende Teil, welcher das Hauptdestillat bildet, wurde sorgfältig fraktioniert, wobei folgende vier Franktionen genommen wurden:

60°–70° (7 g.), 90°–100° (14 g.), 120°–130° (12 g.), 140°–150° (11 g.).(1) Bei der Rektifikation siedeten die einzelnen Fraktionen innerhalb dreier Grade: 66°–69°, 96°–99°, 122°–125°. Sie werden bei Schütteln mit conc. Schwefelsäure warm und teils braun gefärbt und haben folgende Eigenschaften:

	Sp. G. $\frac{17.5^\circ}{4^\circ}$.	Mol. Gew. (nach Dampf-Dichte). (1)	(2)	C : H (nach Elementar Analyse, kein Sauerstoff).	Prozent des Broms welche diese sättigt.(2)
66°–69°	0.6826	85,	86	1 : 2.04	61 %
96°–99°	0.7126	99,	100	1 : 2.03	59 ,,
122°–125°	0.7392	111,	118	1 : 2	60 ,,

Hach den gewonnenen Resultaten ist es höchst wahrscheinlich, dass wir Gemische von Hexan und Hexylen, Heptan und Heptylen, Octan und Octylen in der Hand haben. Die durch conc. Schwefelsäure nicht angegriffenen Teile der Destillate von den Siedepunkten ca. 80°, 110° und 140° wurde durch Nitrieren, u. s. w. als frei von Benzol, Toluol und Xylol erkannt.

Bei der Franktionierung des zw. 150°–200° siedenden Teiles konnten wir keine überwiegende Franktion bekommen, deshalb haben wir das Destillat über 170° und das oberhalb 200° mit dem durch Wasserdampf schwer übergehenden Oele vereinigt.

Das in der Retorte zurückbleibende schwerer flüchtige Oel wurde mit Chlorcalcium getrocknet, unter 50 mm. Druck destilliert, wobei ungefähr die Hälfte zw. 80°–270° überging. Da wir aber fanden, dass das Destillat einige in Wasser unlösliche Phenole enthält, wurde das unter 50 mm. Druck unterhalb 180° siedende Destillat (ca. 80 g.) wiederholt mit verd. Kalilauge, dann mit Wasser gewaschen, mit Chlorcalcium getrocknet und über

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(1) Auf wiederholter Fraktionierung siedete dieſe Teil unverändert.

(2) Die Brommenge, welche für die Sättigung dieser Kohlenwasserstoffe nötig ist, wenn man den Letzteren völlig als Homologe der Ethylenreihe annimmt, ist als 100 gesetzt.

Natrium unter gewöhnlichem Drucke sorgfältig fractioniert, wobei alles zw. 170–270° herausdestilliert. Ungefähr die Hälfte siedet zw. 240–255°. Es giebt keine andere überwiegende Fraktion. Bei der wiederholten Fraktionierung des Destillates 240°–250°, wo innerhalb dreier Grade aufgefangen wurde, ist es uns nicht gelungen, einen hervorragenden Teil zu erhalten. Ebensowie alle niedriger siedenden Destillate, addiert dieser hoch siedender Teil Brom, reagirt teilweise mit conc. Schwefelsäure unter Wärmeentwickelung und Braunfärbung. Er hat folgende Eigenschaften:

Sp. G. $\frac{18°}{4°}$.	Mol. Gew.	C:H (nach Elementar Analyse, kein Sauerstoff).
0.8201	194.188	1 : 1.84

Nach diesem Resultate ist es sehr wahrscheinlich, dass wir hier auch ein Gemisch von Kohlenwasserstoffen vor uns haben und dass darin unter anderem solche von der Zusammensetzung von $C_{14}H_{28}$, $C_{14}H_{26}$, etc. existieren werden. Dieser Teil wird noch eine genauere Untersuchung verdienen.

Die alkalische Waschflüssigkeit wurde angesäuert, mit Benzol durchschüttelt und die Benzollösung mit wasserfreiem Natriumsulfat getrocknet. Nach dem Abdestillieren des Benzols wurde der Rückstand unter 50 mm. Druck fraktioniert, wobei alles zw. 140°–195° übergeht. Eine bedeutend hervorragende Fraktion wurde nicht bemerkt. Die Fraktionen haben alle die Reaktionen der mehrwertigen Phenole.

Die am höchsten siedenden Teile und der Rückstand bei der Destillation unter vermindertem Drucke wurden hauptsächlich als Gemische von Kohlenwasserstoffen und Phenolen erkannt. Aber die Trennung der beiden Körper wird dadurch erschwert, dass die Flüssigkeit beim Schütteln mit Kalilauge eine fast untrennbare Emulsion bildet, die in Aether oder Benzol vollständig übergeht und keine Alkaliverbindung, ausser dem überschüssigen Kali in der wässrigen Lösung, zurücklässt. Es ist bemerkenswert, dass sich die Eigenschaften dieser Teile immer mehr der Urushinsäure selbst nähern, je nachdem der Siedepunkt steigt. Wahrscheinlich bilden diese Substanzen alle Stufen der unvollständigen Zersetzung der Urushinsäure. Zum Schluss wollen wir diese Resultate in einer Tabelle zusammenfassen:

	Urushinsäure (800 g.).			
Gas.	Flüssigkeit (600 g.).			Festkörper.
a) Methan und höhere gesät. Kohlenwasserstoff (18 Liter).	Löslich in Wasser.	Unlöslich in Wasser.		Pechartig.
	a) Geringe Menge der Säure.	Flüchtig mit Wasserdampf (120 g.).	Schwerflüchtig mit Wasserdampf.	
b) Ungesät. Kohlenwasserstoff (60 g. als Bromverbindung).	*b*) Brenzcatechin (30 g.). *c*) Unkrystallisierbare Phenole (8 g.).	C_6H_{12}, C_6H_{14} C_7H_{14}, C_7H_{16} C_8H_{16}, C_8H_{18} etc.	*a*) $C_{14}H_{28}$, $C_{14}H_{26}$ (40 g.). *b*) Phenole (15 g.). *c*) Gemisch von Kohlenwasserstoffen und Phenolen. Sd. P. uber 270°. (300 g.).	

3. Die Oxydation mit Salpetersäure.

Unter den vielen Oxydationsmitteln greift die Salpetersäure die Urushinsäure am heftigsten an. 20 g. Urushinsäure wird in 200 g. Salpetersäure (sp. G. 1.46), welche sich in einem ca. 1 Liter fassenden Kolben befindet, tropfenweise eingetragen, stark geschüttelt und gekühlt, wobei der Lack unter Wärme- und Nitrosedampfentwickelung stark aufschwillt. Wenn alles zugesetzt ist, wird die Salpetersäure mit 200 g. Wasser verdünnt und eine

Stunde lang auf Wasserbade erwärmt, wobei das Meiste in Lösung geht und nur ein kleiner Teil als ein in Wasser unlöslicher, rotbraun gefärbter, halbfester Körper zurückbleibt. Im ganzen wurden 100 g. Urushinsäure oxydiert.(1)

Der halbfeste Körper wurde von der Lösung getrennt, die dann auf Wasserbade eingedampft wurde. Zuerest haben wir den ersteren Körper untersucht. Er ist gegen Salpetersäure nicht ganz beständig, sondern wird allmählich von ihr gelöst. Sein Geruch erinnert an aromatische Nitroverbindungen. Er wurde mit überhitztem Dampf ausgetrieben und das Destillat ausgeaethert. Nach dem Abdestillieren des Aethers bleibt eine geringe Menge einer mit Oel durchtränkten Krystallmasse zurück, welche nach dem Waschen mit Kalilauge und dem Umkrystallisieren aus Alkohol characteristisch riechende, leicht gelb gefärbte, schuppenförmige Krystalle liefert. Aber die Menge war so gering (0.05 g.), dass eine weitere Untersuchung unmöglich war. Der mit überhitztem Dampf nicht flüchtige Rückstand ist in Alkohol und Aether leicht löslich und ist eine Säure, deren Kalium- und Ammonium-Salze in Wasser mit rotbrauner Farbe löslich sind; die Calcium-, Barium-, Silber- und Kupfer-Salze sind in Wasser unlösliche, amorphe Körper. Das Kupfer-Salz wurde, nach dem Waschen mit Wasser und Trocknen bei 110°, analysiert,

Subst.	0.1228 g.	N (nass)	6.05 ccm., (21°, 766 mm.)		
,,	0.1468 ,,	H_2O	0.0624 g.,	CO_2	0.2420 g.
,,	0.3295 ,,	CuO	0.0648 ,,		

C 44.77%, H 4.74%, N 5.61%, Cu 15.71%, O 29.17%.

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(1) Die Urushinsäure wird schon durch verdünntere Salpetersäure (sp. G. 1.2) ziemlich stark angegriffen. Wir haben auch versucht mit solcher Säure 4 Tage lange den Lack zu oxydieren. Das Resultat war gleich, nur mit dem Unterschied, dass fast keine krystallisierbaren Nitrokörper entstehen.

Es ist wahrscheinlich, dass hier eine Mischung von Körpern vorliegt, welche aus den die Nitro- und Carbonsäuregruppe gleichzeitig enthaltenden grossen Molekeln bestehen.

Der in Salpetersäure löslich gewordene Teil giebt beim Abdampfen der Säure eine grosse Menge von Krystallen, welche meistenteils aus Oxalsäure bestehen, aber daneben noch andere Dicarbonsäuren enthalten. Zur Trennung derselben wurde zuerst der Krystallbrei von ihrer Mutterlauge (A) abgesaugt und der Rückstand aus möglichst wenig Wasser wiederholt umkrystalisiert, wobei leicht gelbgefärbte Krystalle vom Smp. 135°–6° isolirt wurden. Dieser Körper wird bei Anwendung von Tierkohle farblos, und nach wiederholter Umkrystallisation aus warmem Wasser schmilzt er schliesslich bei 138–9° und bildet meistens kleine Nadeln, aber auch oft grössere Blättchen. Er ist leicht löslich in Alkohol und Aceton, fast unlöslich in Benzol. Er wurde als eine Säure erkannt, die Alkalisalze sind in Wasser löslich, das Silbersalz aber unlöslich. Diese Eigenschaften, sowie die Analyse der Säure und des Silbersalzes deuten darauf hin, dass wir es hier mit der Korksäure zu thun haben.

Säure 0.1523 g. CO_2 0.3074 g. H_2O 0.1099 g.
gef. C 55.04 % H 8.07 %
ber. ($C_8H_{14}O_4$) „ 55.17 „ „ 8.05 „
Silbersalz 0.4700 g. Ag 0.2595 g.
gef. Ag 55.21 %
ber. ($C_8H_{12}O_4Ag_2$) „ 55.63 „

Die Mutterlauge (A) trübt sich beim Verdünnen mit Wasser, und durch Extraktion mit Aether erhält man daraus ein gelbgefärbtes Oel, welches bei mehrtägigem Stehen teilweise krystallisiert. Diese Krystalle bestehen aus noch sehr unreiner

Korksäure, deren Menge zusammen mit der oben beschriebenen etwa 6 g. beträgt. Die ausgeaetherte wässrige Lösung wurde mit Calciumcarbonat gekocht, filtriert und das Filtrat mit Tierkohle entfärbt. Es wurde dann mit Bleiessig gefällt, abfiltriert, der Rückstand mit Wasser gewaschen und mit Schwefelwasserstoff gespalten. Die vom Bleisulfid abfiltrierte Lösung liefert beim Verdampfen eine geringe Krystallmenge, welche nach dem Trocknen auf Ton ca. 1 g. wiegt. Das Produkt wurde unter 25 mm. Druck destilliert und nach wiederholter Umkrystallisation des Destillats aus Wasser bei 105° getrocknet; Schmelzpunkt 150°–170°. Obwohl es noch unrein ist, wurde es als Silbersalz analysiert, weil die Menge schon stark verringert war:

Subst. 0.1754 g. Ag 0.1086 g.
Ag 61.92%.

Es ist sehr wahrscheinlich, dass wir hier durch höheren Homologen verunreinigte Bernsteinsäure (Smp. 185°, Ag in Silbersalz 65%) in Händen haben.

4. Die Methylierung der Urushinsäure.

1.8 g. Natrium (entsprechend den Sauerstoffatomen in der Urushinsäure) wurde in 40 ccm. abs. Alkohol gelöst und 10 g. Urushinsäure hinzu gegeben, wobei eine schwarzgrüne Lösung entstand. Dann wurden 20 g. Methyljodid in diese Lösung eingetragen, welche sich dabei durch die vorsichgehende Reaktion erwärmt. Nach dem Erkalten wurde die Lösung noch zwei Stunden lang auf dem Wasserbade erwärmt, dann wurde der Alkohol und der Ueberschuss des Methyljodids abdestilliert. Der

Rückstand wurde in Aether gelöst, erst mit verd. Natronlauge,(1) dann wiederholt mit Wasser gewaschen und mit Chlorcalcium getrocknet. Wenn der Aether abgedampft ist, bleibt ein Oel zurück, welches ungefähr gleiche Farbe und Geruch, wie die ursprüngliche Säure besitzt, dessen Löslichkeit in kalten Alkohol aber stark vermindert ist. Es ist leicht löslich in Aether, Chloroform und Benzol. In alkoholischer Lösung wird es durch Eisenchlorid oder Alkali nicht gefärbt. Es ist viel beständiger, als Urushinsäure, selbst gegen Oxydation, und sogar starke Salpetersäure (sp. G. 1.48) oxydiert es nur allmählich. Auch beim Erhitzen bis 300° (Temperatur des Bades) unter 30 mm. Druck destilliert es nicht. Die Analyse und die Methoxylbestimmung (nach ZEISEL) wurden ausgeführt.

	Subst.	CO_2	H_2O	C	H
1)	0.2030 g.	0.5960 g.	0.1806 g.	80.08%	9.95%
2)	0.1856 ,,	0.5431 ,,	0.1631 ,,	79.80 ,,	9.83 ,,
			Im mittel	79.94 ,,	9.89 ,,
Vorläufig nach der Formel $C_{40}H_{54}O_4(CH_3)_4$ ber.				80.17 ,,	10.10 ,,

	Subst.	AgI	CH_3%	
1)	0.2181	0.2705	7.92	Im mittel 7.80%
2)	0.2041	0.2406	7.54	
3)	0.2270	0.2671	7.53	
4)	0.2071	0.2528	7.80	

Dass in der Urushinsäure selbst keine Methoxylgruppen vorhanden sind, ist durch einen besonderen Versuch konstatiert worden. Wenn man annimmt, dass alle Sauerstoffatome in Methoxylgruppen umgewandelt sind, so berechnet sich 9.13% für die

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(1) Zuweilen wird die Lösung durch Waschen mit Natronlauge wieder schwarzgrün. Es ist dies das Zeichen der unvollständigen Methylierung, und man kann sie durch Wiederholung des obigen Verfahrens sicher vervollständigen.

Methylgruppe. Es ist bis jetzt unmöglich, zu entscheiden, ob diese Verschiedenheit aus der Anwesenheit unmethylierbaren Sauerstoffes, oder aus dem etwaigen Versagen der ZEISEL'schen Methode in diesem Falle herzuleiten ist.

5. Die Acetylierung der Urushinsäure.

10 g. Urushinsäure wurden in 60 g. frisch destilliertem Essigsäureanhydrid gelöst und nach dreistündigem Erhitzen der Ueberschuss des Anhydrids abdestilliert. Der Rückstand wurde dann in Benzol gelöst, wiederholt mit verd. Natronlauge und Wasser gewaschen und mit Chlorcalcium getrocknet. Wenn das Benzol abdestilliert ist, hinterbleibt eine weniger als Urushinsäure braun gefärbte, dicke Flüssigkeit. Der Körper ist leicht in Alkohol, Aether und Benzol löslich und leicht verseifbar durch alkoholische Kalilauge. Die Analyse giebt folgendes Resultat:

	Subst.	CO_2	H_2O	C	H
1)	0.1335 g.	0.3634 g.	0.1018 g.	74.24%	8.53%
2)	0.1922 ,,	0.4686 ,,	0.1310 ,,	74.21 ,,	8.51 ,,
			Im mittel	74.23 ,,	8.52 ,,
Vorläufig als $C_{40}H_{54}O_4(C_2H_3O)_4$ ber.				74.75 ,,	8.63 ,,

Wir haben zur Acetylbestimmung das acetylierte Produkt mit alkoholischem Kali verseift, mit Schwefelsäure angesäuert und mit Wasserdampf abdestilliert. Das Destillat wurde mit Bariumhydroxydlösung neutralisiert, die Lösung eingedampft, mit Schwefelsäure versetzt und das geglühte Bariumsulfat gewogen. Aber das Resultat war leider ungenau, denn die Urushinsäure selbst liefert, wie in einen Parallelversuch festgestellt wurde, durch alkoholische Kalilauge wechselnde Mengen flüchtiger Säuren (vielleicht teilweise durch die Oxydation).

	Acetylurushinsäure	$BaSO_4$	Urushinsäure	$BaSO_4$	C_2H_3O% (Corrigiert).
1)	0.4510	0.3569	0.4417	0.1466	19.04
2)	0.5355	0.4094	0.6801	0.0995	23.71
				Im mittel	21.38
Vorläufig als $C_{40}H_{54}O_4(C_2H_3O)_4$ ber.					22.34

Aber wenigstens ist es sicher, dass die Sauerstoffatome der Urushinsäure zum grössten Teil acetyliert worden sind.

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Ueber die Anomalie der starken einwertigen Elektrolyte.

Von

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Einleitung.

Die Unanwendbarkeit des Ostwald'schen Verdünnungsgesetzes auf den starken Elektrolyten war schon seit Anfang der modernen Elektrochemie immer das Objekt lebhafter Diskussionen. Die verschiedenen Gedankenlinien, die man von theoretischer Ueberlegung oder experimenteller Beobachtung bekommt, können in folgender Weise geteilt werden.

1. Das Massenwirkungsgesetz ist gültig.
   a. Die Aequivalentleitfähigkeit ist das Mass für den Dissociationsgrad.
   b. Die Aequivalentleitfähigkeit ist kein Mass für den Dissociationsgrad.
2. Das Massenwirkungsgesetz ist nicht gültig.
   a. Die Aequivalentleitfähigkeit ist das Mass für den Dissociationsgrad.
   b. Die Aequivalentleitfähigkeit ist auch kein Mass für den Dissociationsgrad.

Es wird hier eine kurze Zusammenfassung der hauptsächlichsten Arbeit gegeben.

1. Das Massenwirkungsgesetz ist gültig.

Dass das Massenwirkungsgesetz nicht allgemein anwendbar ist, ist schon klar durch die anomale Natur der Gefrierpunkterniedrigung, da man hier mit der Leitfähigkeit nichts zu tun hat. Aber hier und da ist in einigen speziellen Fällen eine gute Uebereinstimmung mit dem Massenwirkungsgesetz beobachtet.

a. Die Aequivalentleitfähigkeit ist das Mass für den Dissociationsgrad.

Zwischen den organischen Säuren sieht man oft ziemlich starke Säure, deren Leitfähigkeit das Verdünnungsgesetz erfüllt. Nach den Messungen von OSTWALD (Zeitschr. f. physik. Chem., **3**, 170, 241, 369, 1889) ist das Gesetz bis zu den Säuren anwendbar, die Dissociationskonstante von 0.05 (Liter Mol.) haben.

Eine von den stärksten Säuren dieser Klasse ist Dichlorfluoressigsäure. Nach der Messung von SWARTS (Mém. publ. par l'Acad. de Belgique, 51, 1895) bei 24.7° bekommt man eine Dissociationskonstante von ca. 0.5 in Siemenseinheit für Liter Mol.

NOYES und ABBOTT (Zeitschr. f. physik. Chem., **16**, 125, 1895) haben die Thalliumsalze Chlorid, Bromat und Thiocyanid bei 39.75° auf ihre Löslichkeit in reinem Wasser und zu je zwei in gemeinschaftlicher Lösung untersucht. Aus der Löslichkeit wurde der Dissociationsgrad in der reinen wässerigen Lösung berechnet, unter der Annahme, dass das Massenwirkungsgesetz gültig ist. Hierbei ergaben sich von den verschiedenen Kombinationen übereinstimmende Werte für dieselbe Substanz. Die Werte des Dissociationsgrades, die aus der Leitfähigkeit berechnet wurden, stimmen auch vorzüglich mit den von den Löslichkeiten berechneten Werten überein. Die anderen ähnlichen Arbeiten von NOYES (Zeitschr. f. physik. Chem., **11**, 603, 1892), NOYES und WOODWORTH (ibid., **26**, 152, 1898) zeigen auch, dass die Anwendung des Massenwirkungsgesetzes und die Berechnung des Dissociationsgrades aus der Leitfähigkeit annähernd zuverlässig sind. ABEGG und CUMMING (Zeitschr. f. Elektrochem., **13**, 18, 1907) haben die Konzentrationsketten von Silbernitrat bei 25° gemessen. Die nach der einfachen NERNST'schen Formel von den Leitfähigkeiten berechneten Werte stimmen gut mit den beobachteten Werten überein. Da die NERNST'sche Formel das Massenwirkungsgesetz in sich enthält, so scheinen in diesem Falle die Anwendung des Massenwirkungsgesetzes und das Leitfähigkeitsprinzip gültig zu sein. Anderseits sieht man aber, dass das Verdünnungsgesetz für die Leitfähigkeiten der Silbernitratlösungen nicht anwendbar ist.

b. Die Aequivalentleitfähigkeit ist kein Mass für den Dissociationsgrad.

BILTZ (Zeitschr. f. physik. Chem., **40**, 185, 1902) hat verschiedene Salze auf dem Dampfdruck, Gefrierpunkt und Siedepunkt ihrer Lösungen untersucht. Der einzige Fall, wo das Massenwirkungsgesetz anwendbar war, war die Gefrierpunkterniedriegung von Caesiumnitratlösung. In einem Konzentrationsbereich von 0.0077–0.43 normal bekommt man konstante Werte für den bekannten Ausdruck $\frac{\alpha^2}{(1-\alpha)V}$. Aber die aus der Leitfähigkeit bei 25° berechneten Werte für den Dissociationsgrad stimmen nicht mit den kryoskopisch gefundenen überein. Die Leitfähigkeit scheint daher kein exaktes Mass für den Dissociationsgrad zu sein. Der Verfasser schreibt die Abweichung vom Massenwirkungsgesetz im andern Falle zu der Hydratation der Ionen.

ROTHMUND und DRUCKER (Zeitschr. f. physik. Chem., **46**, 827, 1903) haben die Verteilung der Pikrinsäure zwischen Wasser und Benzol bei 18° untersucht. Es ergab sich eine gute Bestätigung des Massenwirkungsgesetzes. Aber die Berechnung aus der Leitfähigkeit weicht ganz von dem Gesetz ab. Eine andere Untersuchung von DRUCKER (ibid., **49**, 563, 1904) auf die Verteilung von Trichloressigsäure, Trichlorbuttersäure und Dichloressigsäure hin zeigt auch die Gültigkeit vom Massenwirkungsgesetz. Aber die Berechnungen sind etwas komplizierter und unsicherer als die mit der Pikrinsäure, da die Halogenfettsäure sich in Benzol polymerisiert. Die Abweichung der Leitfähigkeit von dem Verdünnungsgesetz ist viel kleiner als stärkere Säure. Es wurde darauf aufmerksam gemacht, dass die Unsicherheit der Beweglichkeit von Wasserstoffion einen grossen Einfluss auf die Berechnung der Dissociationskonstante hat. BOGDAN (Zeitschr. f. Elektrochem., **11**, 824, 1905) hat auch eine ähnliche Methode bei der Verteilung von Salpetersäure zwischen Wasser und Aether angewendet und annähernde Gültigkeit vom Massenwirkungsgesetz gefunden. Der Verfasser (ibid., **12**, 489, 1906) hat diesen Versuch weiter fortgesetzt. Er fand, dass die Leitfähigkeit der verdünnten Lösungen von Salpetersäure in äthergesättigtem Wasser das OSTWALD'sche Gesetz erfüllt. Beim Verteilen ist das

Massenwirkungsgesetz auch gültig unter Berücksichtigung von passender Dissociation in der Aetherphase.

DANNEEL (ibid., **11**, 249, 1905) setzt die Beweglichkeit von Ionen als eine lineare Funktion von totaler Konzentration an und hat für Kaliumchlorid und Natriumchlorid eine annähernde Anwendbarkeit des Verdünnungsgesetzes gefunden.

2. Das Massenwirkungsgesetz ist nicht gültig.

a. Die Aequivalentleitfähigkeit ist das Mass für den Dissociationsgrad.

ARRHENIUS (Zeitschr. f. physik. Chem., **11**, 391, 1893; **31**, 197, 1899; **36**, 28, 1901) hält immer seinen Standpunkt fest, dass die aus der Leitfähigkeit berechneten Werte des Dissociationsgrades die richtigen seien. Nach seiner Untersuchung über die Aenderung der katalytischen Wirkung der Essigsäure durch Salzzusatz hat der Zusatz von starken Ionen einen bedeutenden Einfluss auf den Dissociationsgrad der schwachen Säure, und zwar vermehrt er die Dissociation. Dieselbe kann auch mit der starken Elektrolyte selbst stattfinden.

Vom rein empirischen Standpunkte aus wurde die OSTWALD'sche Formel zuerst von RUDOLPHI und VAN'T HOFF in der wohlbekannten Form geändert. Diese wurde von STORCH (ibid., **19**, 13, 1896) und BANCROFT (ibid., **31**, 188, 1899) zu der Form

$$K = \frac{c_i^n}{c_n}$$

verallgemeinert. Darin bezeichnet c_i und c_n respektiv die Konzentration der Ionen und die der nichtdissocierten

Moleküle, und K und n sind zwei Konstante, deren Wert sich je nach dem betreffenden Stoff ändert.

KOHLRAUSCH (Leitvermögen der Elektrolyte, S. 107; Sitzgsber. d. Berl. Akad., **44**, 1002, 1900) hat die zwei folgenden empirischen Formeln für die Beziehung zwischen der Konzentration η, der Aequivalentleitfähigkeit λ, und derselben für die unendliche Verdünnung λ_∞ gegeben:

$$\lambda_\infty - \lambda = a\,\eta^{\frac{1}{3}}$$

$$\frac{\lambda_\infty - \lambda}{\lambda^p} = c\,\lambda^{\frac{1}{2}}$$

a, p und c sind für jeden Elektrolyten charaktersistische Konstante. Wenn man diese Formeln unter der Annahme, dass der Ausdruck $\frac{\lambda}{\lambda_\infty}$ dem Dissociationsgrad gleich ist, umformt, so bekommt man für die erste

$$A = \frac{c^{1.333}}{c_n}$$

und für die zweite

$$B = \frac{c_i^p\, c^{1.5-p}}{c_n}$$

Darin bezeichnen A und B zwei Konstante und c die totale Konzentration.

BARMWATER (Zeitschr. f. physik. Chem., **28**, 115, 1899) hat aus der theoretischen Ueberlegung eine Formel entwickelt, die für sehr verdünnte Lösung mit der ersten Gleichung KOHLRAUSCHS identisch ist. Die Gleichung ist

$$\lambda_\infty - \lambda = g\sqrt[3]{\lambda c} \qquad (g = \text{konstant}).$$

Da λ von sehr verdünnter Lösung fast konstant ist, so resultiert die erste Gleichung KOHLRAUSCHS. Für schwache Elektrolyten nimmt der Verfasser zwei Hypothesen an, ausserdem die in der Haupttheorie enthaltenen. Dieselben sind 1.): dass die schwache Elektrolyte wie Essigsäure sich in der Lösung polymerisiert, 2.): dass aber diese Reaktion nur auf die rotierende Bewegung der Ionen Einfluss hat. In seinem späteren Versuche (ibid., 28, 424, 1899; ibid., 45, 557, 1904; ibid, 56, 225, 1906) über die Leitfähigkeit der gemischten Elektrolyten, sind die Ueberreinstimmungen von dem beobachteten und theoretisch berechneten Werte ziemlich gut.

Liebenow (Zeitschr. f. Elektrochem., 8, 933, 1902) hat von der Hypothese, dass das in der Nähe der Molekel befindliche Ion auf dieselbe zunächst eine drehende, dann eine zerreissende Wirkung ausübt, die folgende Formel entwickelt:

$$\frac{\alpha^2}{(1-\alpha)V} = A + B\left(\frac{\alpha}{V}\right)^{\frac{2}{3}}$$

Darin bezeichnet α den Dissociationsgrad, V die Verdünnung und A und B zwei Konstante. Die aus dieser Formel berechneten Werte für λ stimmen nicht schlecht zu den Zahlen Kohlrauschs.

Liebenow (Zeitschr. f. Elektrochem., 11, 301, 1905) hat auch eine andere Formel

$$\frac{c_i^{2-r}}{c_n} e^{-k\int_{c_{oi}}^{c_i} \frac{d\,c_n}{c_i}} = K$$

entwickelt. Die Annahme, die der Ableitung dieser Formel zugrunde liegt, ist, dass das Gleichgewicht zwischen verschiedenen Sorten von Wassermolekülen beim Auflösen von Salz geändert wird. Die Auflösung des Integrals erfolgt durch sukzessive Näherungsrechnung. Die Uebereinstimmung der berechneten Werte mit den Zahlen KOHLRAUSCHS ist bei Kaliumchlorid sehr gut.

v. STEINWEHR (ibid., **7**, 685, 1901) hat im Anschluss an TAMMANS Ansichten und Experimente über den Binnendruck von Lösungen eine Korrektion zum Massenwirkungsgesetz eingebracht. Die Grösse des Druckeinflusses wurde aus dem Einfluss von Salzzusatz auf die Zuckerinversion annähernd berechnet. Die so korrigierten Zahlen sind weniger veränderlich mit der Verdünnung, als die von der Leitfähigkeit direkt berechneten Werte von $\frac{c_i^2}{c_n}$.

b. Die Aequivalentleitfähigkeit ist kein Mass für den Dissociationsgrad.

DIETERICI (Wied. Ann., **62**, 616, 1897) und PLANCK (Zeitschr. f. physik. Chem., **41**, 222, 1902) haben schon einige Einwände gegen die Leitfähigkeitsmethode gemacht. Die Meinung ist, dass die Anwendung einer dynamischen Methode, wie diejenige der Leitfähigkeit, für die Untersuchung von Problemen statischer Natur nicht berechtigt ist.

Viele Autoren, wie VAN DER WAALS, VAN LAAR, NERNST, JAHN, haben die Theorie für die nicht ideale verdünnte Lösung entwickelt. Die NERNST'sche (Zeitschr. f. physik. Chem., **38**, 487, 1901) und die JAHN'sche (ibid., **37**, 490, 1901; **41**, 257, 1902) sind mit einander sehr verwandt. JAHN geht von den Gleichungen PLANCKS aus. In den einfachen PLANCK'schen Formeln sind der Gesamtenergiegehalt und das Gesamtvolumen einer ideal verdünnten Lösung als eine lineare Funktion von entsprechenden Grössen der vorhandenen Stoffarten dargestellt. JAHN führt ausserdem verschiedene quadratische Glieder in der Gleichung ein. NERNST nimmt eine mit der Lösung koexistierende ideale Gasphase an und bringt die Korrektion in das Teilungsverhalten jeder Stoffart.

Die von beiden Autoren entwickelten Gleichungen für die Gefrierpunktserniedrigung oder für das Massenwirkungsgesetz sind wohl formal verschieden, aber im Inhalt fast gleich.

JAHN ist schon von seiner früheren Arbeit (Zeitschr. f. physik. Chem., **27**, 354, 1898; **33**, 545, 1900; **35**, 1, 1900), wo er das Massenwirkungsgesetz beibehalten wollte, immer der Gegner des Leitfähigkeitsprinzipes geblieben.

JAHN (ibid., **50**, 129, 1904) hat nach seiner Formel die entsprechenden Koeffizienten in Korrektionsglieder aus den Beobachtungen auf die Gefrierpunktserniedrigung und die Konzentrationskette berechnet. Daraus schliesst er, dass die Beweglichkeit des Kalium- und Natriumion im Konzentrationsintervall 0.025–0.1 normal im Betrag von 13–15% sich ändert.

MALMSTRÖM (Zeitschr. f. Elektrochem., **11**, 797, 1905) hat eine Theorie der Lösung entwickelt. Es wurde zuerst unter Benutzung der VAN DER WAALS'schen Gleichung eine Gleichung für die freie Energie des gelösten Stoffes. Die JAHN'sche Formel kann als ein spezieller Fall daraus abgeleitet werden. Der Verfasser hat auch eine neue Zustandsgleichung unter Berücksichtigung des gegenseitigen elektrischen Einflusses von Ionen abgeleitet. Hieraus bekommt man eine andere Formel für das Gleichgewicht.

Die Formeln geben keine Konstante, wenn die Ionenkonzentrationen aus Leitfähigkeit berechnet werden.

Zusammenfassend dürfen wir sagen, dass noch viel übrig bleibt, um diese verwickelte Frage zu lösen. Der NERNST-JAHN'sche Gedankengang ist zumeist rationell. Aber die daraus geschlossene Aenderung der Ionenbeweglichkeit scheint etwas zu gross zu sein. Die folgende Berechnung wurde aufgenommen, um zu untersuchen, ob in irgend einer Weise die Gedankenlinie von NERNST und JAHN mit der von STORCH und BANCROFT verbunden werden kann. Es wurde kein neues experimentales Material beigefügt, sondern nur die wertvollen Beobachtungen verschiedener Autoren frei benutzt.

Aequivalentleitfähigkeit.

Man hat überhaupt keinen direkten Beweis dafür, dass die Beweglichkeit von Ionen konstant bleibt. Nur so weit als die Ueberführungszahl konstant ist und das KOHLRAUSCH'sche Gesetz, verbunden mit dem HITTORF'schen Gesetz die übereinstimmenden Werte für Ionenbeweglichkeit gibt, bleibt es höchst wahrscheinlich, dass die Ionenbeweglichkeit konstant ist. Nach diesem Gedanken muss man, für die höchste Konzentration bis ca. 0.1 normal, nur die Leitfähigkeit der einwertigen binären Elektrolyten als vertrauenswert aufnehmen. Die zweiwertigen dreiionigen Elektrolyten zeigen meistens veränderliche Ueberführungszahl (HOPFGARTNER, Zeitschr. f. physik. Chemie, **25**, 115, 1898; NOYES, ibid., **36**, 74, 1901; JAHN, ibid., **58**, 6, 1907). Bariumnitrat hat nach Noyes eine konstante Ueberführungszahl, aber der von Kohlrausch gegebene Wert für λ_∞ ist ungefähr 4% grösser als der aus der Ueberführungszahl und der Beweglichkeit von Nitration berechnete. Mit den zweiwertigen binären Elektrolyten ist die Sache ebenso (Redlich, ibid., **37**, 707, 1901; Gans, Drude's Ann., **6**, 315, 1901; Jahn, Zeitschr. f. physik. Chem.. **58**, 6, 1907).

In der folgenden Berechnung wurden die Beobachtungen von Kohlrausch und Maltby (Sitzgsber. Berl. Akad., 1899, S. 665) und Kohlrausch und v. Steinwehr (ibid., 1902, S. 581) benutzt. Die Storch-Bancroft'sche Formel ist

$$K=\frac{c_i^n}{c_n}$$

d. i.

$$n \log c_i - \log c_n = \text{konstant.}$$

Wenn man diese Formel auf Kohlrausch's Zahlen anwendet, so sieht man, dass der Wert $\frac{\Delta \log c_n}{\Delta \log c_i}$ nicht konstant ist, sondern sich gewöhnlich mit der Verdünnung vermehrt. Diese Beziehung ist zwar deutlich mit Alkalihaloiden. Es wurde also eine möglichst allgemein anwendbare empirische Formel gesucht, die gleichzeitig möglichst wenige Konstante enthält. Die folgende etwas komplizierte Formel passt sehr gut auf die Beobachtungen:

$$K=\frac{c_i^n}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}$$

d. i. $$ln\, K = n\, ln\, c_i - ln\, c_n - 0.3\frac{c_i^2}{c_n}\, ln\, \frac{c_i}{c_n}$$

d. i. $$ln\, K = n\, ln\, \frac{\lambda}{\lambda_\infty} c - ln\, \frac{\lambda_\infty - \lambda}{\lambda_\infty} c - 0.3\frac{\lambda^2 c}{(\lambda_\infty - \lambda)\,\lambda_\infty}\, ln\, \frac{\lambda}{\lambda_\infty - \lambda}$$

In den obigen Gleichungen und den nachfolgenden Tabellen sind die Bezeichnungen wie folgt:

K	Eine Konstante.
c_i	Die Konzentration des Ions in Gm. Mol. per Liter.
c_n	Dieselbe der neutralen, nicht dissocierten Moleküle.
$c_i + c_n = c$	Die totale Konzentration.
n	Eine Konstante.
λ	Die Aequivalentleitfähigkelt für die Konzentration c.
λ_∞	Dieselbe für die unendliche Verdünnung.

Diese Bezeichnungen werden nachher beibehalten.

Hier sieht man vier Konstanten, K, n, λ_∞ und 0.3. Also hat diese Gleichung eine Konstante mehr, als die **Storch-Bancroft**'sche Formel, aber die vierte Konstante 0.3 ist für alle Substanzen anwendbar.

Die Resultate der Berechnung sind in den folgenden Tabellen zusammengestellt. In Kolonne B stehen die Werte der nach der **Bancroft**'schen Formel berechneten Konstanten. Dieselben wurden nachher für die Berechnung der Gefrierpunktserniedrigung benützt. Die Werte von λ_∞ wurden durch Probieren bestimmt.

Kaliumchlorid: 18°: $\lambda_\infty = 130.00$.

$$K = \frac{c_i^{1.51}}{c_n} \left(\frac{c_i}{c_n} \right)^{-0.3 \frac{c_i^2}{c_n}}, \quad B = \frac{c_i^{1.46}}{c_n}.$$

c	λ	K	B
0.0001	129.07	1.24	2.00
0.0002	128.77	1.31	2.07
0.0005	128.11	1.34	2.04
0.001	127.34	1.32	1.97
0.002	126.31	1.32	1.94
0.005	124.41	1.32	1.89
0.01	122.43	1.32	1.89
0.02	119.96	1.32	1.90

0.05	115.76	1.32	1.94
0.1	112.03	1.33	2.02
0.2	107.96	1.33	—
0.5	102.41	1.30	—
1	98.27	1.21	—
		Mittel	1.97

Natriumchlorid: 18°: $\lambda_\infty = 108.97$.

$$K = \frac{c_i^{1.505}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}, \quad B = \frac{c_i^{1.47}}{c_n}.$$

c	λ	K	B
0.0001	108.10	1.16	1.63
0.0002	107.82	1.23	1.70
0.0005	107.18	1.24	1.67
0.001	106.49	1.24	1.65
0.002	105.55	1.24	1.64
0.005	103.78	1.23	1.62
0.01	101.95	1.23	1.62
0.02	99.62	1.23	1.63
0.05	95.71	1.23	1.66
0.1	92.02	1.23	1.70
0.2	87.73	1.24	—
0.5	80.94	1.27	—
1	74.35	1.27	—
		Mittel	1.65

Lithiumchlorid: 18°: $\lambda_\infty = 98.94$.

$$K = \frac{c_i^{1.502}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}, \quad B = \frac{c_i^{1.48}}{c_n}.$$

c	λ	K	B
0.0001	98.14	1.18	1.47
0.0002	97.85	1.21	1.50

0.0005	97.19	1.17	1.43
0.001	96.52	1.18	1.43
0.002	95.62	1.18	1.44
0.005	93.92	1.18	1.44
0.01	92.14	1.17	1.44
0.02	89.91	1.18	1.45
0.05	86.42	1.18	1.49
0.1	82.42	1.17	1.51
0.2	77.93	1.17	—
0.5	70.71	1.17	—
1	63.36	1.12	—
		Mittel	1.46

Caesiumchlorid : 18° : $\lambda_\infty = 133.3$.

$$K = \frac{c_i^{1.52}}{c_n} \left(\frac{c_i}{c_n} \right)^{-0.3 \frac{c_i^2}{c_n}}, \quad B = \frac{c_i^{1.48}}{c_n}.$$

c	λ	K	B
0.0001	132.30	1.08	1.59
0.0002	132.00	1.17	1.70
0.0005	131.38	1.25	1.77
0.001	130.68	1.28	1.80
0.002	129.52	1.24	1.71
0.005	127.47	1.23	1.68
0.01	125.20	1.20	1.63
—	—	—	—
—	—	—	—
0.1	113.55	1.24	1.77
		Mittel	1.71

Kaliumnitrat: 18°: $\lambda_\infty = 126.40$.

$$K = \frac{c_i^{1.53}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}, \quad B = \frac{c_i^{1.5}}{c_n}.$$

c	λ	K	B
0.0001	125.50	1.03	1.36
0.0002	125.18	1.09	1.44
0.0005	124.44	1.08	1.41
0.001	123.65	1.09	1.41
0.002	122.60	1.10	1.42
0.005	120.47	1.10	1.40
0.01	118.19	1.09	1.39
0.02	115.21	1.08	1.39
0.05	109.86	1.07	1.39
0.1	104.79	1.07	1.40
0.2	98.74	1.08	—
0.5	89.24	1.11	—
1	80.46	1.14	—
		Mittel	1.40

Natriumnitrat: 18°: $\lambda_\infty = 105.38$.

$$K = \frac{c_i^{1.51}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}, \quad B = \frac{c_i^{1.48}}{c_n}.$$

c	λ	K	B
0.0001	104.55	1.12	1.51
0.0002	104.19	1.11	1.46
0.0005	103.53	1.11	1.44
0.001	102.85	1.13	1.46
0.002	101.89	1.13	1.45
0.005	100.06	1.14	1.44
0.01	98.16	1.13	1.44

0.02	95.66	1.13	1.44
0.05	91.43	1.13	1.45
0.1	87.24	1.12	1.46
0.2	82.28	1.12	—
0.5	74.05	1.12	—
1	65.86	1.12	—
		Mittel	1.45

Lithiumnitrat: 18°: $\lambda_\infty = 95.22$.

$$K = \frac{c_i^{1.508}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}.$$

c	λ	K
0.0001	94.46	1.19
0.0002	94.15	1.19
0.0005	93.52	1.16
0.001	92.87	1.17
0.002	91.97	1.16
0.005	90.33	1.17
0.01	88.61	1.16
0.02	86.41	1.16
0.05	82.72	1.16
0.1	79.19	1.16
0.2	75.01	1.17
0.5	67.98	1.17
1	60.77	1.16

Kaliumiodat: 18°: $\lambda_\infty = 98.37$.

$$K = \frac{c_i^{1.534}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}.$$

Natriumiodat: 18°: $\lambda_\infty = 77.32$.

$$K = \frac{c_i^{1.54}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}.$$

c	λ	K	λ	K
0.0001	97.64	.96	76.69	.82
0.0002	97.34	.97	76.44	.85

0.0005	96.72	.97	75.83	.81
0.001	96.04	.97	75.19	.80
0.002	95.04	.96	74.30	.80
0.005	93.19	.96	72.62	.80
0.01	91.24	.96	70.86	.81
0.02	88.64	.96	68.56	.81
0.05	84.06	.95	64.43	.81
0.1	79.67	.96	60.46	.81
0.2	74.34	.96	55.45	.78

Lithiumiodat: 18°: $\lambda_\infty = 67.27$. Kaliumbromid: 18°: $\lambda_\infty = 132.18$.

$$K = \frac{c_i^{1.54}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}. \qquad K = \frac{c_i^{1.5}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}, \quad B = \frac{c_i^{1.45}}{c_n}.$$

c	λ	K	λ	K	B
0.0001	66.66	.74	131.15	1.25	2.06
0.0002	66.43	.77	130.86	1.35	2.14
0.0005	65.87	.75	130.15	1.37	2.08
0.001	65.27	.75	129.38	1.37	2.04
0.002	64.43	.74	128.32	1.38	2.00
0.005	62.89	.75	126.40	1.37	1.98
0.01	61.23	.75	124.40	1.37	1.96
0.02	59.05	.75	121.87	1.37	1.96
0.05	55.26	.75	117.78	1.37	2.02
0.1	51.50	.75	114.22	1.38	2.11
0.2	46.88	.73	110.40	1.37	—
0.5	38.98	.68	105.37	1.31	—
1	31.21	.68	—	—	—
				Mittel	2.04

Kaliumiodid: 18°: $\lambda_\infty=130.95$. Kaliumthiocyanat: 18°: $\lambda_\infty=121.25$.

$$K=\frac{c_i^{1.495}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}. \qquad K=\frac{c_i^{1.5}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}.$$

c	λ	K	λ	K
0.0001	129.76	1.12	120.22	1.14
0.0002	129.50	1.28	120.02	1.34
0.0005	128.97	1.44	119.38	1.36
0.001	128.25	1.46	118.64	1.35
0.002	127.21	1.44	117.65	1.35
0.005	125.33	1.44	115.81	1.34
0.01	123.44	1.44	113.95	1.34
0.02	121.10	1.44	111.59	1.34
0.05	117.26	1.44	107.74	1.35
0.1	113.98	1.44	104.28	1.35
0.2	—	—	—	—
0.5	—	—	95.69	1.31
1	—	—	91.61	1.22

Kaliumchlorat: 18°: $\lambda_\infty=119.60$. Kaliumfluorid: 18°: $\lambda_\infty=111.22$.

$$K=\frac{c_i^{1.52}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}. \qquad K=\frac{c_i^{1.52}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}.$$

c	λ	K	λ	K
0.0001	118.63	1.00	110.47	1.19
0.0002	118.35	1.09	110.22	1.27
0.0005	117.68	1.12	109.57	1.21
0.001	116.92	1.13	108.89	1.21
0.002	115.84	1.13	107.91	1.19
0.005	113.84	1.13	106.16	1.19
0.01	111.64	1.11	104.28	1.18
0.02	108.81	1.11	101.87	1.18

0.05	103.74	1.09	97.73	1.18
0.1	99.19	1.10	94.02	1.19
0.2	93.73	1.12		
0.5	85.28	1.14		

Natriumfluorid: 18°: $\lambda_\infty = 90.13$. Thalliumchlorid: 18°: $\lambda_\infty = 130.98$.

$$K = \frac{c_i^{1.52}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}. \qquad K = \frac{c_i^{1.65}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}.$$

c	λ	K	λ	K
0.0001	89.35	.93	130.33	.49
0.0002	89.06	.97	130.00	.50
0.0005	88.49	.99	129.18	.49
0.001	87.86	1.01	128.23	.49
0.002	86.99	1.02	126.81	.49
0.005	85.27	1.01	123.73	.49
0.01	83.48	1.01	120.21	.49
0.02	81.10	1.00		
0.05	77.03	1.00		
0.1	73.14	1.00		

Thalliumnitrat: 18°: $\lambda_\infty = 127.40$. Silbernitrat: 18°: $\lambda_\infty = 115.65$.

$$K = \frac{c_i^{1.58}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}. \qquad K = \frac{c_i^{1.55}}{c_n}\left(\frac{c_i}{c_a}\right)^{-0.3\frac{c_i^2}{c_n}}.$$

c	λ	K	λ	K
0.0001	126.63	.76	115.01	1.10
0.0002	126.30	.79	114.56	.94
0.0005	125.61	.79	113.88	.94
0.001	124.70	.79	113.14	.95
0.002	123.48	.79	112.07	.95
0.005	121.11	.78	110.03	.95

0.01	118.38	.79	107.80	.95
0.02	—	—	—	—
0.05	107.93	.79	99.50	.94
0.1	101.19	.78	94.33	.95

In der folgenden Tabelle sind die Werte von λ_∞, n und die Mittelwerte von K im Konzentrationsbereich 0.001–0.1 normal zusammengestellt. Die von Kohlrausch für λ_∞ gegebenen Werte sind auch unter Kolonne λ_k wiedergegeben.

	λ_k	λ_∞	n	K
$K\,Cl$	130.10	130.00	1.510	1.32
$Na\,Cl$	108.99	108.97	1.505	1.23
$Li\,Cl$	98.88	98.94	1.502	1.18
$Cs\,Cl$	133.60	133.30	1.520	1.24
$K\,NO_3$	126.50	126.40	1.530	1.09
$Na\,NO_3$	105.33	105.38	1.510	1.13
$Li\,NO_3$	95.18	95.22	1.502	1.16
$K\,IO_3$	98.49	98.37	1.534	.96
$Na\,IO_3$	77.42	77.32	1.540	.81
$Li\,IO_3$	67.36	67.27	1.540	.75
$K\,Br$	132.30	132.18	1.500	1.37
$K\,I$	131.10	130.95	1.495	1.44
$K\,CNS$	121.30	121.25	1.500	1.35
$K\,ClO_3$	119.70	119.60	1.520	1.11
$K\,F$	111.35	111.22	1.520	1.19
$Na\,F$	90.15	90.13	1.520	1.01
$Te\,Cl$	131.47	130.98	1.650	.49
$Te\,NO_3$	127.75	127.40	1.580	.79
$Ag\,NO_3$	115.80	115.65	1.550	.95

Die Werte für λ_∞ erfüllt das Kohlrausch'sche Gesetz gut, wie man aus der folgenden Tabelle ersieht.

	K	Dif.	Na	Dif.	Li	Dif.	Tl
Cl	130.00	21.03	108.97	10.03	98.94	32.04	130.98
NO_3	126.40	21.02	105.38	10.16	95.22	32.18	127.40
IO_3	98.37	21.00	77.37	10.10	67.27		
F	111.22	21.09	90.13				

Für die Säuren hat man Unsicherheit, da die Beweglichkeit des Wasserstoffions noch nicht sicher bestimmt ist. KOHLRAUSCH (Sitzgsber. Berl. Akad., 1901, S. 1026) setzt die Beweglichkeit des Wasserstoffions bei 18° zu 318 an. In dem Handbuch von OSTWALD und LUTHER ist der Wert 314 gegeben. Nach NOYES und SAMMET (Zeitschr. f. physik. Chem., **43**, 49, 1903) und JAHN (ibid., **58**, 6, 1907) ist die Ueberführungszahl des Wasserstoffions gleich 0.833. Hieraus berechnet man den Wert 329.8 für die Beweglichkeit des Wasserstoffions. Der Unterschied zwischen den bezeichneten Werten ist ziemlich gross. In den Abhandlungen von DRUCKER (Zeitschr. f. Elektrochem., **13**, 81, 1907) und KOHLRAUSCH (ibid., **13**, 333, 1907) wurden einige Kritiken über diesen Punkt gemacht, aber die Sache ist noch nicht entschieden.

In der folgenden Berechnung mit der Pikrinsäure und Dichloressigsäure wurde die Beobachtung von DRUCKER (Zeitschr. f. physik. Chem., **49**, 565, 567, 1904) benutzt. Die Werte für λ_∞ wurden wie früher nur empirisch bestimmt.

Pikrinsäure: 18°: $\lambda_\infty = 341.5$.

$$K = \frac{c_i^{1.8}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}, \quad B = \frac{c_i^{1.82}}{c_n}.$$

c	λ	K	B
0.001088	338.1	.36	—
0.002175	336.6	.42	.45

0.004350	332.9	.41	.44
0.008700	327.1	.42	.45
0.01740	318.0	.42	.46
0.03480	302.3	.41	.44
		Mittel	.45

Drucker gibt den Wert 342 für λ_∞.

Dichloressigsäure: 18°: $\lambda_\infty=351.0$.

$$K=\frac{c_i^{1.8}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}},\quad A=\frac{c_i^2}{c_n}.$$

c	λ	K	A
0.001202	340.0	0.137	0.0740
0.00240	329.5	0.114	0.0515
0.00481	317.4	0.119	0.0510
0.00962	297.0	0.115	0.0513
0.01924	271.3	0.115	0.0557
0.03848	240.0	0.116	0.0612
0.07695	206.5	0.116	0.0690
0.1539	168.2	0.114	0.0718

Die Werte A sind diejenigen, die von Drucker nach dem Verdünnungsgesetz unter Benutzung des Wertes $\lambda_\infty=345$ berechnet wurden.

Für die Monobromessigsäure, die auch von Drucker bei 18° gemessen wurde, ist der Wert vom Ausdruck $\left(\frac{c_i}{c_n}\right)^{0.3\frac{c_i^2}{c_n}}$ fast gleich eins. Die Abweichungen hatten keinen Einfluss auf die dritte Stelle von Konstanten und können vernachlässigt werden. Der Wert von n ist auch gleich 2, d. h. das einfache Verdünnungsgesetz ist anwendbar. Die Sache ist gleich auch mit schwächeren Säuren.

Man sieht also aus obigen Berechnungen, dass die Formel:

$$K = \frac{c_i^n}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}$$

ganz allgemein für jede Sorte von einwertigen Elektrolyten anwendbar ist. Da die Ausdrücke $\left(\frac{c_i}{c_n}\right)^{0.3\frac{c_i^2}{c_n}}$ gemeinsam für jeden Elektrolyten sind, so nehmen wir an, dass diese Korrektion einer allgemeinen Eigenschaft von Ionen entspricht. Andererseits sind die Werte n von jedem Molekül charakteristisch und ändern sich je nach der Natur von neutralen Molekülen.

Man denkt nach Nernst (Zeitschr. f. physik. Chem., **38**, 488, 1901) eine Lösung, die auf n_1, n_2, n_3 Molekeln gelöster Stoffe N Moleküle Wasser enthält und eine in Berührung mit der Lösung existierende Dampfphase, in der die Dampfdrücke von gelösten Molekülen gleich π_1, π_2, π_3 sind und der des Wassers gleich p ist. Man nimmt an, dass für jeden Dampf die Gesetze von perfektem Gas anwendbar sind.

Von einwertigem Elektrolyt, setzen wir an:

n_1 = Die Molekülzahl des neutralen Moleküls.
$n_2 = n_3$ = Dieselbe von Kathion oder Anion.
π_1 = Der Dampfdruck von neutral. Molekülen.
$\pi_2 = \pi_3$ = Derselbe von Kathion oder Anion.

Zunächst nehmen wir Folgendes an:

$$\pi_1 = A_1 \frac{n_1}{N}\left(\frac{n_2}{N}\right)^s$$

$$\pi_2 = A_2 \frac{n_2}{N}\left(\frac{n_2}{n_1}\right)^{r\frac{n_2^2}{n_1 N}}$$

Für verdünnte Wasserlösungen können wir ansetzen:

$$\frac{n_1}{N} = b\,c_n, \qquad \frac{n_2}{N} = b\,c_i\,;$$

folglich haben wir :

$$\pi_1 = a_1 \, c_n \, c_i^s \qquad \text{(1)}$$

$$\pi_2 = a_2 \, c_i \left(\frac{c_i}{c_n} \right)^{l \frac{c_i^2}{c_n}} \qquad \text{(2)}$$

In obigen Gleichungen bezeichnen A_1, A_2, a_1, a_2, S, r und l alle Konstanten, und b das Molekularvolumen des Wassers in Litern.

Nun ergibt sich in der Dampfphase das Aequilibrium :

$$\frac{\pi_2^2}{\pi_1} = \text{konstant} \qquad \text{(3)}$$

Setzen wir (1) und (2) ein, so ergibt sich :

$$\frac{c_i^2 \left(\frac{c_i}{c_n} \right)^{2l \frac{c_i^2}{c_n}}}{c_n \, c_i^s} = \text{konstant}$$

Setzen wir an :

$$2 - s = n, \qquad 2\,l = -0.3$$

dann bekommt man die Formel :

$$\frac{c_i^n}{c_n} \left(\frac{c_i}{c_n} \right)^{-0.3 \frac{c_i^2}{c_n}} = K.$$

Die Annahmen (1) und (2) können mit den Beobachtungen auf die elektromotorische Kraft der Konzentrationskette und auf das Teilungsverhältnis geprüft werden.

Konzentrationskette.

Nach NERNST (l. c.) ist die Beziehung zwischen den Dampfdrücken und Konzentrationen folgende :

$$N \frac{dp}{p} + n_1 \frac{d\pi_1}{\pi_1} + 2 n_2 \frac{d\pi_2}{\pi_2} = 0 \qquad \text{(4)}$$

Nach HELMHOLTZ ist das Potentialinkrement dE von der einer einwertigen Anion umkehrbar arbeitenden Lösung gleich :

$$dE = -\frac{RT}{F} u_k \frac{1}{c} \frac{dp}{p} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Darin bezeichnet R die Gaskonstante $=8{,}315$ Joule, F 96540 Coulomb, T die Absoluttemperatur, u_k die Ueberführungszahl von Kathion und $C = \frac{n_1 + n_2}{N}$ die totale Molekularkonzentration.

Nach der Gleichung (3) ergiebt sich nun:

$$\frac{d\pi_1}{\pi_1} = 2 \frac{d\pi_2}{\pi_2}$$

Hieraus ergiebt sich von der Gleichung (4):

$$N \frac{dp}{p} + 2(n_1 + n_2) \frac{d\pi_2}{\pi_2} = 0$$

d. i.

$$\frac{1}{c} \frac{dp}{p} = -2 \frac{d\pi_2}{\pi_2}$$

Deshalb hat man von (5):

$$dE = \frac{RT}{F} u_k \, 2 \frac{d\pi_2}{\pi_2}.$$

Integriert man zwischen π_2'' und π_2', so ergiebt sich:

$$E = \frac{RT}{F} u_k \, 2 \, (ln \, \pi_2'' - ln \, \pi_2'),$$

Aus der Gleichung (2) haben wir nun:

$$ln \, \pi_2 = ln \, a_2 + ln \, c_i + l \frac{c_i^2}{c_n} ln \frac{c_i}{c_n}.$$

Hieraus ergiebt sich:

$$E = \frac{RT}{F} u_k \, 2 \left(ln \frac{c_i''}{c_i'} + l \frac{c_i''^2}{c_n''} ln \frac{c_i''}{c_n''} - l \frac{c_i'^2}{c_n'} ln \frac{c_i'}{c_n'} \right) \ldots\ldots(6)$$

worin

$$l = -0.15.$$

In den folgenden Berechnungen wurden die Messungen von Jahn (Zeitschr. f. physik. Chem., **33**, 559, 1900; ibid., **41**, 295,

1902) von den Konzentrationsketten, die aus Kalium bezw. Natriumchlorid bestehen und die von Chlorion umkehrbare Elektrode haben, benutzt. c bezeichnet die totalen Konzentrationen in Mol. pro Liter, E *beob.* die beobachteten elektromotorischen Kräfte, E *ber.* die Werte berechnet nach der obigen Formel (6), E_n die nach der einfachen NERNST'schen Formel berechneten, E_j die von JAHN berechneten. Die Werte von λ für entsprechende Konzentrationen sind nach JAHN für Kaliumchlorid aus der empirischen Formel

$$\lambda = 131.75 - 43.314\, c^{\frac{1}{3}}$$

und für Natriumchlorid aus der Formel

$$\lambda = 110.75 - 40.887\, c^{\frac{1}{3}}$$

berechnet.

Kaliumchlorid.

$n_k = 0.497, \qquad T = 291.$

c	λ	E *beob.*	E *ber.*	E_n
0.033473	117.79	0.05403	0.05434	0.05578
0.0033467	125.27			
0.016693	120.68	0.03806	0.03819	0.03907
0.0033467	—			
0.011174	122.07	0.02856	0.02876	0.02937
0.0033467	—			
0.0083496	122.96	0.02176	0.02182	0.02225
0.0033467	—			
0.0066959	123.59	0.01643	0.01661	0.01693
0.0033467	—			
0.033494	117.79	0.07028	0.07097	0.07291
0.0016697	126.61			

0.016693	120.68	0.05424	0.05479	0.05616
0.0016697	—			
0.011138	122.08	0.04497	0.04526	0.04637
0.0016697	—			
0.0083294	122.97	0.03844	0.03839	0.03932
0.0016697	—			
0.0067000	123.58	0.03330	0.03321	0.03402
0.0016697	—			
0.0055685	124.07	0.02895	0.02878	0.02950
0.0016697	—			

c	λ	E beob.	E ber.	E_n	E_j
0.05009	115.78	0.02125	0.02115	0.02198	0.02128
0.02000	119.99				
0.03507	117.57	0.01288	0.01302	0.01348	0.01309
0.02000	119.99				
0.03003	118.29	0.02561	0.02578	0.02655	0.02602
0.01000	122.42				
0.01999	119.99	0.01608	0.01632	0.01676	0.01650
0.01000	122.42				
0.01000	122.42	0.01595	0.01624	0.01663	—
0.00505	124.34				
0.02000	119.99	0.03215	0.03258	0.03341	—
0.00505	124.34				

Natriumchlorid.

$u_k=0.396$, $T=291$.

c	λ	E beob.	E ber.	E_n
0.033439	97.58	0.05614	0.05670	0.05775
0.0016738	105.89			
0.016734	100.29	0.04360	0.04386	0.04457
0.0016738	—			

0.011172	101.61	0.03608	0.03627	0.03681
0.0016738	—			
0.0083642	102.45	0.03073	0.03082	0.03124
0.0016738	—			
0.0066860	103.05	0.02652	0.02657	0.02692
0.0016738	—			

c	λ	*E beob.*	*E ber.*	E_n	E_j
0.06005	94.74	0.01255	0.01271	0.01309	0.01279
0.03002	98.04				
0.05007	95.68	0.01670	0.01693	0.01742	0.01700
0.02000	99.65				
0.03999	96.77	0.01268	0.01280	0.01317	0.01287
0.02000	99.65				
0.03003	98.04	0.02058	0.02055	0.02105	0.02071
0.01000	101.94				
0.02000	99.65	0.01293	0.01301	0.01330	0.01314
0.01000	101.94				
0.02000	99.65	0.02558	0.02619	0.02672	—
0.00500	103.76				
0.01000	101.94	0.01323	0.01317	0.01341	0.01339
0.005000	103.76				

Die berechneten Werte sind noch etwas grösser als die beobachteten, aber der Unterschied ist höchstens wenige zehntausendstel Volt. *E ber.* stehen näher zu den beobachteten, als die Werte E_j, die von JAHN nach seiner Formel berechnet wurden. Man kann allgemein sagen, dass die Uebereinstimmung zwischen den berechneten und den beobachteten Werten ziemlich befriedigend ist und dass die bezeichnete Annahme in diesem Falle bestätigt wird.

Teilungsverhältnis.

Wenn ein Elektrolyt zwischen Wasser und einem anderen Lösungsmittel geteilt wird und im bezeichneten Lösungsmittel keine Dissociation oder Polymerisation stattfindet, so ist die Konzentration (z) im zweiten Lösungsmittel proportional mit dem Dampfdruck (π_1) des neutralen Moleküls in der koexistierenden Dampfphase. Es ergiebt sich deshalb nach der Gleichung (1):

$$z = h\, c_n\, c_i^s. \quad (h = \text{konstant}) \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Ein starker Elektrolyt, welcher in dieser Beziehung ausführlich untersucht wurde, ist die Pikrinsäure (ROTHMUND und DRUCKER, Zeitschr. f. physik. Chem., 46, 827; 1903). Es wurde die Pikrinsäure bei 18° zwischen Wasser und Benzol geteilt und das Verhältnis sorgfältig bestimmt. Um die Resultate mit der obigen Formel zu prüfen, muss man zuerst die Werte von λ für entsprechende Konzentrationen wissen. Da die beschriebene komplizierte Formel nicht bequem für die Interpolation ist, wurde die folgende empirische Formel benützt. Diese passt gut zu den Beobachtungen im Konzentrationsbereich 0.002–0.017 normal.

$$\lambda = 342.9 - 372.5\, c^{\frac{2}{3}}.$$

c	λ *beob.*	λ *ber.*
0.002175	336.6	336.6
0.004350	332.9	333.0
0.008700	327.1	327.1
0.01740	318.0	317.9

In der folgenden Tabelle sind die Konzentrationen vom neutral Molekül (c_n) im Wasser, die Konzentration im Benzol (z) und die Werte (h) von dem Verhältnis zwischen z und $c_n\, c_i^s$ gegeben.

Der Wert s ist gleich 0.2 nach der Berechnung für Leitfähigkeit (s. o.).

c	z	c_n	$h=\frac{z}{c_n\, c_i^{0.2}}$.
0.01994	0.06996	0.00148	105
0.01701	0.05225	0.00116	104
0.01357	0.03453	0.00079	105
0.01011	0.01993	0.00047	106
0.00913	0.01647	0.00040	104
0.00710	0.01011	0.00026	106
0.003273	0.002248	0.000065	109
0.002079	0.000932	0.000029	112

Man kann auch in umgekehrter Weise berechnen. Nach Rothmund und Druckers Auffassung ist hier das einfache Massenwirkungsgesetz anwendbar, und daraus berechneten die Autoren folgende Werte für die Konstante:

$$\frac{c_i^2}{c_n}=0.164$$

$$\frac{c_n}{z}=0.0281.$$

Setzen wir an:

$$c=c_i+c_n,$$

so sieht man leicht:

$$c=0.0281\,z+\sqrt{0.164\times 0.0281\,z}.$$

Die Werte von c berechnet aus den Werten von z nach dieser Formel stimmen gut mit den beobachteten Werten überein. Wenn man die obige Gleichung nach z löst, so bekommt man:

$$z=\frac{0.164+2c}{2\times 0.0281}\left\{1-\sqrt{1-\left(\frac{2c}{0.164+2c}\right)^2}\right\}$$

Für die Berechnung ist die folgende annähernde Form bequemer:

$$z=\frac{0.164+2c}{2\times 0.0281}\left\{\frac{1}{2}\left(\frac{2c}{0.164+2c}\right)^2+\frac{1}{8}\left(\frac{2c}{0.164+2c}\right)^4\right\}$$

Es wird hier diese Formel als eine empirische Gleichung benutzt, die die Beziehung zwischen z und c zeigt.

In der folgenden Tabelle sind die Werte z aus der obigen Gleichung und c_n und c_i direkt aus den beobachteten Werten von λ berechnet.

c	c_n	z	$h=\frac{z}{c_n\, c_i^{0.2}}$.
0.001088	0.0000108	0.000253	92
0.002175	0.0000312	0.00100	110
0.00435	0.000110	0.00390	106
0.00870	0.000367	0.0149	106
0.01740	0.00120	0.0546	104
0.03480	0.00399	0.1886	(95)

Die Werte von h, ausser demjenigen in der Klammer, sind konstant unter der Grenze der Versuchsfehler.

Aus den oben gegebenen Berechnungen von beiden Seiten kann man das Teilungsverhältnis der Pikrinsäure gleich gut erklären nach der Annahme:

$$\pi_1=a_1\, c_n\, c_i^s,$$

wie nach dem einfachen Massenwirkungsgesetz. Nur muss man nach dem Massenwirkungsgesetz die Werte von Leitfähigkeit als unzuverlässig abwerfen, während man im anderen Falle diese dem Teilungsverhältnis anpassen kann.

Gefrierpunktserniedrigung.

Die Beziehung zwischen dem Dampfdruck und dem Gefrierpunkt ist nach DIETERICI (Wied. Ann., **52**, 263; 1894) von der folgenden Gleichung gegeben:

$$ln\,\frac{p_0}{p}=\frac{t\,\rho}{RT\,T_0}\left(1-\frac{c_1-c_2}{2}\,\frac{T_0}{\rho}\,\frac{t}{T}\right)$$

Darin ist $\frac{p_0}{p}$ das Verhältnis der Dampfdrücke vom reinen Lösungsmittel und der Lösung; ρ die Molekularschmelzwärme, T_0 der Gefrierpunkt des reinen Lösungsmittels und $T=T_0-t$ derjenige der Lösung; c_1-c_2 ist die Differenz der Molenkularwärmen vom flüssigen und festen Lösungsmittel. Bei Gefrierpunktserniedrigungen bis zu wenigen Dezigraden von Wasserlösungen können die Korrektionen vernachlässigt werden, wenn man den Fehler von wenigen Tausendsteln nicht berücksichtigt. Dann ergiebt sich die einfache Formel:

$$ln\,\frac{p_0}{p}=\frac{t\,\rho}{RT^2}\;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Nach NERNST hat man nun die Beziehung:

$$N\frac{dp}{p}+n_1\,\frac{d\pi_1}{\pi_1}+2n_2\,\frac{d\pi_2}{\pi_2}=0\quad\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Ferner setzen wir an:

$$\frac{n_1}{N}=b\,c_n,\quad \frac{n_2}{N}=b\,c_2$$

$$c_n=M_n,\quad c_i=M_i,\quad c_n+c_i=c=M;$$

$$\pi_1=a_1\,c_n\,c_i^s\ldots\ldots\ldots\ldots\ldots(1);\qquad \pi_2=a_2\,c_i\left(\frac{c_i}{c_n}\right)^{l\frac{c_i^2}{c_n}}\ldots\ldots\ldots\ldots\ldots(2)$$

Darin c, c_n, c_i sind die in Mol. pro Liter ausgedrückten Konzentrationen, und M, M_n, M_i die Konzentrationen, die in Mol. pro 1000 gr. Wasser ausgedrückt sind.

Von (1) bekommt man:

$$ln\,\pi_1 = ln\,a_1 + ln\,c_n + s\,ln\,c_i.$$

Differenziert man diese Gleichung, so ergiebt sich:

$$\frac{d\pi_1}{\pi_1} = \frac{d\,c_n}{c_n} + s\frac{d\,c_i}{c_i}.$$

Aehnlicherweise ergiebt sich von der Gleichung (2):

$$ln\,\pi_2 = ln\,a_2 + ln\,c_i + l\frac{c_i^2}{c_n}\,ln\frac{c_i}{c_n},$$

$$\frac{d\pi_2}{\pi_2} = \frac{d\,c_i}{c_i} + l\left\{\frac{c_i}{c_n}\,d\,c_i - \frac{c_i^2}{c_n^2}\,d\,c_n + ln\frac{c_i}{c_n}\left(\frac{2\,c_i}{c_n}\,d\,c_i - \frac{c_i^2}{c_n^2}\,d\,c_n\right)\right\}$$

Setzt man die Werte für $\frac{d\pi_1}{\pi_1}$ und $\frac{d\pi_2}{\pi_2}$ in die Gleichung (4), so bekommt man:

$$-\frac{1}{b}\,\frac{dp}{p} = \frac{n_1}{N}\,\frac{d\,c_n}{c_n} + \frac{n_1}{N}\,s\,\frac{d\,c_i}{c_i} + 2\,\frac{n_2}{N}\,\frac{d\,c_i}{c_i}$$
$$+2\,l\,\frac{n_2}{N}\left\{\frac{c_i}{c_n}\,d\,c_i - \frac{c_i^2}{c_n^2}\,d\,c_n + ln\frac{c_i}{c_n}\left(\frac{2\,c_i}{c_n}\,d\,c_i - \frac{c_i^2}{c_n^2}\,d\,c_n\right)\right\}.$$

Nach den Annahmen für die Werte $\frac{n_1}{N}$ und $\frac{n_2}{N}$ bekommt man:

$$-\frac{1}{b}\,\frac{dp}{p} = d\,c_n + s\,\frac{c_n}{c_i}\,d\,c_i + 2\,d\,c_i$$
$$+2\,l\left\{\frac{c_i^2}{c_n}\,d\,c_i - \frac{c_i^3}{c_n^2}\,d\,c_n + ln\frac{c_i}{c_n}\left(\frac{2\,c_i^2}{c_n}\,d\,c_i - \frac{c_i^3}{c_n^2}\,d\,c_n\right)\right\} \quad \ldots(9)$$

Diese Gleichung ist nicht direkt integrierbar. Aber bei starken Elektrolyten ist die Summe der Integrale vom zweiten und vierten Gliede nur ein Korrektionsglied von höchstens einigen Prozenten der Totalwerte. Deshalb kann man ohne viele Fehler eine

Annäherungsmethode aufnehmen. Also nehmen wir hier die STORCH-BANCROFT'sche Formel an.

$$c_i^{2-p} = B\, c_n.$$

d. i.
$$(2-p)\,\frac{d\,c_i}{c_i} = \frac{d\,c_n}{c_n}.$$

Wenn man diese Werte in die Gleichung (9) einsetzt, so ergiebt sich:

$$-\frac{1}{b}\,\frac{dp}{p} = d\,c_n + 2\,d\,c_i + \frac{s}{2-p}\,d\,c_n$$
$$+2\,l\,B\,\{(p-1)\,c_i^p\,d\,c_i + p\,(ln\,B)\,c_i^p\,d\,c_i + (p^2-p)\,(ln\,c_i)\;c_i^p\,d\,c_i\}.$$

Da

$$d\{c_i^{p+1}\,ln\,c_i\} = (1+p)\,c_i^p\,ln\,c_i\,d\,c_i + c_i^p\,d\,c_i,$$

so ist die letzte Gleichung gleich:

$$-\frac{1}{b}\,\frac{dp}{p} = d\,c_n + 2\,d\,c_i + \frac{s}{2-p}\,d\,c_n$$
$$+\frac{2\,l\,B}{1+p}\Big\{(p-1)\,d\,c_i^{1+p} + p(ln\,B)\,d\,c_i^{1+p} + (p^2-p)\,d\,(c_i^{1+p}\,ln\,c_i) - \frac{p^2-p}{1+p}\,d\,c_i^{1+p}\Big\}.$$

Durch Integration zwischen p' und p entsprechend c' und c bekommt man:

$$\frac{1}{b}\,ln\,\frac{p'}{p} = c_n + 2c_i + \frac{s}{2-p}\,c_n + \frac{2\,l\,B}{(1+p)^2}\,c_i^{1+p}\{p-1+p(1+p)\,ln\,B + (p^2-1)\,p\,ln\,c_i\}$$
$$-c_n' - 2c_i' - \frac{s}{2-p}\,c_n' - \frac{2\,l\,B}{(1+p)^2}\,(c_i')^{1+p}\{p-1+p(1+p)\,ln\,B + (p^2-1)\,p\,ln\,c_i'\}.$$

Wenn man mathematisch exakt bis zu $c=0$ integriert, so bekommt man anomalische Resultate, da der Grenzwert des Ausdruckes $c_i^{1+p}\,ln\,c_i$ unendlich wird. Deshalb integriert man z. B. bis zu der Konzentration $c_i = 10^{-1000}$. Dann ergiebt sich:

$$(c_i')^{1+p}\,ln\,c_i' = -\,10^{-1000\,(1+p)} \times 2.303 \times 1000.$$

Diese Werte und diejenigen anderer Glieder, die c_i' und c_n' enthalten, sind ganz vernachlässigbar, da p immer positiv ist und zwischen 0 und 1 liegt.

Nehmen wir an, dass der Dampfdruck von 10^{-1000} normal Lösung demjenigen von reinem Wasser p_0 gleich ist, so bekommen wir:

$$\frac{1}{b} \, ln \, \frac{p_0}{p} = c_n + 2\,c_i + \frac{s}{2-p}\,c_n$$
$$+ \frac{2\,l\,B}{(1+p)^2}\,c_i^{1+p}\{p-1+p\,(1-p)\,2.303 \log B + (p^2-1)\,p\,2.303 \log c_i\}$$

Nach der Gleichung (8) ergiebt sich:

$$\frac{t\,\rho}{b\,R\,T^2} = c_n + 2\,c_i + \frac{s}{2-p}\,c_n$$
$$+ \frac{2\,l\,B}{(1+p)^2}\,c_i^{1+p}\{p-1+p(1-p)2.303 \log B + (p^2-1)p\,2.303 \log c_i\} \ldots (10)$$

In den folgenden Berechnungen ist der Wert $\frac{b\,RT^2}{\rho}$ gleich 1.86 gesetzt. l ist für alle Substanzen gleich -0.15, aber s, p, und B sind verschieden je nach den Substanzen, t ist die beobachtete Gefrierpunktserniedrigung, und *L beob.* ist der Wert $\frac{t}{1.86}$. λ ist von der für jede Substanz gegebenen empirischen Formel berechnet, und daraus sind die Werte *L ber.* nach der Gleichung (10) berechnet. L_r ist der entsprechende Wert, der nach der einfachen RAOULT'schen Formel berechnet wurde.

Kaliumchlorid.

t nach JAHN (Zeitschr. f. physik. Chem., **50,** 144, 145, 1905).
$\lambda = 131.33 - 41.88\, c^{\frac{1}{3}}$ nach JAHN.

$s=0.49,\quad p=0.54,\quad B=1.97,\quad \lambda_\infty=130.00$

c	t	λ	*L beob.*	*L ber.*	L_r
0.1002	0.3470	111.88	0.1865	0.1852	0.1864
0.07576	0.2640	113.61	0.1419	0.1408	0.1420
0.05117	0.1799	115.78	0.0967	0.0959	0.0968
0.05043	0.1765	115.86	0.0949	0.0945	0.0954
0.04050	0.1426	116.95	0.0767	0.0762	0.0769
0.03777	0.1340	117.26	0.0721	0.0712	0.0718
0.03024	0.1071	118.28	0.0576	0.0572	0.0578
0.02534	0.0893	119.03	0.0480	0.0480	0.0485

Natriumchlorid.

t nach JAHN (l. c.).
$\lambda = 110.48 - 39.90\, c^{\frac{1}{3}}$ nach JAHN.

$s=0.495,\quad p=0.53,\quad B=1.65,\quad \lambda_\infty=108.97$

c	t	λ	*L beob.*	*L ber.*	L_r
0.1004	0.3484	91.93	0.1873	0.1862	0.1851
0.07582	0.2648	93.59	0.1424	0.1414	0.1409
0.05035	0.1770	95.75	0.0952	0.0947	0.0946
0.04112	0.1453	96.72	0.0781	0.0776	0.0776
0.03803	0.1341	97.06	0.0721	0.0719	0.0719
0.03058	0.1087	98.00	0.0584	0.0580	0.0581
0.02520	0.0895	98.78	0.0481	0.0480	0.0481

t nach OSAKA (Zeitschr. f. physik. Chem., **41,** 562, 1902).
$\lambda = 110.75 - 40.887\, c^{\frac{1}{3}}$ nach JAHN (für verdünntere Lösungen).

c	t	λ	L *beob.*	L *ber.*	L_r
0.010069	0.03646	101.92	0.01960	0.01952	0.01959
0.008470	0.03037	102.42	0.01633	0.01637	0.01643
0.006834	0.02438	102.99	0.01311	0.01325	0.01329
0.005179	0.01878	103.67	0.01011	0.01007	0.01011
0.003495	0.01274	104.55	0.00685	0.00682	0.00685
0.001778	0.00662	105.80	0.00355	0.00349	0.00350

Lithiumchlorid.

t nach JAHN (l. c.).
$\lambda = 100.54 - 39.13\, c^{\frac{1}{3}}$ nach JAHN.

$s = 0.498,\quad p = 0.52,\quad B = 1.46,\quad \lambda_\infty = 98.94$

c	t	λ	L *beob.*	L *ber.*	L_r
0.09732	0.3431	82.54	0.1844	0.1810	0.1785
0.07462	0.2648	84.07	0.1424	0.1395	0.1380
0.05053	0.1794	86.07	0.0964	0.0951	0.0945
0.03771	0.1352	87.42	0.0727	0.0713	0.0710
0.02503	0.0909	89.09	0.0489	0.0477	0.0476

Caesiumchlorid.

t nach JAHN (l. c.)
$\lambda = 135.47 - 47.26\, c^{\frac{1}{3}}$ nach JAHN.

$s = 0.48,\quad p = 0.52,\quad B = 1.71,\quad \lambda_\infty = 133.3$

c	t	λ	L *beob.*	L *ber.*	L_r
0.1041	0.3572	113.24	0.1921	0.1939	0.1926
0.07719	0.2677	115.35	0.1439	0.1446	0.1440

0.05182	0.1818	117.85	0.0978	0.0978	0.0976
0.03890	0.1378	119.46	0.0741	0.0738	0.0738
0.02560	0.0914	121.54	0.0491	0.0489	0.0489

Kaliumbromid.

t nach Jahn (l. c.).
$\lambda = 133.19 - 41.49\, c^{\frac{1}{3}}$ nach Jahn.

$s = 0.50, \quad p = 0.55, \quad B = 2.04, \quad \lambda_{\infty} = 132.18$

c	*t*	λ	*L beob.*	*L ber.*	L_r
0.1018	0.3493	113.82	0.1878	0.1880	0.1895
0.07642	0.2639	115.59	0.1419	0.1420	0.1433
0.05087	0.1775	117.82	0.0954	0.0953	0.0962
0.03831	0.1345	119.20	0.0723	0.0722	0.0729
0.02541	0.0902	121.00	0.0485	0.0482	0.0486

Kaliumnitrat.

t nach Loomis (Wied. Ann., **59**, 504, 1896).
λ nach Kohlrausch. $\lambda_{0.025}$ ist in folgender Weise berechnet.

$$\lambda_{0.02} - \lambda_{0.025} = \frac{\lambda_{0.02} - \lambda_{0.05}}{0.05^{\frac{1}{3}} - 0.02^{\frac{1}{3}}} (0.025^{\frac{1}{3}} - 0.02^{\frac{1}{3}}).$$

$s = 0.47, \quad p = 0.5, \quad B = 1.40, \quad \lambda_{\infty} = 126.40$

c	*t*	λ	*L beob.*	*L ber.*	L_r
0.2	0.6388	98.74	0.3435	0.3647	0.3562
0.1	0.3314	104.79	0.1782	0.1852	0.1829
0.05	0.1705	109.86	0.0917	0.0939	0.0935
0.025	0.0864	113.38	0.0465	0.0474	0.0474
0.02	0.0703	115.21	0.0378	0.0382	0.0382
0.01	0.0346	118.19	0.0186	0.0193	0.0194

Natriumnitrat.

t nach LOOMIS (l. c.).
λ nach KOHLRAUSCH. $\lambda_{0.025}$ berechnet in gleicher Weise wie für $K\,NO_3$.

$s=0.49$, $p=0.52$, $B=1.45$, $\lambda_\infty=105.38$

c	t	λ	*L beob.*	*L ber.*	L_r
0.2	0.6689	82.28	0.3597	0.3649	0.3562
0.1	0.3426	87.24	0.1842	0.1853	0.1828
0.05	0.1722	91.43	0.0926	0.0940	0.0934
0.025	0.0866	94.51	0.0466	0.0475	0.0474
0.02	0.0689	95.66	0.0370	0.0382	0.0382
0.01	0.0355	98.16	0.0191	0.0194	0.0193

Pikrinsäure.

t nach OSAKA (Zeitschr. f. physik. Chem., **46**, 844, 1903).
$\lambda=342.9-372.5\,c^{\frac{2}{3}}$.

$s=0.2$, $p=0.18$, $B=0.45$, $\lambda_\infty=341.5$

c	t	λ	*L beob.*	*L ber.*	L_r
0.01785	0.06014	317.5	0.03234	0.0348	0.03448
0.01624	0.05493	319.0	0.02953	0.0317	0.03141
0.01384	0.04864	321.4	0.02615	0.0271	0.02686
0.01149	0.04140	323.9	0.02226	0.0225	0.02239
0.01145	0.04082	324.0	0.02195	0.0226	0.02231
0.00839	0.03083	327.5	0.01658	0.0165	0.01644
0.00460	0.01757	332.6	0.00945	0.0091	0.00908
0.00456	0.01763	332.7	0.00948	0.0090	0.00900

Wie man aus obigen Zusammenstellungen ersieht, ist die Uebereinstimmung zwischen den beobachteten und den berechneten Werten nicht immer gut. Aber beim Vergleichen der aus der Leitfähigkeit bei 18° berechneten Werte direkt mit den von der Gefrierpunktserniedrigung bekommenen Werten, hat man angenommen, dass $ln\frac{p_0}{p}$ von der Temperatur unabhängig ist. Wenn man denkt, dass ausserdem einige Annäherungen und Vernachlässigungen bei der Berechnung aufgenommen wurden, so dürfte man sagen, dass die Uebereinstimmung meistens befriedigend ist.

Es werden hier einige qualitative Bemerkungen aus den obigen Tabellen gegeben.

Kaliumchlorid dissociert in der Nähe von 0.1 normal nach Leitfähigkeit mehr als Natriumchlorid, aber seine Gefrierpunktserniedrigung ist kleiner als die des letzt genannten. Die Berechnung nach der Gleichung (10) zeigt aber, dass das Kaliumchlorid wirklich kleineren Wert von $ln\frac{p_0}{p}$ hat.

Vom Lithiumchlorid zeigt die einfache Berechnung aus der Leitfähigkeit viel kleinere Dissociation als nach dem Gefrierpunkt. Wenn man die Korrekturen nach der Gleichung (10) einführt, so wird der Unterschied viel geringer.

Kaliumbromid zeigt nach der einfachen Berechnung gerade das Gegenteil von Lithiumchlorid, aber nach der Einführung der Korrektion stimmen die berechneten mit den beobachteten Werten sehr gut überein.

Kaliumnitrat, Natriumnitrat und Pikrinsäure zeigen bei Einführen der Korrektion viel mehr Unterschied zwischen den beobachteten und den berechneten Werten, als nach einfachen Berechnungen. Die Werte $ln\frac{p_0}{p}$ bei 0° sind kleiner, als diejenigen bei 18°.

Verdünnungswärme.

Die Wärmeentwicklung Q bei Zusatz von 1 Mol. Wasser zu einer grossen Menge der Lösung ist nach KIRCHHOFF:

$$Q = -RT^2 \frac{d\,ln\,\frac{p_0}{p}}{d\,T}.$$

Deshalb ist die Wärmeentwicklung W beim Verdünnen:

$$W = -RT^2 \int \frac{d\,ln\,\frac{p_0}{p}}{d\,T}\,dm$$

darin bezeichnet dm das Inkrement der Wassermoleküle. Von dem absoluten Wert des Integrals kann man nichts sagen, aber im allgemeinen: je positiver der Ausdruck $\frac{d\,ln\,\frac{p_0}{p}}{d\,T}$ ist, desto negativer wird der Wert von W.

Wenn man die Tabelle für Gefrierpunkte beobachtet, so ersieht man, dass der Koeffizient $\frac{d\,ln\,\frac{p_0}{p}}{d\,T}$ viel positiver bei Nitraten, als bei Chloriden ist. Also muss die Verdünnungswärme von Nitraten viel negativer, als diejenige von Chlorid sein.

Die folgenden Zahlen sind von den in LANDOLTS Tabelle gegebenen THOMSEN'schen Beobachtungen berechnet. Die Zahlen geben in Kilogrammkalorien die Wärmeentwicklung, welche eintritt, falls eine Lösung von 2 gr. Aequivalent Salz in 100 Mol. Wasser auf eine Lösung von m Mol. verdünnt wird.

m	$NaNO_3$	$NaCl$	NH_4NO_3	NH_4Cl
200	−0.572	−0.25	−0.44	−0.016
400	−0.904	−0.35	−0.65	−0.016

Man sieht übereinstimmend mit der obigen Ueberlegung, dass die Verdünnungswärme von Nitraten viel negativer ist, als diejenige von Chloriden.

Zusammenfassung.

1. Es wurde eine empirische Formel:

$$K=\frac{c_i^{2-s}}{c_n}\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}$$

vorgeschlagen. Diese Formel passt gut mit den Beobachtungen der Leitfähigkeit von jeder Sorte von einwertigen Elektrolyten.

2. In Verknüpfung mit der NERNST'schen Theorie von Lösungen wurden zwei Annahmen gemacht:

$$\pi_1=a_1\, c_n\, c_i^s,$$

$$\pi_2=a_2\, c_i\left(\frac{c_i}{c_n}\right)^{-0.3\frac{c_i^2}{c_n}}.$$

3. Die erste Annahme passt gut zu den Beobachtungen von Konzentrationsketten.

4. Die zweite Annahme scheint auch durch das Teilungsverhältnis bestätigt zu sein.

5. Die aus den zwei Annahmen berechneten Werte für Gefrierpunktserniedrigung stimmen meistens mit den Beobachtungen gut überein.

6. Die Veränderung von $ln\frac{p_0}{p}$ mit der Temperatur, zeigt qualitativ dieselbe Beziehung wie die Verdünnungswärme.

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Coagulation of Colloidal Aluminium Hydroxide by Electrolytes.

By

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1. Introduction.

Physical chemistry, in its application to the problems of biology, achieved many brilliant conquests with comparative ease, particularly by means of the theory of osmotic pressure and that of the mass-action. But the progress has been impeded by several circumstances. Particularly the colloidal nature of the substances which form living bodies seemed to present insurmountable difficulties. Yet through the combined labour of physical chemists and physiologists these difficulties are being removed one by one; and at present there is no branch of physical chemistry which is cultivated with greater ardour and whose progress is watched with keener interest than the so-called colloid-chemistry. Of all the results obtained in this field the most definite and at the same time the most interesting from the chemical stand-point are those concerning the coagulation of colloidal solutions by electrolytes. The experimental works of SCHULZE, PICTON and LINDER, HARDY, BILTZ, FREUNDLICH and others have thrown much light on the complicated phenomena.

It is only the so-called suspension colloids which are so sensitive to electrolytes.[1] Most inorganic colloids belong to this class, and the greater part of the experimental researches have been carried out with such. Of these the colloidal solution of arsenious sulphide is the one most frequently studied on account of the ease with which it can be obtained free from contamination, and on account of its stability. It is the positive and negative ions which cause the coagulation. Where the suspended particles are negatively charged, as is the case with arsenious sulphide, the coagulation is called forth by positive ions; while positively charged particles such as ferric hydroxide are precipitated by negative ions. The strength of the action evidently depends on the valency of the ions, because the higher the valency the stronger the action. And the difference between the action of mono- and divalent ions, as well as that between di- and trivalent ions is enormous.

Such are some of the salient features of the results hitherto obtained. They are only quasiquantitative, because the time effects are often very pronounced in the case of coagulating colloids and preclude any exact determination. Moreover the methods hitherto employed in determining the concentration of electrolytes which call forth coagulation in a given colloidal solution leave much to be desired. Some investigators have measured the minimum concentration of the electrolytes at which distinct turbidity is observed; others have estimated the concentration at which the coagulum separates out leaving clear supernatant liquid free from suspended particles; while still another has determined the strength of the electrolyte solutions which so far coagulate

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[1] There are intermediate forms between suspension colloids and hydrophile colloids. These may be sensitive to electrolytes as is evidently the case with legumine, whose coagulum forms the principal constituent of our food-stuff tôfu.

the colloidal solutions that none pass through filter paper of certain definite brand. But as SCHULZE pointed out more than twenty years ago, all these methods must give different values, because they are only fit, so to speak, to determine certain definite points on the curves of coagulation. This is due to the fact that coagulation comprises a whole series of changes, the magnitude of suspended particles increasing continuously with the increasing concentration of the active ion. At a certain stage the average particles begin to reflect so much light that the solution appears turbid. When the particles attain such magnitude that they can no longer remain suspended in the medium they separate out as coagulum. For complete precipitation still greater concentration of the active ion is necessary. If we could determine the average magnitude of the particles as a function of the concentration of the ion concerned, a clear idea of the phenomena might be obtained. Indeed it may not be impossible to accomplish this by means of the ultramicroscope. It will however be a very laborious task; and the results, being obscured by various unavoidable sources of errors, may not correspond to the pains taken. But if we could find a specific property of the colloidal solution which varied continuously with the growing magnitude of the suspended particles, we might employ it as an index of the degree of coagulation; and by measuring this property we might attain our object much more readily.

The inner friction or viscosity of colloidal solutions is evidently a specific property corresponding to the foregoing description, and being in general quite easy of measurement, seems to be particularly well fitted for the study of the problem under discussion. In order to test this supposition the coagulation of colloidal aluminium hydroxide by various electrolytes has been studied with the aid of the viscosimeter, and the results obtained fulfil the expectation to a remarkable degree as is shown in the following pages.

2. The Colloidal Solution of Aluminium Hydroxide.

The colloidal solution of aluminium hydroxide employed in the following experiments is the one first prepared by the English chemist, WALTER CRUM,[1] more than half a century ago. He obtained a basic acetate of aluminium as a fine insoluble crystalline powder by heating a concentrated solution of aluminium acetate. On prolonged boiling with water the basic salt goes into solution, the acetic acid being given off with the steam, while aluminium hydroxide remains in the colloidal state. All the soluble impurities can be removed by thoroughly washing the basic acetate. When the boiling is carried out in a large platinum vessel, care being taken to exclude contamination from the air, it is possible to get rid of the acetic acid almost completely. In this way a remarkably pure solution of colloidal aluminium hydroxide can be prepared with great ease. It is slightly opalescent, but almost clear to the transmitted light, somewhat viscous and oily to the touch when concentrated. This solution is very stable. Kept in a vessel of hard Jena-glass it has remained apparently quite unaltered in its appearance and properties during the lapse of more than three years. Parallel experiments carried out with this old solution and with a solution newly prepared agreed in all particulars.

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[1] Journ. Chem. Soc. London, 1, (1853), 216.

The coagulation of such a solution of colloidal aluminium hydroxide by various agents was observed by WALTER CRUM and described in the following terms:

"A solution containing $\frac{1}{4}$ percent of alumina is converted into a transparent jelly, when mixed with half its bulk of water acidulated with $\frac{1}{2500}$ of sulphuric acid. The jelly has therefore only $\frac{1}{600}$ of its weight of alumina, and $\frac{1}{7500}$ of sulphuric acid.

"By pressure in a bag the liquid part of this jelly was readily separated, and the solid was reduced to $\frac{1}{60}$ or $\frac{1}{70}$ of its original volume. Pure water did not dissolve this residue, neither did an excess of sulphuric acid, even at a boiling heat. On examination it was found that the solid portion had imbibed almost the whole of the sulphuric acid. It existed there in the proportion of about 1 equivalent of acid to 15 of alumina.

"The coagulating power of the various agents may be ascertained with tolerable accuracy by employing an aluminous solution so dilute as to contain not more than 1 part of alumina in 800 of water, and shaking it in a phial with about half its volume of a coagulating solution. In this manner it was found that 1 atom of citric acid (tribasic) coagulates as powerfully as 3 atoms of sulphuric acid, and tartaric acid (bibasic) as much as 2. 2 atoms of oxalic acid are required to produce the same effect as 1 of sulphuric acid. Of muriatic and nitric acids, not less than 300 equivalents must be employed to produce an effect equal to that of 1 equivalent of sulphuric acid—the volume of the acid being always $\frac{1}{2}$ that of the aluminous solution. No acid has the power of redissolving the coagulum.

"Of the other acids which have been tried, the chromic, molybdic, racemic, suberic, salicylic, benzoic, gallic, lactic, cinnamic, butyric, valerianic, carbazotic, camphoric, uric, meconic, comenic and hemipinic acids all coagulate the solution ; but their exact power has not be ascertained.

"The acetic, formic, boracic, arsenious, and cyanuric acids do not coagulate, at least when moderately concentreted.........

"The alkalies have a strong coagulating power. About 2 equivalents of potash produce an effect equal to 1 of sulphuric acid, and the same is the case with soda, ammonia, and lime. The coagulation takes place before the acetic acid which remains in the aluminous solution is fully saturated ; for when the alkali, in a very dilute state, is added with caution, the coagulum which it produces has still an acid reaction. This coagulum, like that from sulphuric acid, is insoluble in any acid, whether cold or hot, as well as in pure water. It dissolves, however, in a boiling solution of potash or soda, and when the alkaline solution is afterwards saturated by an acid, the ordinary terhydrate of alumina is thrown down.

"Large quantities, however, of the acetic salts (ready formed) may be added before they coagulate the aluminous solution. When the solid part of the coagulum produced by a strong solution of acetate of soda was afterwards freed from that salt by pressure, it redissolved in pure water, and the solution was again coagulated by a fresh addition of the salt. An experiment with acetate of lime gave the same result.

"The nitrates and chlorides coagulate also with great difficulty.

"Solutions of sulphate of soda, magnesia, and lime coagulate as readily as a liquid containing the same quantity of sulphuric acid in the free state. On examining one of these mixtures, the sulphuric acid was found in the solid part of the coagulum, as before, and the alkali in the fluid part, united with the acetic acid which had remained in the aluminous solution after boiling.

"The digested solution of alumina which has not been deprived of its acetic acid by boiling, requires about twice as much sulphuric acid to coagulate it as does the boiled solution, and thirty or forty times as much alkali. The coagulation is complete before the acetic acid is entirely saturated.

"One of the most characteristic properties of the digested and altered acetate of alumina is its loss of the power of acting as a mordant. The ordinary acetate, as is well known, forms a yellow opaque precipitate with decoction of quercitron. That which has been thoroughly digested is merely coagulated by that decoction—the colour of which is but little altered, and the coagulum is translucent. The same effect is produced with decoctions of logwood, brazilwood, etc."

This description shows how well the solution is suited to the experimental study of the phenomena of coagulation of a colloidal solution by electrolytes. The solution employed in the greater part of the present study is an old one made by Prof. IKEDA. On analysis it was found to contain 0.457% of alumina. It was diluted 4.4 times, so that the solution actually employed contained 0.1 per cent (or more exactly 0.104%) of alumina.

When the electrodes of a secondary battery of 120 volts were inserted in the two branches of a U-tube filled with the more concentrated solution of alumina, the liquid near the negative electrode became milky in about half an hour, while that in the vicinity of the opposite electrode lost its opalescence and became quite clear. This observation proves beyond doubt that the suspended particles of aluminium hydroxide are positively charged. The same has already been found to be true for the colloidal solutions of ferric and aluminium hydroxide prepared by dialysis. Hence coagulation phenomena similar to those observed in the latter solution are to be expected in the present study.

3. The Method of Measurement.

The apparatus and the method of measuring viscosity employed in this work are those recommended by OSTWALD; they are too well known to require description. A capillary tube of a rather wide bore was purposely chosen for the viscosimeter in order to minimise the effect of small particles which might separate out from the solution and adhere to the side of the tube. This had the unfortunate result of making the flow of the liquid too rapid and so the correction to be applied on account of the kinetic energy acquired by it became unduely large. But as it is quite useless to aim at any high degree of exactness in a work of this nature, this correction has been neglected. The omission is the more justifiable as the viscosity is measured not for its own sake but only as an index to the degree of coagulation, and so only relative values are to be considered. For the same reason the time of flow was measured with an ordinary watch, the readings being taken to the second.

As the temperature exercises considerable influence on viscosity, the apparatus was immersed in a thermostadt with glass sides. The temperature was kept constant at 25°, and the greatest fluctuation during the whole period of the work, which lasted several months, did not exceed $\frac{1}{5}$ of a degree.

To make a measurement, 2 c.c. of the colloidal solution and an equal volume of an electrolyte solution were introduced into the wider tube of the viscosimeter, and mixed thoroughly. Then the mixture was sucked up into the bulb. The measurement of the time of flow was repeated several times with one and the same mixture, and the mean was taken. As a rule single determinations did not differ by more than a second. Between two observations with different mixtures the apparatus was heated with concentrated sulphuric acid, washed thoroughly with distilled water, and dried.

The following details of a series of observations made with potassium sulphate as electrolyte will give an idea of how the work was carried out.

TABLE I.

Concentration of SO_4K_2 in equivalent normal.	Time of flow in seconds.	Mean t
0	26, 25, 25, 24, 25, 24.5, 25, 25.	25
0.0005	27, 26, 25.5, 26.	26
0.0007	28, 28, 28, 28.5.	28
0.0010	42, 42, 42, 41.5, 41.5.	42
0.0025	42, 42, 41, 42, 42.5.	42
0.0050	42, 41.5, 42, 42, 41.5.	42
0.050	40, 42, 42.5, 42, 42.	42

The viscosity of the aluminous solution, containing 0.05% of alumina and free from electrolyte, differed but slightly from that of pure water. If we take the ratio of the time of flow of various mixtures to that of the solution to which no electrolyte has been added we get relative viscosities η.

TABLE 2.

Concentration of SO_4K_2	0	0.0005	0.0007	0.001	0.0025	0.005	0.05
t	25	26	26	42	42	42	42
η	1.00	1.04	1.12	1.68	1.68	1.68	1.68

These numbers show clearly that with the concentration of 0.001 molar of potassium sulphate the coagulation was complete and the further addition of the electrolyte had no effect. It is also to be noted that the coagulation began at a concentration as low as 0.0005 and was considerable at 0.0007. In this way we get a tolerably good idea of the degree of coagulation effected by different concentrations of the electrolyte.

4. The Influence of Temperature.

In order to be able to make generalisations which should hold good over a wide range of temperature we had to study the influence which temperature exercises on the phenomena of coagulation. As a typical electrolyte, potassium sulphate was chosen, and the viscosity was further measured at three different temperatures, viz. 6°, 40°, and 60°. The results obtained are contained in the following tables.

TABLE 3.

Temperature = 6°.

Concentration of SO_4K_2	0	0.0005	0.0025	0.004	0.05
t	42	43	70	71	71
η	1.00	1.02	1.66	1.69	1.69

TABLE 4.

Temperature = 40°.

Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
t	20	21	32	32	32
γ	1.00	1.05	1.60	1.60	1.60

TABLE 5.

Temperature = 60°.

Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
t	15	16	24	24	24
γ	1.00	1.06	1.60	1.60	1.60

The absolute values of viscosity vary considerably with the temperature, but the values of γ remain nearly constant. For the sake of easier comparison all the results including those at 25° are collected in the next table.

TABLE 6.

Value of γ.

Concentration of SO_4K_2 / Temperature	0	0.0005	0.0025	0.005	0.05
6°	1.00	1.02	1.66	1.69	1.69
25°	1.00	1.04	1.68	1.68	1.68
40°	1.00	1.05	1.60	1.60	1.60
60°	1.00	1.06	1.60	1.60	1.60

As may be seen, the general course of coagulation with the increasing concentration of the electrolyte remains nearly the same at different temperatures. And if it were not too venturesome we might say that the higher the temperature the lower will be the concentration of the electrolyte necessary to cause noticeable coagulation. The relative viscosity of the completely coagulated solution tends to decrease with the rising temperature. But as the general features remain the same between 6° and 60°, we may draw pretty general conclusions from observations at the single chosen temperature of 25°.

5. Effect of the Concentration of the Colloidal Solution.

As has been demonstrated by CRUM the electrolyte is decomposed in the act of coagulation, the anion being retained by the gel formed. Hence the concentration of the electrolyte which causes complete coagulation must vary with the concentration of the colloidal solution. In order to test this point the following measurements were made.

TABLE 7.

Concentration of the colloidal solution=0.025% alumina.

Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
t	25	26	33	34	34
η	1.00	1.04	1.32	1.36	1.36

TABLE 8.

Concentration of the colloidal solution=0.0125% alumina.

Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
t	24	24	28	29	29
η	1.00	1.00	1.17	1.21	1.21

TABLE 9.

Concentration of the colloidal solution=0.005% alumina.

Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
t	23	23	26	26	26
η	1.00	1.00	1.13	1.13	1.13

In order to facilitate the comparison, all the values of η are collected in the following table together with the results obtained with 0.05% colloidal solution. (See § 3).

TABLE 10.

Concentration of SO_4K_2 % Al_2O_3	0	0.0005	0.0025	0.005	0.05
0.05	1.00	1.04	1.68	1.68	1.68
0.025	1.00	1.04	1.32	1.36	1.36
0.0125	1.00	1.00	1.17	1.21	1.21
0.005	1.00	1.00	1.13	1.13	1.13

Within the experimented range, the concentration of the electrolyte, which causes complete coagulation, appears to be the same for the colloidal solutions of different concentrations. In order to observe the effect above mentioned the concentration had to be varied within far wider range. Hence any generalisation from the observations made on the aluminous solution containing 0.05% Al_2O_3 will apply to all the solutions whose concentrations are not very large.

The value of $\eta-1$ for the completely coagulated solution is not quite proportional to the concentration, as might have been expected, but varies more slowly. Even when the viscosity of pure water instead of the respective aluminous solution is taken as the standard of comparison, strict proportionality does not obtain. But this is after all not very strange, because the apparent viscosity observed in the these experiments can not be a very simple function of the number of suspended particles.

The simplest empirical equation, which represents the relation, will have the form :

$$\eta_{\text{lim}} - 1 = \alpha\, c^{\beta}$$

where c stands for the concentration of the colloidal solution, and α and β are constants. In the present case it has been found by trial that $\alpha=10$ and $\beta=0.9$.

Concentration c.	0.05	0.025	0.0125	0.005
$\eta_{\text{lim}}-1$ (found).	0.68	0.36	0.21	0.13
$\eta_{\text{lim}}-1$ (calculated).	0.68	0.36	0.20	0.09

6. The Effect of Time.

As the colloidal solution is essentially an unstable system and its coagulation is generally a change to a more stable state, time must exercise some effect on the phenomena. This has been confirmed in the case of arsenious sulphide. But in the present case no marked effect was observed. This is well shown by the constancy of the viscosity of various solutions, partially or completely coagulated, during the time in which repeated measurements of the time of flow were made. Yet when a completely coagulated solution is allowed to stand for a comparatively long time the viscosity gradually diminishes. For example, in a solution whose relative viscosity was initially 1.76, it became after

66 hours 1.68 and after 22 hours more, 1.64. To what this diminution is due can only be surmised.

No particular attention was paid to the mode of mixing the colloidal solution with that of the electrolyte.

7. Coagulative Power of Various Electrolytes.

In the foregoing investigations we have seen that the relative viscosity η of the colloidal solution is nearly independent of temperature and not much influenced by time. On the other hand it has been found to be a function of the concentration of the colloidal substance, and it might well be affected by the previous history of the solution. The aluminous solution employed throughout the following experiments was of the same origin and concentration (0.05% of alumina); hence the values of η observed are strictly comparable. We are thus in a position to study the effect of the nature and concentration of various electrolytes on the coagulation of the colloidal aluminium hydroxide.

Most of the substances employed were purified by recrystallisation, but some could be obtained only in such small quantities that they had to be used as they were. Of the alkalies, caustic soda was made from metallic sodium, while the others were the ordinary materials of the laboratory. The solutions of $Ag(CN)_2K$, PO_4Na_3 and the like were prepared by adding the components in proper proportions. Mellithic acid was prepared from mellithrite. The colouring matters were ordinary samples, while the solution of egg-albumin was obtained by dialysing the white of hen's eggs.

The results of the measurements arranged in the order of the increasing valency of the negative ions of the electrolytes are contained in the following table. The concentrations are given in equivalent normal.

TABLE 11.

No.	Concentr. / Substance	0.00017	0.00025	0.0005	0.00072	0.001	0.0017	0.0025	0.005	0.05
1	NO_3 K	—	—	—	—	1.00	1.00	1.00	1.00	1.00
2	ClO_3 K	—	—	—	—	1.00	1.00	1.00	1.00	1.00
3	MnO_4 K	—	—	—	—	1.00	1.00	1.00	1.04	1.20
4	Cl K	—	—	—	—	1.00	1.00	1.00	1.00	1.53
5	Br K	—	—	—	—	1.00	1.00	1.00	1.00	1.00
6	I K	—	—	—	—	1.00	1.00	1.00	1.00	1.74
7	CNS K	—	—	—	—	1.00	1.00	1.00	1.00	1.00
8	CN K	—	—	—	—	—	1.00	1.32	1.84	1.88
9	$Ag(CN)_2$ K	—	—	—	—	1.00	1.00	1.08	1.16	1.48
10	NO_3 H	—	—	—	—	1.00	1.00	1.00	1.00	1.00
11	Cl H	—	—	—	—	1.00	1.00	1.00	1.00	1.00
12	Picric acid	1.00	1.00	1.00	—	1.08	—	—	1.60	(1.88)[1]
13	HO Na	—	—	—	—	—	1.08	1.22	1.74	1.84
14	HO K	—	—	—	—	—	1.00	1.04	1.30	1.88
15	$(HO)_2$ Ba	—	—	—	—	—	1.00	1.00	1.04	1.88
16	SO_4 K_2	—	1.00	1.04	1.58	1.68	1.68	1.68	1.68	1.68
17	CrO_4 K_2	—	1.00	1.00	1.00	1.00	1.00	1.17	1.75	1.75
18	Cr_2O_7 K_2	—	1.00	1.00	1.00	1.00	1.08	1.58	1.75	1.75
19	B_4O_7 Na_2	—	1.00	1.00	1.12	1.20	1.32	1.36	1.40	1.68
20	$Pt(CN)_4$ K_2	1.00	1.00	1.00	1.00	1.00	1.04	1.16	1.52	1.72
21	CO_3 Na_2	—	1.00	1.00	1.00	1.00	1.00	1.26	1.79	1.79
22	SO_4 H_2	—	1.00	1.58	1.58	1.58	1.58	1.58	1.58	1.58
23	Succinic acid	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
24	Na Succinate	1.00	1.00	1.00	1.00	1.00	1.26	1.58	1.68	1.68
25	Oxalic acid	1.00	1.05	1.06	1.08	1.10	1.26	1.26	1.26	1.26
26	NH_4 Oxalate	1.00	1.02	1.10	1.15	1.21	1.23	1.26	1.26	1.26
27	K Oxalate	1.00	—	1.00	1.04	1.10	1.32	1.32	1.32	1.32

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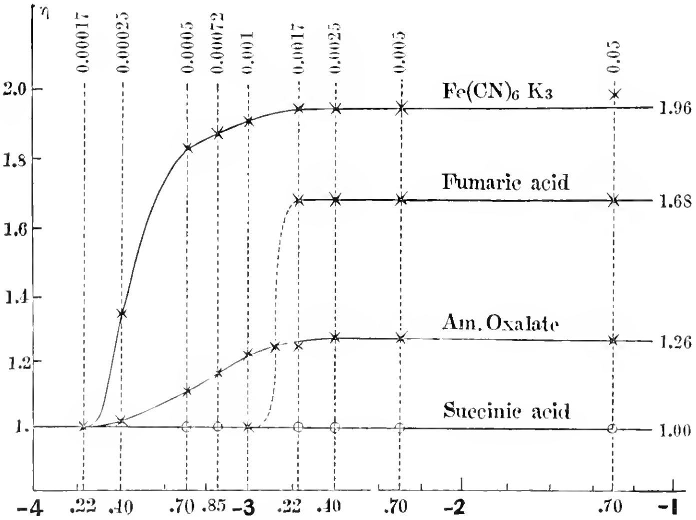
[1] This value corresponds not to the concentration 0.05 but to 0.01.

No.	Concentr. Substance	0.00017	0.00025	0.0005	0.00072	0.001	0.0017	0.0025	0.005	0.05
28	Tartaric acid	1.00	—	1.00	1.27	1.63	1.72	1.84	1.84	1.84
29	Malonic acid	1.00	—	—	—	—	—	—	—	1.00
30	Fumaric acid	1.00	—	—	—	1.00	1.68	1.68	1.68	1.68
31	Maleic acid	1.00	—	—	—	—	—	—	—	1.00
32	Na Maleate	1.00	—	—	—	—	1.00	1.16	1.74	1.89
33	Itaconic acid	1.00	—	—	—	—	—	—	—	1.00
34	Na Itaconate	1.00	—	—	—	—	1.00	1.16	1.63	1.68
35	$PO_4 H_3$	—	—	—	—	1.00	1.05	1.05	1.05	1.74
36	$PO_4 H Na_2$	—	—	—	—	1.00	1.00	1.79	1.89	1.89
37	$PO_4 Na_3$	—	—	—	—	1.00	1.00	1.89	1.95	1.95
38	$Fe (CN)_6 K_3$	1.00	1.36	1.84	1.88	1.92	1.96	1.96	1.96	2.00
39	Citric acid	—	—	—	1.00	1.39	1.74	1.84	1.84	1.84
40	K Citrate	—	—	—	1.00	1.74	1.75	1.85	1.90	1.90
41	$Fe (CN)_6 K_4$	1.08	1.52	2.16	2.20	2.20	2.24	2.24	2.24	2.24
42	Mellithic acid	1.00	1.16	1.42	2.00	2.00	2.00	2.05	2.05	2.05

An inspection of the foregoing table reveals the following facts. In the cases where the coagulation takes place, the relative viscosity shows a noticeable rise only when the concentration of the electrolytes reaches certain values. From this point the viscosity increases with the increasing concentration to a certain limit, and then ceases to be influenced by the further addition of the electrolyte. Sometimes the increase of viscosity with increasing concentration is gradual, while in other cases it is quite sudden. Again the limiting value, to which the relative viscosity tends, shows considerable difference in different cases. A diagram, in which the logarithm of the concentration is taken as the abscissa and the relative viscosity as the ordinate, brings these facts most clearly into view. Ammonium



oxalate (26),[1] potassium ferricyanide (38), and fumaric acid (30) are chosen as typical cases and represented in the annexed diagram. In the case of ammonium oxalate, incipient coagulation took place at the very low concentration of 0.0002, the concentration at which complete coagulation was effected was 0.0025 and the final value of the relative viscosity was very low being only 1.26. In the case of potassium ferricyanide the concentration of the incipient coagulation was about the same, but complete coagulation was reached at the somewhat lower concentration of about 0.0015, while the limiting value of the relative viscosity was as high as 1.96. In the case of fumaric acid no coagulation was observed at 0.001 while at 0.0017 it was already complete. The limiting value of η is here middling, being 1.68.

For a complete characterisation of an electrolyte with respect to its coagulative power on a chosen colloidal solution a curve such as shown in the foregoing diagram is necessary. But for

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[1] The numbers in the brackets refer to the number in Table 11.

the purpose of comparison of various electrolytes among themselves, it will be more convenient to chose certain characteristic points on the curves, than to employ the curves themselves; and the distinct points which are particularly well fitted for the purpose seem to be those above mentioned, viz.: the concentration of the incipient coagulation, and the lowest concentration at which complete coagulation takes place.

The smallest concentration of an electrolyte at which coagulation actually begins can not of course be determined with great precision. Moreover, its experimental value depends on the exactness of the method of measurement. In the present investigation the method employed is a rather rough one, therefore the values found can only be approximate. Yet they may serve as the basis of a broad comparison.

In Table 12 the electrolytes are classified according to the magnitude of the concentration under consideration.

In the first column are placed the electrolytes whose coagulative power is very slight, since they fail to cause even incipient coagulation at the comparatively high concentration of $\frac{1}{20}$ normal. They are all electrolytes with monovalent anions. The organic acids included are indeed dibasic, but they are all so weak that their dissociation hardly proceeds beyond the first stage, and if the free divalent anion be present at all it must be in such a minute quantity that they do not affect the colloidal solution in any noticeable degree.

In the second column are contained only two halides, potassium chloride and iodide. It is a rather curious fact that the coagulative power of the bromide is so weak and does not lie between those of the two halides. To exclude any mistake the measurements were repeated, but with the same result.

TABLE 12.

above 0.05	between 0.05 and 0.005	between 0.005 and 0.001	below 0.001
$NO_3 K$	Cl K	$Mn O_4 K$	Picric acid
$ClO_3 K$	I K	CN K	K oxalate
Br K		$Ag (CN)_2 K$	Tartaric acid
CNS K		HO Na	Citric acid
$NO_3 H$		HO K	K Citrate
Cl H		$(HO)_2 Ba$	$SO_4 K_2$
Succinic acid		$CrO_4 K_2$	$SO_4 H_2$
Malonic acid		$Cr_2O_7 K_2$	Oxalic acid
Maleic acid		$Pt (CN)_4 K_2$	NH_4 Oxalate
Itaconic acid		$CO_3 Na_2$	$Fe (CN)_6 K_3$
		$B_4O_7 Na_2$	Mellithic acid
		Na Succinate	$Fe (CN)_6 K_4$
		Na Maleate	
		Na Itaconate	
		Fumaric acid	
		$PO_4 H_3$	
		$PO_4 HNa_2$	
		$PO_4 Na_3$	

In the third column are included electrolytes with monovalent anions. Of these the permanganate is the weakest and its position is rather doubtful. Three are alkalies, which have a pretty strong coagulative power, as first pointed out by CRUM. The remaining two are potassium cyanide and potassium silver-cyanide. Why they act comparatively so strongly is not known. Of the other twelve electrolytes belonging to this class, nine have divalent anions, the remaining three being phosphoric acid and its salts. Phosphoric acid, although it is tribasic, may not be dissociated to such an extent that the trivalent anion PO_4''' exists in any significant concentration; but in the solution of trisodium phosphate this must undoubtedly be the case.

In the last class, whose members have such a strong action on the colloid that they produce incipient coagulation at a concentration below $\frac{1}{1000}$ equivalent normal, there is only one electrolyte with monovalent anion, viz., picric acid. Of the anions of the remaining eleven electrolytes, six are divalent, three are trivalent, one is tetravalent and one may be hexavalent.

According to SCHULZE, the coagulative power of an electrolyte is chiefly determined by the valency of its ions. On the whole, this rule holds in the present case, though there are several noteworthy exceptions. The other chemical and physical properties of the anion seem to exercise considerable influence on the coagulative power.

When we take the lowest concentration of the electrolytes necessary for complete coagulation as the basis of comparison, we get the results shown in Table 13.

This mode of comparison comes nearer to the methods employed by former investigators, particularly SCHULZE and FREUNDLICH, because what they measured may also be looked upon as the lowest concentrations of complete coagulation.

Among fifteen electrolytes which require greater concentrations than $\frac{1}{20}$ equivalent normal, there is only one whose anion is polyvalent, i. e. phosphoric acid.

In the next column are found five electrolytes with monovalent anions, the remaining four having divalent ones. In the third column are placed nine electrolytes with divalent anions and five electrolytes with trivalent anions. In the last column

TABLE 13.

above 0.05	between 0.05 and 0.005	between 0.005 and 0.001	between 0.001 and 0.00025
NO_3 K	CN K	CrO_4 K_2	SO_4 K_2
ClO_3 K	HO Na	Cr_2 O_7 K_2	SO_4 H_2
MnO_4 K	HO K	CO_3 Na_2	Mellithic acid
Cl K	$(HO)_2$ Ba	Na Succinate	Fe $(CN)_6$ K_4
Br K	Picric acid	NH_4 Oxalate	
I K ?	B_4O_7 Na_2 ?	Oxalic acid	
CNS K	Pt $(CN)_4$ K_2	K Oxalate	
Ag $(CN)_2$ K	Na Maleate	Fumaric acid	
NO_3 H	Na Itaconate	Tartaric acid	
Cl H		PO_4 H Na_2	
PO_4 H_3		PO_4 Na_3	
Succinic acid		K Citrate	
Malonic acid		Citric acid	
Maleic acid		Fe $(CN)_3$ K_3	
Itaconic acid			

are two having divalent anions, while one has tetravalent and the remaining one has an anion of possible hexavalency. Thus the rule of SCHULZE is here brought out much more clearly than in Table 12.

The limiting value of relative viscosity is also a characteristic quantity for an electrolyte with respect to its coagulative power. But it is perhaps more rational to compare the increase of viscosity $\eta_{lim}-1$ caused by various electrolytes. The lowest value was found in the case of oxalic acid and ammonium oxalate, being only 0.26. The highest value was reached in potassium ferricyanide, and is about five times as large being 1.24.

As the value of $\eta_{\text{lim}}-1$ depends on the concentration of the colloidal solution, it is not very well fitted for the characterisation of an electrolyte. But perhaps it might be possible to eliminate this effect by employing the empirical equation given at the end of § 5:

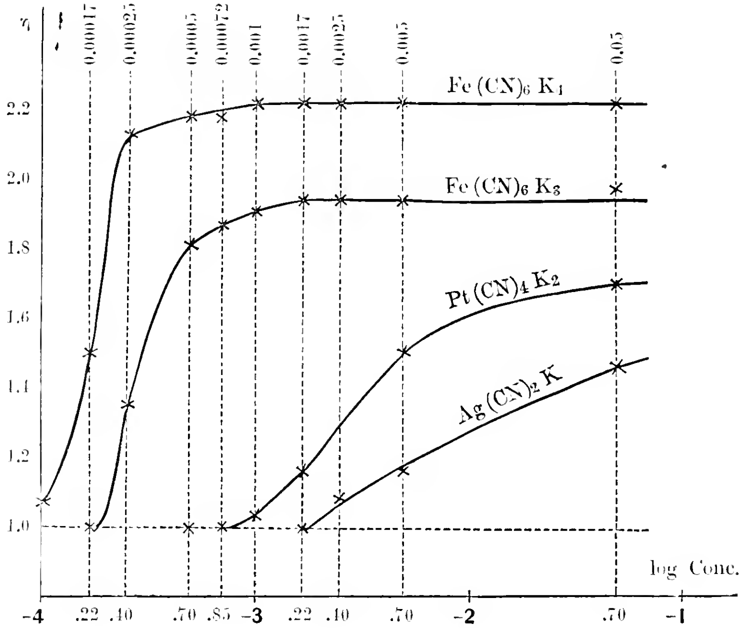
$$\eta_{\text{lim}}-1=\alpha\, c^{\beta}.$$

It is not improbable that the empirical constant β retains its value for different electrolytes and that α alone varies with different cases; but this point must be left for further study.

Another fact deserves mention in this place. The values of $\eta_{\text{lim}}-1$ for electrolytes with particularly well developed coagulative power, are also high. Thus strong electrolytes with trivalent anions have $\eta_{\text{lim}}-1$ between 0.9 and 1.0, while in one electrolyte with tetravalent anion it is as high as 1.24.

What the different values of $\eta_{\text{lim}}-1$ may mean physically and chemically it is difficult to say. They point no doubt to some difference in the physical structure of the coagulum. Microscopic observation may reveal in what the difference lies.

In order to study the effect of the valency of ions on the coagulative power, it is necessary to compare electrolytes of chemically allied natures but of different valencies. For this purpose we chose potassium salts of cyanogen complexes, $Ag(CN)_2K$ (9), $Pt(CN)_4K_2$ (20), $Fe(CN)_6K_3$ (38), and $Fe(CN)_6K_4$ (41). The relation between η and the concentration of the electrolytes is shown in the annexed diagram. All the three aspects of the coagulative power, which we have been discussing, are brought so clearly before the eye, that it is needless to dilate upon them in this connection. In short, the rule of SCHULZE finds the



fullest cofirmation in all details. As to the quantitative relation proposed by HARDY and WHETHAM,[1] it may be tested in the following manner. The concentration necessary for complete coagulation is :

$Pt(CN)_4K_2$	$Fe(CN)_6K_3$	$Fe(CN)_6K_4$
0.1	0.0015	0.0005

If *n* be the valency of the anion, then the *n*th root of the concentration ought to have one and the same value.

$Pt(CN)_4K_2$	$Fe(CN)_6K_3$	$Fe(CN)_6K_4$
0.3	0.11	0.15

The order of the numbers is the same, but the difference is too great to be ascribed to experimental error.

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[1] Journal of Physiology, **21**, (1899), 301.

When the concentration is large enough, even electrolytes with the weakest coagulative power can cause considerable increase in the relative viscosity as is illustrated by the following observations on nitric acid.

TABLE 14.

Concentration	0	0.05	0.5	2.5
η	1.00	1.00	1.40	1.52

But when the concentration of an electrolyte is so large, the viscosity is generally increased to some extent even without coagulation taking place. Hence it will be necessary to apply proper correction to obtain more exact results. In the present investigation we have limited ourselves to the study of more dilute solutions.

Although it seemed highly improbable that positive ions should exercise any considerable coagulative power on the colloidal aluminium hydroxide, we studied the effect of the nitrates of the following six cations,

Na, Ag, Ba, Co, Ni, UO_2,

in order to reach experimental certainty on the subject. Up to the concentratien of $\frac{1}{20}$ equivalent normal the results were quite negative. Thus we are naturally led to the conclusion that it is anions which cause the coagulation.

The fact, that succinic, maleic, and itaconic acid are quite inactive up to the highest concentration tested, while their sodium salts exercise considerable coagulative power even in tolerably dilute solutions, is in accordance with this conclusion. But the most interesting fact of all is that the coagulative power of fumaric acid is so well developed while the stereoisomeric maleic acid is quite inactive. The dissociation constant of maleic acid considered as a monobasic acid is indeed far greater than that of fumaric acid, being 0.00117 as against 0.000093; but in the dissociation constant[1] with respect to the second hydrogen ion the relation is reversed, being only 0.00000039 for maleic acid and 0.000018 for fumaric acid. These latter constant were found for 100°. At 25° their values may be somewhat different, yet the order of magnitude will remain nearly the same. This explains why the dissociation constant as monobasic acid calculated from the electrolytic conductivity remains very nearly constant for maleic acid, while it increases, though at first very gradually, with increasing dilution for fumaric acid. Hence the concentration of the divalent anion must be very much greater in the solution of fumaric acid than in that of maleic acid. This accounts for the great difference in the coagulative power of the two acids.

The coagulative power of tartaric acid has been found to be markedly greater than that of fumaric acid; this may be looked upon as the consequence of the greater dissociation constant of the second hydrogen ion for this acid, the constant being 0.000059 or more than three times larger than that of fumaric acid. This doubtless also applies to oxalic acid.

The indifferent organic substances, ethyl alcohol, phenol and mannite, were tested, and found to lack coagulative power, at least in not too high concentrations. Such is doubtless the case

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[1] W. A. Smith: Zeits. für physik. Chem., **25**, (1898), 241.

with most organic substances which form real (not colloidal) solutions and do not undergo electrolytic dissociation.

Mannite solution, to which boric acid had been added, was also found quite inactive, although it formed complex acids of considerable strength.[1] Boric acid itself exerts no coagulative action.

Crum observed the coagulating action of some decoctions of certain dye-stuffs. The solutions of many colouring matters are colloidal, and when the suspended particles have negative electric charge, this is to be expected, particularly according to the observations of Biltz.[2] We made observations on the solutions of helianthin, fuchsin, and eosin, and also on that of tannin; and found their coagulative power very strong as shown in the following table.

TABLE 15.

Substance \ Concentr.	0.00017	0.00025	0.0005	0.001	0.005	0.01
Eosin	1.04	—	2.08	—	2.12	2.12
Fuchsin	1.00	1.00	1.00	1.02	1.60	1.88
Helianthin	1.04	1.40	—	1.84	—	2.08
Tannin	1.00	1.00	1.04	—	1.36	1.84

It is known that eosin has cathodic cataphoresis and the same is probably the case with other substances in the table.

It was also observed that the colloidal solution of aluminium

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[1] Magnanini: Zeits. für physik. Chem., **6**, (1890), 58.

[2] Berichte d. deutschen chemischen Gesellschaft, **37**, (1904), 1113.

hydroxide was coagulated by saliva. This is doubtless due to the protein present in it. We have tested the coagulative power of egg-albumin and obtained the following result.

TABLE 16.

Concentration	0.0108	0.0431	0.431%
η	1.07	1.11	1.35

Summary.

1. The measurement of viscosity was found to be particularly well fitted for the study of the coagulation phenomena of the colloidal solution of aluminium hydroxide.

2. The degree of coagulation was found to increase in some cases suddenly and in others more gradually with the increasing concentration of the electrolytes.

3. Only anions were found to exercise coagulative power. This is in accordance with the rule of HARDY, for the colloidal solution shows anodic cataphoresis.

4. The coagulative power of the anions increased rapidly with the increasing valency, in confirmation of SCHULZE's rule.

5. The final degree of coagulation caused by the increasing concentration of various electrolytes differed considerably in different cases, and seemed to be characteristic of the action of each electrolyte.

6. Neither the concentration of the colloidal solution nor

the temperature, nor duration of the experiment seemed to affect in any marked degree the general relations found.

The foregoing study was undertaken and prosecuted under the guidance of Prof. IKEDA to whom my best thanks are due.

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On the Partition of Silver between Zinc and Lead.

By

G. N. Potdar.

The study of the melting points of alloys has demonstrated beyond a doubt that the laws of dilute solutions apply to metallic mixtures in which one of the components greatly preponderates over the others. Consequently the law of the constant partition coefficient must also obtain for them. The experimental verification, however, has so seldom been undertaken that it may not be uninteresting to add a well defined instance. For this purpose I have at the suggestion of Prof. IKEDA, investigated the system zinc-lead-silver, because it has some additional interest in connection with PARKES' process of desilverisation of lead.

This system has already been studied by WRIGHT and THOMPSON.[1] They melted the three metals in various proportions at temperatures ranging between 750° and 850°, and allowed the melt to stand eight hours in order that the separation of the two layers might be complete. They then determined the composition of these layers by analysis. The results obtained by them are given in Table 1.

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[1] Proceedings of the Royal Society of London, **48**, (1890), 25-45.

TABLE 1.

Composition of the lighter layer.			Composition of the heavier layer.		
Silver.	Lead.	Zinc.	Silver.	Lead.	Zinc.
0	.0157	.9843	0	.9870	.0130
.0934	.0251	.8815	0002	.9864	.0134
.1546	.0463	.7991	.0010	.9838	.0152
.2207	.0696	.7097	.0032	.9761	.0207
.2228	.0756	.7016	.0025	.9708	.0267
.2795	.0617	.6588	.0088	.9623	.0289
.3949	.0346	.5705	.0112	.9698	.0190
.4182	.0390	.5428	.0146	.9658	.0196
.4811	.0346	.4843	.0160	.9714	.0126
.4893	.0382	.4725	.0226	.9646	.0128
.5186	.0447	.4367	.0535	.9327	.0138
.5398	.0478	.4124	.0778	.9076	.0146
.6107	.0723	.3170	.0936	.8862	.0202
.6193	.1028	.2779	.1075	.8695	.0230
.6889	.1828	.1283	—	—	—

As can readily be seen, the partition coefficient of silver between the lighter and the heavier layer varies continuously with the concentration, and this leads us to infer the existence of such molecular complexes as Ag_n or $Ag_n\ Zn_m$ in the former. But the concentrations of silver in the lighter layer as studied, are nearly all so high that the laws of dilute solutions can no longer be applied. Yet their results, especially in the region where the concentration of silver in the lighter phase is not too small, appear to deserve closer study. The triangular diagram shown in Fig. 1 has been drawn using WRIGHT and THOMPSON's data. The characteristic change of curvature between 10% and 40% of silver in the lighter phase, mirrowed in miniature towards the lead end of the heavier phase branch, is very interesting as

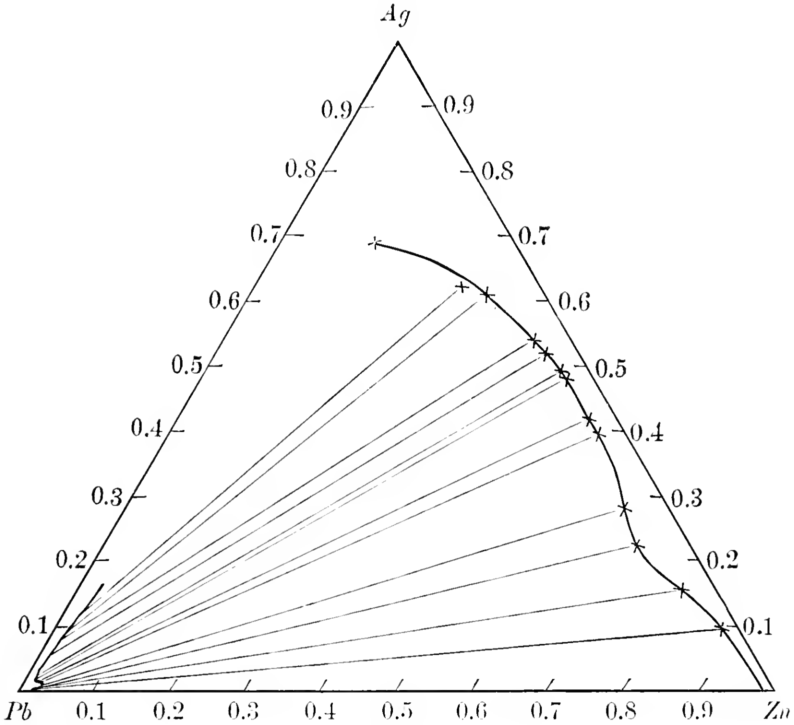

Fig. 1.

indicating the existence of a compound, perhaps $Ag_2 Zn_5$, in the solution. But as the quantitative theory of the concentrated solution has not yet been worked out, it is at present impossible to attempt to account for the course of the curve in detail.

The same authors have also studied the system zinc-lead-tin,[1] in which the partition of tin between the two layers remains nearly constant, so long as the concentration of tin does not become too great. In this case the partition coefficient being not far from unity, the experimental determination seems to have been easier. The results are given in Table 2 and represented in the annexed diagram Fig. 2.

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[1] Proceedings of the Royal Society of London, **48**, (1890), 29.

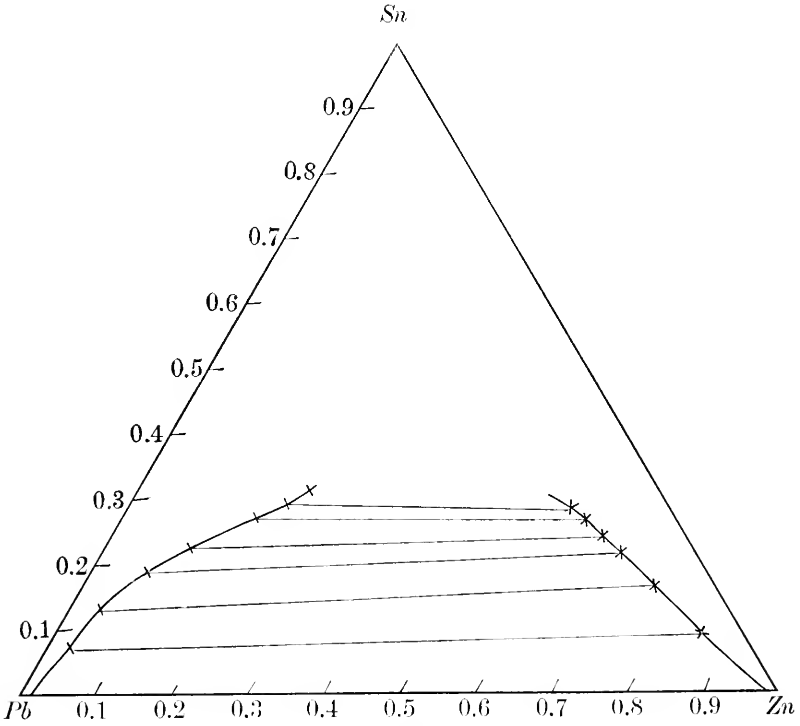

Fig. 2.

TABLE 2.

Heavier layer.			Lighter layer.			Partition coefficient.
Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.	
0	.9870	.0130	0	.0157	.9843	—
.0701	.8987	.0312	.0928	.0539	.8533	1.324
.1277	.8298	.0425	.1636	.0800	.7564	1.281
.1929	.7317	.0754	.2156	.1004	.6840	1.118
.2284	.6580	.1136	.2394	.1139	.6467	1.048
.2712	.5490	.1790	.2662	.1213	.6125	.982
.2947	.5007	.2046	.2837	.1295	.5868	.963
.3166	.4574	.2260	—	—	—	—

In the present experiments weighed portions of lead, silver and zinc were melted in a glass tube somewhat larger than an ordinary test-tube. This tube, being attached to an asbestos cardboard, was suspended in a larger vessel, for which the cardboard served as a lid. For this outer vessel a very big test-tube about 20 cm. in height and 4.5 cm. in diameter was found most suitable. In order to obtain a constant temperature phosphorus pentasulphide was kept boiling in this vessel.

Of the three metals used, the lead and the silver were commercially pure, the metallic impurities contained in them being in such minute quantities as not to affect the determination of the partition coefficient to any appreciable extent; the zinc was chemically pure.

The method of procedure was as follows. Zinc rods and pieces of lead were first filed to remove any oxide that might have been formed on them. The lead was melted in a porcelain crucible and the silver added to it. When the latter was completely dissolved, the mass was allowed to solidify, and cut in pieces of proper size. These together with pieces of zinc were introduced into the melting tube, care being taken to have the zinc pieces at the bottom. The tube was then fitted in the outer vessel in which powdered phosphorus pentasulphide had been put. At first a rapid current of carbon dioxide gas, purified and dried by being passed through sodium bicarbonate solution and concentrated sulphuric acid, was introduced into the inner tube to displace all the air, and then a very slow and steady current of the gas was kept up all through the experiment in order to reduce the loss of the metals by oxidation. The outer vessel was heated by the

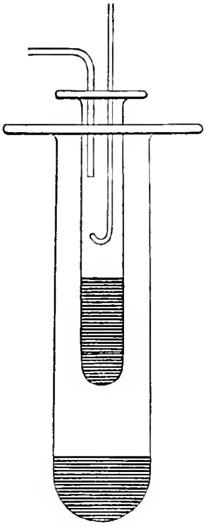

Fig. 3.

strong flame of a ring burner, the upper part of the tube being covered with asbestos paper to diminish the loss of heat by radiation. The height of the flame was so regulated that the dark brown vapour of the phosphorus pentasulphide reached to within a few centimeters of the top of the vessel and remained nearly constant the whole time. The metals in the inner tube lay well below the upper limit of the vapour so that all danger of cooling from above was excluded. Within a short time the metals became melted, and the mass was thoroughly stirred three times at intervals of five minutes. For this purpose a thin glass rod bent at one end was used. Finally the mass was kept in the melted condition for about five hours and a half, in order to secure a complete separation of the two layers. At the end of this period the flame was removed and the whole allowed to cool as rapidly as possible, so that the layers might not be disturbed and the alloys might solidify without a redistribution of the components.

The solidified lump of the metals consisted of two layers, the lighter in which zinc predominated and the heavier in which lead preponderated, each containing a small percentage of the other metal and the silver being unequally divided between them. These layers were cut in pieces with a saw parallel to the line of demarcation and the silver contents of the pieces were separately determined, VOLHARD's method of titration being employed. For the pieces from the lighter layer, which contained the greater portion of the silver, a decinormal solution of ammonium thiocyanate was used; while for the pieces from the heavier layer a twentieth to fiftieth normal solution was employed according to the amount of the silver contents.

The calculation of the ratio of the silver contents of the two layers from the results of analysis gave very fluctuating values. Thus in some cases this ratio, or the partition coefficient of silver between zinc and lead, was found to be as low as 45, while in others it was something like 150 or more. Not only was this discrepancy to be found with different samples, but pieces from the same lump cut at different distances from the line of demarcation gave different percentages of silver. Thus it was found in the lighter layer that the pieces nearer the line were richer in silver than those much removed from the same; while the heavier layer showed an utter irregularity of distribution. After many trials in the case of the heavier layer it was found that the alloy was much contaminated with particles of zinc, especially on the surface, and that at some points the contamination had penetrated to some extent into the mass of the alloy. This may have happened owing to the particles of zinc oxide, already existing in the metal used or formed during the process of heating, persistently adhering to the sides of the glass tube and helping to retain particles of zinc, which would thus refuse to rise to the layer above even after vigorous stirring. The discrepancies in the zinc layer may have been due to the formation of minute crystals of a silver-zinc compound which tended to accumulate in the lower part of the layer even during the short time required for the mass to solidify.

To remove these irregularities the zinc layer was analysed as a whole mass. The whole of the lighter layer and a small part of the heavier layer next to it was cut with a saw, dissolved in nitric acid and titrated for silver as usual. In the solution the lead was determined as peroxide deposited electrolytically. The amount of zinc in the mass was determined by difference.

Previous to making these determinations, the solubility of lead in zinc, and that of zinc in lead were separately estimated. For this purpose about 30 grammes of zinc and about 45 grammes of lead were kept fused in a tube under exactly similar conditions. After the mass had become cool, the percentage of lead dissolved in the zinc was determined electrolytically. For the determination of zinc in the lead the latter metal was removed as sulphate, and then the zinc was precipitated as sulphide and finally determined as oxide. From six determinations, the mean value found for the solubility of lead in the zinc at about 540°, the temperature of boiling phosphorus pentasulphide, was 1.35 percent, and for that of zinc in the lead, 1.33 percent.

By the aid of these values it was possible to estimate the amount of the heavier layer which accompanied the lighter layer taken for analysis. The actual amount of the lighter layer analysed being thus known, the percentage of silver in it could be readily calculated.

To remove the discrepancies in the heavier layer there was no other way than to remove the zinc particles, which was done with a file and a knife. This was tedious work and it took many hours before the contamination was completely removed. The presence of zinc particles was discernible by the different hardness of the two metals, and also by etching with dilute nitric acid, by which the presence of the zinc particles was clearly depicted by the darkening in colour due to the innumerable small particles of silver disseminated in them.

The amount of zinc taken for a single fusion was either 20 or 30 grammes; that of lead either 45 or 60 grammes; while the amount of silver varied from 0.2 to a little above 2 grammes. The results obtained are contained in the following table.

TABLE 3.

No.	Percentage of silver in the lighter layer.	Percentage of silver in the heavier layer.	Partition coefficient.
1.	0.75	0.0030	250
2.	0.99	0.0037	267
3.	2.14	0.0096	223
4.	2.31	0.0069	334
5.	3.16	0.0099	319
6.	3.64	0.0110	330
7.	3.65	0.0112	326
8.	3.92	0.0199	197
9.	4.43	0.0198	226
10.	5.24	0.0192	273
11.	5.42	0.0169	320
12.	5.45	0.0194	281
13.	5.54	0.0144	384
14.	6.26	0.0197	317

These results leave much to be desired. But the accurate determination of small quantities of silver contained in large amounts of the heavier layer is particularly difficult, and a tolerably wide range of error must be allowed even on this head alone. In the table the results are arranged in the order of the increasing percentage of silver in the lighter layer, and the partition coefficient does not show any tendency to rise or fall with the same. Hence we must conclude that it is actually constant at least for the more dilute solutions of silver in zinc and lead. This proves beyond doubt that whatever compounds of silver and zinc may occur in the lighter phase, other than those corresponding to the molecular formula $Ag\,Zn_m$ must be in such minute quantities that they do not influence the partition coefficient materially.

As to the numerical value of the partition coefficient the general mean of all the results obtained was 289. This is perhaps too low, because even a small amount of the lighter phase contaminating the heavier tends to decrease the observed partition coefficient, and as we have seen this source of error is particularly difficult to eliminate. If we omit the three lowest values (Nos. 3, 8, and 9) the average is raised to 309, which may not be very far from the truth. We may therefore affirm that at about 540° silver is about three hundred times more soluble in zinc than in lead.

The principal feature of PARKES' process of desilverisation is the partition of silver between solid zinc and liquid lead. In the first place argentiferous lead is melted and heated to a little above the melting point of zinc when a certain amount of the latter metal is added and the mixture stirred. The melt is then allowed to cool slowly. Scum consisting principally of zinc and containing silver (together with gold, copper, etc.) rises to the surface and is continually skimmed off. The temperature is allowed to fall nearly to the melting point of lead. Usually a second and sometimes a third or farther addition of zinc is made, the temperature being raised each time. In this way the desilverisation may be made practically complete.

The amount of zinc remaining in the desilvered lead depends upon the temperature at which the process is brought to an end; because the solubility of solid zinc varies considerably with the temperature. The following diagram will serve to make the matter clear. It is purposely not drawn to the scale, in order to bring out the essential features more clearly. *A* and *F* are respectively the melting point of lead and zinc. *B* and *E* are eutectic points, while *C* represents the temperature and the composition of the heavier liquid phase, which is in equilibrium with the lighter liquid phase and solid zinc. *BC* is the curve of solubility of solid zinc in lead, and the curve *CDE* shows the mutual solubility of liquid zinc and lead in each other. The curve *CDE* and a point on the curve *BC* have been determined by Spring and Romanoff,[1] but their results agree neither with the determinations of Wright and Thompson nor with my own, nor with the experience of practical metallurgists. I prefer therefore to rely on the data of Wright and Thompson and my own, though they are rather meagre. From these it appears that the curve *CD* proceeds upwards nearly perpendicularly and by extrapolation the composition of the point *C* is estimated at 1.2 percent zinc, the temperature being that of the eutectic point *E*, which is only slightly below 420° the melting point of pure zinc. Working at the temperature of boiling mercury, that is about 358°, and employing the ap-

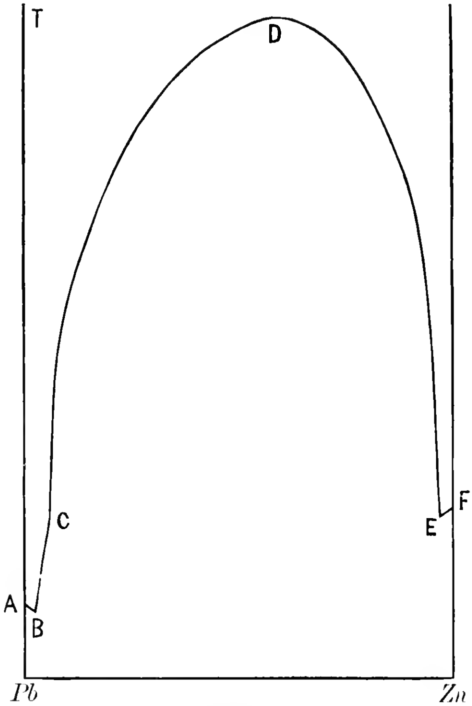

Fig. 4.

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[1] Zeits. anorg. Chem., **13**, (1897), 29–35. That they have taken the liquid phases as such, and not the solidified layers is much in their favour; but they did not wait long enough before taking the samples for analysis. At lower temperatures the separation of the two layers may have been incomplete, and so vitiated their results.

paratus described above, I found the solubility of solid zinc in melted lead to be 0.55%. Assuming the curve *BC* to be a straight line the composition of the point *B* is estimated at about 0.2% of zinc, the temperature being but very slightly below 325°, the melting point of lead.

Hence if the last scumming in PARKES' process takes place between the temperatures 325° and 360° as it appears to be the case in practice, the amount of zinc remaining in the desilvered lead will lie between 0.2 to 0.6%. That this amount is so small is important for the economical success of the process. The quantites of zinc added in excess of this are available for the extraction of silver.

The recent exhaustive study of zinc-silver alloy by PETRENKO[1] in TAMMANN's laboratory has shown the existence of a series of compounds and solid solutions. But in the temperature range which comes into consideration in PARKES' process none of the compounds has a realm of independent existence, so that we shall have a series of surfaces of solubility of zinc-silver solid solutions in lead, provided no ternary solid phase is formed. Hence it is clear that the partition coefficient must vary with the concentration, and the variation itself must show sudden changes at certain points. Yet for very dilute solid solutions the partition coefficient must be practically constant; for the law of dilute solutions also applies to solid solutions.

I have tried to test this conclusion experimentally, but without success. The temperature chosen was 358°, the boiling point of mercury. The three metals were melted together in a bath of sulphur vapour, then transferred into one of mercury vapour

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[1] Zeits. anorg. Chem., **48**, (1906), 347.

and kept in it for about one hour, when most of the zinc separated out as scum. The scum was separated by filtering off the melted mass through closely packed glass wool under the pressure of about ten inches of mercury. The scum and the filtrate were analysed separately. The former contained most of the silver, and not a small quantity of lead which adhered to the particles of zinc-silver alloy. The latter contained such minute quantities of silver that its exact determination was difficult. This was accomplished by dissolving the mass in nitric acid and concentrating the solution (when the greater part of the lead separated out as nitrate and was removed) and then titrating it with a dilute solution of thiocyanate.

In three experiments the concentration of silver in solid zinc varied from 0.171 to 0.233% and the partition coefficient from 1300 to 5700. The discrepancy is no doubt due to the contamination of the liquid phase by solid particles which passed through the glass wool. But whether the highest value be near the truth or not can not be decided; for in this case the determination of the silver retained in the melted lead is very uncertain. Yet it is quite clear that the partition coefficient of silver between solid zinc and liquid lead is enormously large, and this fact explains the practical completeness with which the lead is desilverised in practice.

I very much regret that I must leave this investigation in this unsatisfactory form; for the time at my disposal is nearly over, and I can neither repeat nor extend the determinations.

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VOL. XXV., ARTICLE 10.

Studies on the Chemical Theory of Solutions.
Part I.

By

K. Ikeda, *Rigakuhakushi.*

CONTENTS.

Introduction.

The theory of dilute solutious, with which the name of VAN T'HOFF is most prominently associated, has been one of the chief agencies in the rapid development of physical chemistry in the last two decades. But its applicability is by its very nature limited, and for further progress a more general theory, such as will enable us to treat quantitatively problems of solutions of any composition, must be worked out. This want has been generally felt, and attempts to meet it have been made by various physicists and chemists.

Among these the elaborate molecular theory of binary mixtures by VAN DER WAALS stands preëminent, and has led to many investigations theoretical as well as experimental. But his theory is bound up with the equation that bears his name, and requires complicated mathematical apparatus in solving even apparently simple problems. For systems in which chemical reactions take place, or in which the number of components exceeds two, the difficulties become so great that no noteworthy progress has as yet been achieved in these directions.

A simpler method of procedure might perhaps lead to the goal more quickly. It has been demonstrated by the investigations of DAHMS, HARTMANN, LECHATELIER, LINEBARGER, SCHROEDER, VAN LAAR, YOUNG, ZAWIDZKI, and others, that there are some solutions in which the quantitative relations of the heterogeneous equilibria are remarkably simple. These approximate pretty closely to what has been called the "ideal solusion." But the majority of the solutions hitherto studied show more or less marked deviations from these simple relations. Are we to consider these simple cases as accidental and try to establish a theory which would embrace the manifoldness of the phenomena in one general consideration? Or are we to look at these simplest relations as normal and try to account for the deviations by introducing appropriate hypotheses? The teaching of the history of chemistry leaves us no doubt on this point. The anomalous behaviour of vapours, which appeared at first to endanger the universal validity of the gas laws, led to the establishment of the *chemical* hypothesis of association and dissociation, a hypothesis which has proved so fruitful and assisted in no small degree in the development of rational views on chemical affinity. Again the anomalies of the salt solutions with respect to the theory of the dilute solution have found their natural explanation in the *chemical* hypothesis of electrolytic dissociation, under whose banner physical chemistry has achieved so many conquests. What then could be more natural than to assume the simple and regular behaviour of certain solutions as normal and to consider the deviations from such as due to reversible chemical reactions taking place in the solution? And as the manifoldness of chemical reactions is inexhaustible, the resources of this hypothesis must be so too. It is indeed not difficult to imagine that most of the complex relations actually observed could be accounted for in this way. The theory of solution based on such a hypothesis may be called *chemical* in contrast to such a physical theory as that of VAN DER WAALS.

In working out the consequences of particular hypothesis there is always danger of becoming one-sided and losing sight of other possibilities. Yet for the first attempts it would be better not to be too circumspect, lest one should be lost in the maze of the variety of things which must be taken into consideration at the same time. Had the propounder of the theory of electrolytic dissociation sought for all the various factors which might have some bearing upon the deviations from the simple laws of the dilute solution and attempted to interweave these into his fundamental conceptions, he would certainly have produced a more general theory, but it is very doubtful whether he could have achieved so much for the real progress of the science. The present studies have been prosecuted in the same spirit, directness and simplicity of treatment having been striven for rather than generality and rigour. The deviations from the ideal behaviour are considered to be caused by chemical changes alone. In this way it is hoped that the general behaviour of solutions may be made comprehensible, and more particularly that the quantitative relations of heterogeneous equilibria may be elucidated. Conversely it may also be expected that the state of chemical equilibrium in concentrated solutions will be deduced from the study of heterogeneous equilibria. This application, when it can really be made, will prove to be of considerable importance to various branches of chemistry.

It may, however, be urged that in the liquid state the individual properties of the components and the influences of their mutual actions, which are also of a specific nature, are predominant, and that the deviations from the ideal behaviour caused by these factors may be much more considerable than is the case with rarefied gases or dilute solutions, so that quite anomalous relations may obtain without any chemical change taking place. This objection is of course irrefutable. But in a great many cases where chemical reactions are avowedly excluded, close approximation to the ideal behaviour has been observed. We have therefore some reason to suppose that the deviations caused by the physical factors are in general not so great that the deviations called forth by considerable chemical changes become entirely indistinguishable. At any rate we may deduce various types of homogeneous and heterogeneous equilibria by assuming various chemical reactions in the solution, and compare them with observed cases. Exact numerical agreement is of course not to be looked for, but more or less close approximation should be found in many cases, especially when the components are not of a too divergent nature.

When the chemical theory has been worked out to a certain extent and established on the sure foundation of observation, it will be time to take the physical factors into consideration and construct a more complete theory of solution.

CHAPTER I.

THE IDEAL SOLUTION.

§ 1. The General Nature of the Ideal Solution.

The behaviour of the ideal solution in various relations must be investigated in the first place because it forms the foundation of the present study. By the ideal solution is meant a homogeneous liquid mixture in which the following two conditions are fulfilled :

1. The volume of the solution is the sum of the volumes of the components (in the liquid state) under the same pressure and at the same temperature.

2. The energy of the solution is the sum of the energies of the components (in the liquid state) under the same pressure and at the same temperature.

These conditions may be expressed by the following equations:

$$V = n_1 v_1 + n_2 v_2 + \cdots\cdots\cdots, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

$$E = n_1 \varepsilon_1 + n_2 \varepsilon_2 + \cdots\cdots\cdots, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where V and E are the volume and energy of the solution, n_1, n_2,......... are the number of mols (gramme-molecules), v_1, v_2,......... the so-called molecular volumes, and ε_1, ε_2......... energies per mol of the components $\mathfrak{S}_1$, $\mathfrak{S}_2$,......... These conditions must hold at all temperatures and pressures.

The first condition is what is called by VAN DER WAALS the law of AMAGAT. While the law of DALTON is a so-called "Grenzgesetz" to which the gas mixtures approximate the more closely the greater the rarefaction, the law of AMAGAT has a wide range of application, gases under high pressures being known to obey it in some cases. It is quite probable that it would hold, at least approximately, for most gaseous mixtures in which chemical reaction is excluded, because even liquids form solutions with extremely small change of volume when they are unassociated.

The second condition is also fulfilled at least approximately by these liquid mixtures, because the heat disturbances observed on mixing are mostly quite small, being in some cases apparently nil. Hence it is also highly probable that gases under pressures, high or low, should fulfill the condition more or less closely.

When these conditions are satisfied, the chemical potentials of the components have a very simple form just as in a mixture of ideal gases:

$$\left.\begin{array}{l}\mu_1 = \zeta_1 + RT\,ln\,C_1 \\ \mu_2 = \zeta_2 + RT\,ln\,C_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \end{array}\right\} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

where μ_1, μ_2,......... are the molecular chemical potentials, ζ_1, ζ_2, ... the molecular thermodynamic potentials in the isolated state, and C_1, C_2,......... the molar fractions (the thermodynamic or numerical concentrations) of the components $\mathfrak{S}_1$, $\mathfrak{S}_2$,..........

The relation expressed by (3) can be readily deduced from (1) and (2). From the latter we see that the work gained by mixing must be proportional to absolute temperature, and from (1) that it is independent of pressure. When the temperature is sufficiently raised and the pressure sufficiently lowered the mixture as well as the components is in a state approaching that of ideal gases and the work obtainable by reversible mixing of the components is equal to

$$-n_1 RT\,ln\,C_1 - n_2\,RT\,ln\,C_2 - \cdots\cdots\cdots,$$

which is proportional to the absolute temperature. The work obtainable by the formation of the solution can therefore be represented by the same expression. Z, the thermodynamic potential (or the available energy at constant temperature and pressure) of the solution must be equal to the sum of the available energies of the components minus the work obtainable during the formation of the solution. Hence

$$Z = n_1\zeta_1 + n_2\zeta_2 + \cdots\cdots + n_1\,RT\,ln\,C_1 + n_2\,RT\,ln\,C_2 + \cdots\cdots,$$

which on differentiation with respect to n_1, n_2,......... gives:

$$\mu_1 = \frac{\partial Z}{\partial n_2} = \zeta_1 + RT\,ln\,C_1$$

$$\mu_2 = \frac{\partial Z}{\partial n_2} = \zeta_2 + RT\,ln\,C_2$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

In the foregoing deductions it is not necessary to make any assumption as to the molecular weights of the components in the liquid state.

It is enough to use those in the gaseous state. But the molecular weight of a gaseous substance is determined theoretically by the amount of work obtainable by its diffusion or expansion. As substances can be made to pass continuously from the gaseous to the liquid state, and as the work obtainable by the interdiffusion of the components is identical in both, the molecular weights of the components in the liquid state must be considered to remain the same as in the gaseous state. In fact all the components which mix with one another with very small changes of volume and energy are without exception unassociated liquids.

From the amount of work obtainable by reversible mixing we can readily calculate the strength of the osmotic pressure exerted on a semipermeable septum if we assume the liquids to be incompressible. When the mixing is accomplished by means of an osmotic apparatus having as many semipermeable pistons as there are components, then the work must be

$$n_1\pi_1v_1 + n_2\pi_2v_2 + \cdots\cdots = -n_1\,RT\,ln\,C_1 - n_2\,RT\,ln\,C_2 - \cdots\cdots$$

where π_1, π_2,········ are the osmotic pressures exerted by the solution on the pistons allowing the passage of $\mathfrak{S}_1$, $\mathfrak{S}_2$,········ respectively. As n_1, n_2,········ can be varied independently of one another, it follows

$$\pi_1v_1 = -RT\,ln\,C_1$$

or

$$\pi_1 = \frac{-RT\,ln\,C_1}{v_1}$$

which of course gives VAN T'HOFF's relation for the cases in which C_1 approaches unity.

The physical properties of the ideal solutions are mostly of an additive nature. That the heat capacity and the compressibility must belong to this category follows from conditions (1) and (2). Refraction of light calculated according to the formula of GLADSTONE and DALE or that of LORENZ and LORENTZ agrees in some cases almost exactly with the supposition. Other optical properties such as the absorption of light or the rotation of the plane of polarisation are probably also additive. The molecular surface tension of such solutions has been shown to be of the same nature by Ramsay and Aston (Zeits. physik. Chem., **15**, 89; 1894). No doubt with the extension of exact measurements of various properties such examples would be greatly increased.

§ 2. The Equilibrium between Gaseous and Liquid Phases.

(*a*) *Vapour Pressure at a Constant Temperature.*

In the following the gas phases are assumed to be so rarefied that the gas laws are applicable without restriction. In such case the relations obtaining are remarkably simple.

The chemical potential of the components in the liquid phase may, under the circumstances, be considered as constant at a constant temperature and independent of pressure. The chemical potential of the components in the gas phase varies of course with pressure. For the component $\mathfrak{S}_1$ it is

$$\mu_1' = z_1' + RT\,ln\,P + RT\,ln\,C_1', \text{ .... } (4)$$

where z_1' is the molecular thermodynamic potential of the isolated component in the gaseous state at the temperature T and under the unit pressure, while C_1' is the molar fraction of the component in the gas phase.

If the isolated component $\mathfrak{S}_1$ has the vapour pressure P_1 at the temperature T_1 then we have

$$z_1 = z_1' + RT\,ln\,P_1.$$

When the solution is in equilibrium with its vapour

$$\mu_1 = \mu_1',$$

hence

$$z_1' + RT\,ln\,P_1 + RT\,ln\,C_1 = z_1' + RT\,ln\,P + RT\,ln\,C_1'$$

or

$$C_1P_1 = C_1'P = p_1 \quad \text{..........................}(5)$$

in which p_1 denotes the partial pressure of $\mathfrak{S}_1$ in the gas phase. A similar consideration applies to other components. This important relation can be expressed in the following words:

> At a given temperature the partial pressure of a component in the gas phase is equal to the vapour tension of the component in the pure state multiplied by the molar fraction of the component in the liquid phase.

The total pressure P is of course equal to the sum of the partial pressures.

In a binary system we have

$$C_2' = 1 - C_2'$$

and

$$p_1 + p_2 = P.$$

If we take the molar fraction C_1' as abscissa and the pressure as ordinate we get the diagram shown in Fig. 1. As the curves of the partial pressures p_1 and p_2 are straight lines, that of the total pressure is also a straight line.

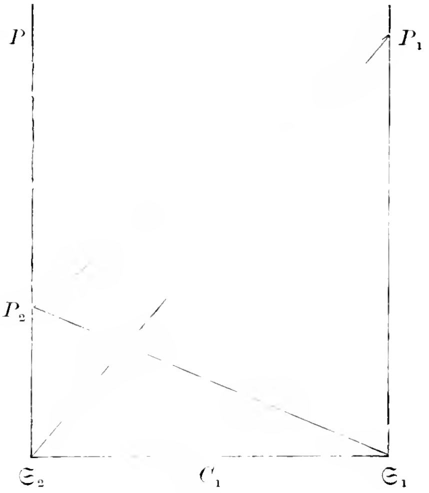

Fig. 1.

The fact that the composition-pressure curve is a straight line for a binary ideal solution was first established by F. GUTHRIE (Phil. Mag., V, **18**, 517; 1884). He found that contraction on mixing of two liquids is generally accompanied by the evolution of heat, and expansion of volume by the absorption of heat. He also observed that in the former case the curves of total vapour pressure are convex to the axis of composition, while in the latter case they are concave. He reasoned from these facts that for a mixture in the formation of which neither a change of volume nor of heat takes place the vapour tension curve must be a straight line. He found his anticipation nearly realised in the mixture of ethyl chloride and iodide.

The results of the experimental studies of LINEBARGER, HARTMANN, LEHFELD, and ZAWIDZKI have been incorporated in the standard work of ROOZEBOOM (Heterogene Gleichgewichte, II, 21), hence it is not necessary to discuss them here. In all the cases where the curves of total as well as of partial pressure are straight lines the components are substances known, by the method of surface tension, to be unassociated. Some mixtures of presumably normal liquids give curves which are not quite straight, but the curvatures are mostly quite small. Doubtless many liquids usually supposed to be normal are associated to a slight extent.

According to VAN DER WAALS the conditions necessary for straight vapour pressure curves are the following:

(*a*) The heat of the evaporation of the mixture is the sum of the heats of the evaporation of the components.

(*b*) The critical pressures of the two components are equal.

That (*a*) is the consequence of (2) is evident, while (*b*) has no direct relation with (1). KOHNSTAMM (Zeits. physik. Chem., **36**, 52; 1901) tried to verify the condition (*b*), but could not reach any satisfactory result owing to the inaccuracy of the data on critical pressure.

According to YOUNG (Journ. Chem. Soc., **83**, 45; 1903) the chemical similarity of the components is one of the conditions for straight vapour pressure curves. Yet ZAWIDZKI has found the mixture of benzene and carbon tetrachloride to have such curves. If the idea of chemical similarity could be applied to such cases, it would be too indefinite to be of much value as a criterion. Yet there seems to be some truth in YOUNG's assertion, because chemically allied substances mix with one another mostly without much change of energy or of volume.

In a ternary system the vapour pressures, total as well as partial, are represented by planes as shown in Fig. 2, while the surface of the total pressure has the form of a sail spread between three points, when the composition is that of the gas phase. The plain and the curved surfaces of the total pressure are represented by the following equations:

$$P = C_1 P_1 + C_2 P_2 + C_3 P_3$$

$$\frac{1}{P} = \frac{C_1'}{P_1} + \frac{C_2'}{P_2} + \frac{C_3'}{P_3}$$

where C_1', C_2', C_3' are the molar fractions of the components in the gas phase, and P_1, P_2, P_3 are the vapour pressures of the pure components at the given temperature.

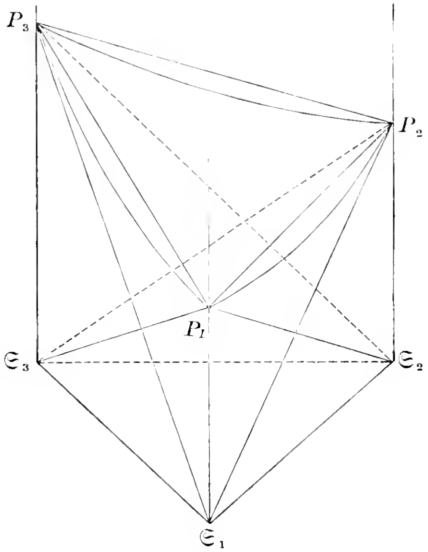

Fig. 2.

It is quite clear that these equations can be extended and applied to the ideal system of any number of components.

There seem to be some solid solutions whose vapour pressure corresponds tolerably closely to that of an ideal solution. For example, Speranski (Zeits. physik. Chem., **51**, 55; 1905) found that the vapour pressure curve of the solid solution of p-dichlorobenzene and p-dibromobenzene was very nearly a straight line throughout the whole range of his experiment, which extended up to 45% mol dibromobenzene. The temperature was varied between 40.3°C. and 66.1°C. without any noticeable influence on the result. This mixture was studied by Küster (Zeits. physik. Chem., **51**, 235; 1905) who employed a dynamical method for the measurement of the small vapour pressures. He found that the curve of the partial pressure of p-dichlorobenzene is nearly a straight line, while that of p-dibromobenzene is concave towards the axis of composition and has a maximum. If the data were exact they would be of considerable interest, because they contradict the relation of Duhem-Margules which ought to be universally applicable.

(*b*) *Isothermal Distillation.*

Fractional distillation is one of the most important operations employed in separating the various components from mixtures. It is daily practised in laboratories and factories, but the exact quantitative theory of the process remains to be developed. This is no doubt due to the lack of insight into the exact relation between temperrture, pressure, and the compositions of the phases, gaseous and liquid. For ideal solutions such insight is given and a part of the problem can be solved with comparative ease. For example, take the subject of isothermal distillation. In this case we not only have to determine how the compositions of the distillate and the residue vary with pressure, but we must also calculate the quantity of the distillate.

To begin with a binary mixture, let the initial conditions of the solution be as follows:

N_1 = number of mols of $\mathfrak{S}_1$
N_2 = " " " " $\mathfrak{S}_2$
P_0 = vapour pressure.

Then we have

$$P_0 = \frac{N_1}{N_1+N_2} P_1 + \frac{N_2}{N_1+N_2} P_2 ;$$

hence if the initial pressure be given, the composition can be calculated by the following equation

$$\frac{N_1}{N_1+N_2} = \frac{P_0-P_2}{P_1-P_2} ;$$

and if the initial weight of the solution be known, N_1 and N_2 can be determined.

At any moment let the pressure be P and the number of mols of the components in the residue be n_1 and n_2 respectively. Then in the infinitesimal evaporation the following relation must hold:

$$dn_1 : dn_2 = C_1' : C_2'$$

But by the equation (5) we have

$$C_1' = \frac{P_1}{P} \frac{n_1}{n_1+n_2}, \qquad C_2' = \frac{P_2}{P} \frac{n_2}{n_1+n_2} ;$$

hence

$$\frac{1}{P_1} \frac{dn_1}{n_1} = \frac{1}{P_2} \frac{dn_2}{n_2},$$

which on integration becomes

$$\frac{1}{P_1} ln \frac{n_1}{N_1} = \frac{1}{P_2} ln \frac{n_2}{N_2} \qquad \text{..........................(6)}$$

This expression combined with the equation

$$\frac{n_1}{n_1+n_2}=\frac{P-P_2}{P_1-P_2}$$

suffices to determine the values of n_1 and n_2. In the distillate there are N_1-n_1 mols of the first component, and N_2-n_2 mols of the second. In this way the compositions and quantities of the distillate and residue are determined in terms of pressure, and the problem is solved.

In the ternary system the composition of the residue suffers a definite course of change during the process of isothermal distillation. This can be represented by a curve in the triangular diagram. The nature of this curve was first investigated by SCHREINEMAKERS (Zeits. physik. Chem., 36, 422; 1901) and is called the distillation curve. So long as the temperature is kept constant the composition of the residue can vary only along this curve. How this comes to pass can be briefly explained in the following manner.

Let g in Fig. 3 represent the composition of the liquid phase and g' that of the gas phase in equilibrium with it. As the distillation goes on the composition of the residue will be displaced a little in the direction of the line $g'g$ according to the well known theorem of the ternary mixture. Hence gg' is the tangent of the curve, and thus the direction of the curve is determined. After a certain amount of liquid has been distilled, the liquid phase will have the composition f, while that of the

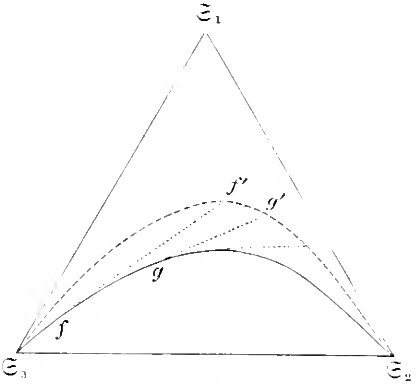

Fig. 3.

gas phase will be f', and the curve will proceed in the direction $f'f$, etc., etc.

In the case of an ideal solution we have

$$p_1 = C_1'P = C_1P_1$$
$$p_2 = C_2'P = C_2P_2$$
$$p_3 = C_3'P = C_3P_3$$

and
$$P = C_1P_1 + C_2P_2 + C_3P_3.$$

Hence

$$C_1' = \frac{C_1P_1}{C_1P_1 + C_2P_2 + C_3P_3}$$

$$C_2' = \frac{C_2P_2}{C_1P_1 + C_2P_2 + C_3P_3}$$

As the tangent to the distillation curve passes through the point C_1, C_2 as well as the point C_1', C_2' we have

$$\frac{dC_2}{dC_1} = \frac{C_2 - C_2'}{C_1 - C_1'} = \frac{C_2\{C_1P_1 + C_2P_2 + (1 - C_1 - C_2)\,P_3 - P_2\}}{C_1\{C_1P_1 + C_2P_2 + (1 - C_1 - C_2)\,P_3 - P_1\}} \text{......(7)}$$

Which may also be written

$$\frac{dC_2}{dC_1} = \frac{C_2\,(P - P_2)}{C_1\,(P - P_1)}.$$

Suppose the first component to be the most volatile and the second component to be the least volatile of the three, then

$$P - P_2 > 0, \qquad P - P_1 < 0\,;$$

and as both C_1 and C_2 are necessarily positive

$$\frac{dC'_2}{dC'_1} < 0.$$

In other words C_2 must decrease as C_1 increases. The curve of isothermal distillation has therefore the form represented by $\mathfrak{S}_1 A \mathfrak{S}_2$, etc., Fig. 4. When there is but little $\mathfrak{S}_1$ in the solution $\frac{dC'_2}{dC'_1}$ must be very large, and when $C_1 = 0$ the curve coincides with the axis $\mathfrak{S}_3\mathfrak{S}_2$. Hence if there is much of $\mathfrak{S}_3$ in the original solution the curve will have a form like $\mathfrak{S}_1 C \mathfrak{S}_2$. On the contrary, when there is but little of $\mathfrak{S}_3$ the curve will have a form like $\mathfrak{S}_1 B \mathfrak{S}_2$. If $C_3 = 0$,

$$(P-P_2):(P-P_1) = -C_1 : C_2$$

and

$$\frac{dC_2}{dC_1} = -1,$$

so that the curve coincides with the axis $\mathfrak{S}_2\mathfrak{S}_1$.

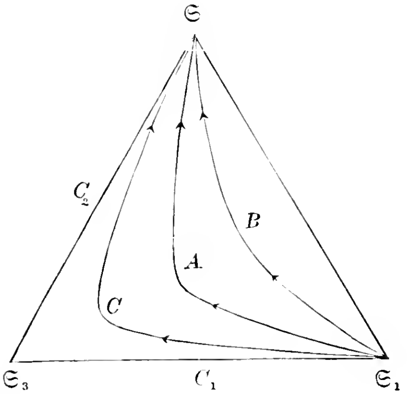

Fig. 4.

The equation (7) can be written

$$\frac{dC_2}{dC_1} = -\frac{C_2\{(P_1-P_2)\,C_1+(P_3-P_2)\,(1-C_1-C_2)\}}{C_1\{(P_1-P_2)\,C_2+(P_1-P_3)\,(1-C_2-C_3)\}},$$

which can be readily transformed into

$$(P_2-P_3)\frac{dC_1}{C_1}+(P_3-P_1)\frac{dC_2}{C_2}-(P_1-P_2)\frac{dC_1+dC_2}{1-C_1-C_2} = 0.$$

On integration we get

$$C_1^{P_2-P_3}\,C_2^{P_3-P_1}\,C_3^{P_1-P_2} = \mathfrak{C}_1^{P_2-P_3}\,\mathfrak{C}_2^{P_3-P_1}\,\mathfrak{C}_3^{P_1-P_2} \ldots\ldots(8)$$

where $\mathfrak{C}_1$, $\mathfrak{C}_2$, and $\mathfrak{C}_3$ are the initial molar fractions of the components. This is the equation of the curve of isothermal distillation.

The composition and the quantity of the residue during the process of isothermal distillation of a ternary mixture can be calculated in exactly the same manner as in the case of a binary system. We have

$$dn_1 : dn_2 : dn_3 = C_1' : C_2' : C_3'$$

which becomes by (5)

$$\frac{1}{P_1}\frac{dn_1}{n_1}=\frac{1}{P_2}\frac{dn_2}{n_2}=\frac{1}{P_3}\frac{dn_3}{n_3}.$$

This can be readily integrated to

$$\frac{1}{P_1}\,ln\,\frac{n_1}{N_1}=\frac{1}{P_2}\,ln\,\frac{n_2}{N_2}=\frac{1}{P_3}\,ln\,\frac{n_3}{N_3}\ \ldots\ldots\ldots\ldots\ldots(a)$$

We have also the relation

$$P=\frac{n_1}{n_1+n_2+n_3}P_1+\frac{n_2}{n_1+n_2+n_3}P_2+\frac{n_3}{n_1+n_2+n_3}P_3.\quad\ldots\ldots(b)$$

These three equations of (a) and (b) are sufficient to determine the values of n_1, n_2, and n_3.

(c) *The Boiling Point of an Ideal Solution.*

As explained under (a) the relation between the total pressure on one hand and the vapour pressures of the pure components and composition on the other is very simple at a constant temperature. Hence if the vapour pressure of the components be given as a function of temperature, the relation between boiling point and composition can be readily ascertained. Now let the vapour pressure of the components be expressed by:

$$P_1=\varphi_1(T),\qquad P_2=\varphi_2(T),\qquad \text{etc.}$$

and let $\mathfrak{P}$ be the constant pressure under which the solution boils, then we have

$$p_1+p_2+\cdots\cdots=C_1\,\varphi_1(T)+C_2\,\varphi_2(T)+\cdots\cdots=\mathfrak{P}\ldots\ldots\ldots(9)$$

The variation of the vapour pressure of each component with the temperature is given by the equation of CLAPEYRON-CLAUSIUS:

$$\frac{\partial\,ln\,P_1}{\partial T}=\frac{q_1}{RT^2},\qquad \frac{\partial\,ln\,P_2}{\partial T}=\frac{q_2}{RT^2},\qquad \text{etc.}$$

where q_1, q_2,……… represent the molecular heat of evaporation. The limitations to which the application of the equations are subject are too well known to be mentioned in this place. q_1, q_2,……… diminish with rising temperatures, but the exact form of the function is not known. Within a short range of temperature, say thirty to fifty degrees, and particularly in the region where the vapour pressure is not very large, q_1, q_2,……… may be considered constant without causing much error.[1] The equations can then be integrated into

$$P_1 = e^{a_1 - \frac{q_1}{RT}}, \qquad P_2 = e^{a_2 - \frac{q_2}{RT}}, \quad \text{etc.} \ldots\ldots\ldots\ldots(A)$$

where a_1, a_2,……… are constants. In cases where the differences between the boiling points are not great the equation (9) can be written

$$C_1 e^{a_1 - \frac{q_1}{RT}} + C_2 e^{a_2 - \frac{q_2}{RT}} + \cdots\cdots = \mathfrak{P} \quad \ldots\ldots\ldots\ldots(10)$$

TROUTON'S law simplifies the matter considerably. According to this law the ratio between the molecular heat of evaporation and the absolute temperature of the boiling point is constant for various substances. This has been verified for many unassociated liquids under ordinary atmospheric pressure. But there is no doubt that the law is also applicable to cases in which the pressure is considerably smaller. Only the ratio must increase with decreasing pressure. Thus under ordinary atmospheric pressure,

---

[1] Otherwise we have the usual equation with more than two constants in the form $ln\,P = A - \frac{B}{T} + C\,ln\,T + DT + \cdots\cdots\cdots$ But then the constants can no longer be determined with necessary definiteness from empirical data, because slight experimental errors cause considerable shifting between the values of the constants. Hence the approximate equation is employed advisedly, not only to lessen mathematical complicacy, but also to make the deductions more definite.

$$\frac{q_1}{RT_1} = \frac{q_2}{RT_2} = \cdots\cdots\cdots = 10.9 \text{ nearly},$$

while under a pressure of 200 m.m. mercury the following values have been found :

Substance.	Ether.	Iodobenzene.	Benzene.	Carbon tetrachloride.
$\frac{q}{RT}$	12.9	12.6	12.5	12.7

The values of q have been calculated by means of the CLAPEYRON-CLAUSIUS equation from the vapour pressures determined by RAMSAY and YOUNG.

As $\frac{q_1}{RT_1}$, $\frac{q_2}{RT_2}$,......... are equal, a_1, a_2,......... must also be equal, the numerical value depending on the unit of pressure employed. Hence if we put

$$\frac{q_1}{RT_1} = \frac{q_2}{RT_2} = \cdots\cdots\cdots = b$$

then

$$a_1 = a_2 = \cdots\cdots\cdots = b + ln\, \mathfrak{P}.$$

The equations (A) then become

$$P_1 = e^{a_1 - \frac{q_1}{RT}} = \mathfrak{P}\, e^{b\left(1 - \frac{T_1}{T}\right)},$$

$$P_2 = e^{a_2 - \frac{q_2}{RT}} = \mathfrak{P}\, e^{b\left(1 - \frac{T_2}{T}\right)},$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots.$$

in which T_1, T_2,......... are the only constants characteristic of the components. The equation (10) now reduces to

$$C_1\, e^{b\left(1 - \frac{T_1}{T}\right)} + C_2\, e^{b\left(1 - \frac{T_2}{T}\right)} + \cdots\cdots\cdots = 1 \quad \cdots\cdots\cdots(11)$$

When C_1, C_2,......... are given, the boiling point T of the solution can be calculated by this equation. But it is only for a binary mixture that the composition can be determined from the boiling point. For solutions with more than two components the equation becomes indeterminate.

Young and Fortey (Journ. Chem. Soc., **83**, 45; 1905) tested the applicability of the equation (9) to various binary solutions approximating more or less closely to the ideal solution. Of these the mixture of chloro- and bromobenzene satisfied conditions (1) and (2) most closely, and they found that the boiling point of the mixture could be represented quite well by equation (9). For $\varphi(T)$ they employed Biot's formula. The calculation with equation (11) is of course much simpler, while the agreement is nearly as good, as is shown in the following table:

Boiling point.	132.0°	136.75°	142.16°	148.16°	156.0°
Molar fraction of C_6H_5Br	0	.2501	.5000	.7364	1.000
Ditto calculated	—	.253	.498	.739	—

The differences between the observed and calculated molar fractions do not exceed 3%, which corresponds to about .05° in the measurement of temperature, and seems to be nearly equal to the limit of error. The value of b employed in the calculation is 10.9, and is nearly equal to the mean value.

If only one component be volatile, then

$$\mathfrak{P} = p_1 = C_1 P_1$$

or

$$C_1 \varphi_1 (T) = \mathfrak{P}$$

In the cases where the simple equation (A) is sufficed

$$C_1 e^{a_1 - \frac{q_1}{RT}} = e^{a_1 - \frac{q_1}{RT_1}}$$

or taking the logarithm

$$ln\, C_1 = \frac{q_1}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

This equation is inapplicable to cases in which C_1 is very small, because then P_1 will be very large and cannot be well expressed by the simple equation (A). But in other cases C_1 can be calculated from the boiling point by equation (12).

If we express the sum of molar fractions of all the involatile components by C, then $C_1 = 1 - C$, and we get

$$-ln\,(1-C) = \frac{q_1}{RTT_1}(T - T_1). \quad \ldots\ldots\ldots\ldots\ldots (13)$$

$T - T_1$ is what is called the elevation of the boiling point, and increases with increasing C. Equation (13) might well be employed for the determination of the molecular weight, etc. in the cases where the solution is not dilute but approximately ideal. When the solution is very dilute, C is very small in comparison with unity and we may write C instead of $-ln\,(1-C)$, and T_1^2 instead of TT_1, and equation (13) passes into

$$C = \frac{q_1}{RT_1^2}(T - T_1)$$

which is the well known equation of VAN T'HOFF.

§ 3. Equilibrium between Ideal Solutions and Pure Solids.

The problems of the equilibrium between solid and liquid phases are full of interest. Yet the treatment of them has hitherto been almost exclusively qualitative, the exceptions being those cases which could be solved by the theory of dilute solutions, and some other simple cases which will be mentioned further on. In the case of ideal solutions it is quite easy to establish general quantitative relations and these may serve as the norm in the investigation of actual cases. Even with the ideal solutions there are so many problems that the discussion must be restricted to the more important ones. The influence of pressure has not been taken into consideration because it is in general quite insignificant.

(*a*) *Isothermal Relations.*

Equation (3) demonstrates the applicability of the law of mass action to ideal solutions of any composition. It is indeed very inconvenient to use the idea of spatial concentration in the case of concentrated solutions and this must be replaced by that of molar fraction. GULDBERG and WAAGE reached the conclusion that the active mass of a pure solid substance is constant at a constant temperature. From this standpoint the relations of solubility at a constant temperature can be readily surveyed and described.

When the solid phase has the composition $\mathfrak{S}_{1\nu_1}\mathfrak{S}_{2\nu_2}\ldots\ldots\ldots$ the composition of the solution which is in equilibrium with the solid must satisfy the following equation:

$$C_1^{\nu_1}\, C_2^{\nu_2} \ldots\ldots = K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

$\nu_1, \nu_2, \ldots\ldots\ldots$ are the so called molecular coefficients or exchange numbers (HELM). K is a function of temperature and pressure. But as the influence of the latter is generally very slight K may be considered to be constant when the temperature is constant.

Equation (14) which represents the law of mass action in this case, can be deduced in the following manner. Let Z'' be the thermodynamic potential of one mol of the solid phase, then,

$$Z'' = \nu_1\,\mu_1 + \nu_2\,\mu_2 + \cdots\cdots\cdots.$$

because one mol of the solid phase produces on melting ν_1 mols of $\mathfrak{S}_1$, ν_2 mols of $\mathfrak{S}_2$, etc., and in the state of equilibrium there could be neither gain nor loss of available energy on fusion. But as has been established in § 1,

$$\left.\begin{array}{l} \mu_1 = z_1 + RT\,ln\,C_1 \\ \mu_1 = z_2 + RT\,ln\,C_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \end{array}\right\} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(3)$$

hence

$$Z'' = \nu_1\,z_1 + \nu_2\,z_2 + \cdots\cdots + \nu_1\,RT\,ln\,C_1 + \nu_2\,RT\,ln\,C_2 + \cdots\cdots,$$

and as Z'', z_1, z_2,········ can be considered to be nearly independent of pressure, they are constant at a constant temperature. Therefore

$$\nu_1\,ln\,C_1 + \nu_2\,ln\,C_2 + \cdots\cdots = ln\,K = \text{const.}$$

which is equation (14) in logarithms.

Equation (14) admits of some interesting deductions. For this purpose we will put

$$\left.\begin{array}{l} \dfrac{\nu_1}{\nu_1+\nu_2+\cdots\cdots} = \gamma_1 \\ \dfrac{\nu_2}{\nu_1+\nu_2+\cdots\cdots} = \gamma_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \end{array}\right\} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(15)$$

and

$$\gamma_1^{\nu_1}\,\gamma_2^{\nu_2}\cdots\cdots = \kappa \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(16)$$

γ_1, γ_2,········ are the molar fractions of $\mathfrak{S}_1$, $\mathfrak{S}_2$,········ in the melt of the pure compound, and it is quite clear that

$$K \begin{matrix} < \infty \\ > 0 \end{matrix}.$$

For example, for the binary compound $\mathfrak{S}_1\mathfrak{S}_2$ K is less than $\frac{1}{4}$ and for the compound $\mathfrak{S}_{1_2}\mathfrak{S}_2$ K is less than $\frac{4}{27}$.

When the solid is a component, we have by (14),

$$C_1 = K.$$

In a binary system this is represented by a point on the line of composition (Fig. 5, A). In a ternary system the equation is represented by a straight line parallel to one of the axes of composition (Fig. 5, B); while in a quaternary system, by a plane parallel to one of the planes of the tetrahedron of composition (Fig. 5, C).

When the solid is a binary compound, then we have

$$C_1^{\nu_1} C_2^{\nu_2} = K.$$

In the case of a binary system this becomes

$$C_1^{\nu_1}(1-C_1)^{\nu_2} = K.$$

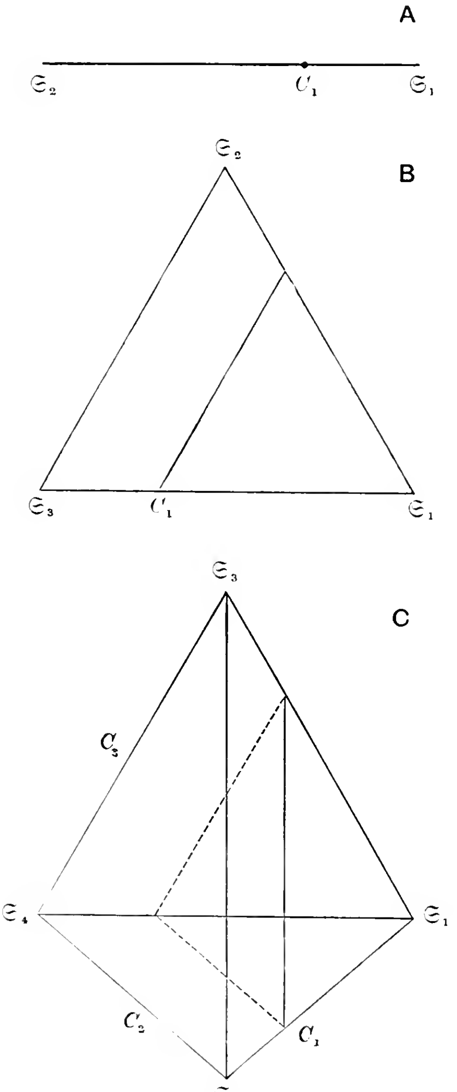

Fig. 5.

There are two positive values of C_1 which satisfy the equation, and these are represented by two points on the line of composition, situated on the opposite sides of the point $C_1=\gamma$ (Fig. 6, A). In systems with more than two components we have the additional condition

$$C_1+C_2<1.$$

This, combined with the foregoing equation, gives a solubility curve of the form shown in Fig. 6, B for a ternary system. γ is a point at which

$$C_1=\frac{\nu_1}{\nu_1+\nu_2}.$$

In a quaternary system the surface of solubility is a ruled surface whose general form is represented by Fig. 6, C.

When the solid is a ternary compound $\mathfrak{S}_{1\nu_1}\mathfrak{S}_{2\nu_2}\mathfrak{S}_{3\nu_3}$, the curve of solubility in a ternary system has the form shown in Fig. 7, A. The symmetry of the curve depends of course on the symmetry relations between the coefficients ν_1, ν_2, and ν_3.

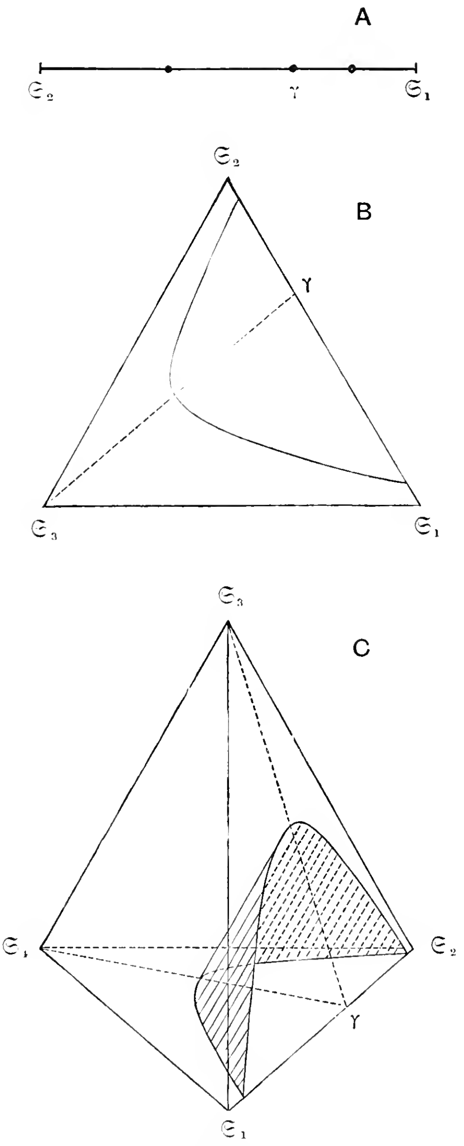

Fig. 6.

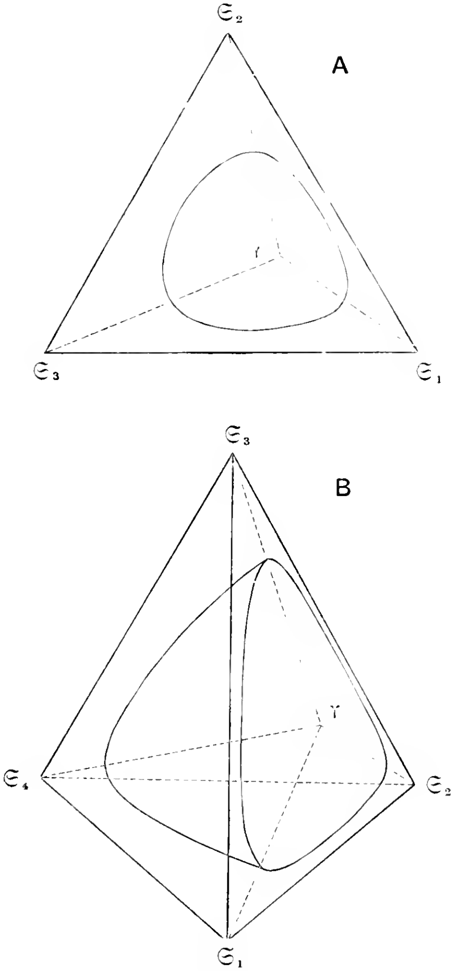

Fig. 7.

In a quaternary system the surface of solubility has the form represented by Fig. 7, B. When the molar fraction of $\mathfrak{S}_4$ exceeds a certain value, the product $C_1^{\nu_1} C_2^{\nu_2} C_3^{\nu_3}$ can no longer be equal to K, but falls below it. Hence the surface must have a maximum point, for which the value of $\mathfrak{S}_4$ is the maximum. This point lies on the straight line connecting the points $\mathfrak{S}_4$ and γ.

When the solid is a quaternary compound, the surface of solubility will be a closed one, having the form shown in Fig. 8.

It must be remembered that no compound exists in the ideal solution itself, because the formation of a com-

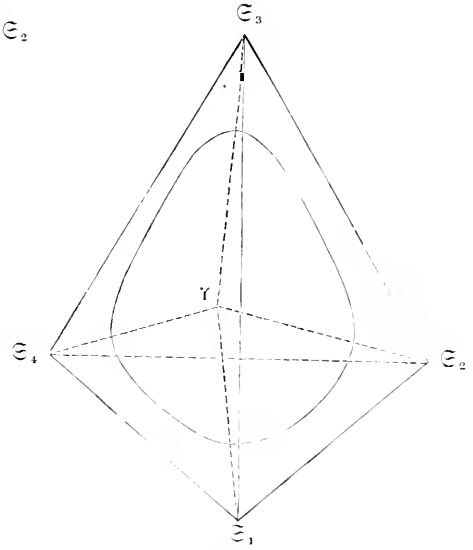

Fig. 8.

pound would be accompanied by changes of energy and volume, and would thus be incompatible with conditions (1) and (2). The equilibrium between a solid compound and an ideal solution is therefore comparable to that between ammonium carbamate and the gaseous mixture of ammonia and carbon dioxide. As the difference of densities between a solid and a liquid is not so great as between a solid and a gas it is quite probable that more or less of the compound exists in the liquid solution also. Hence the curves and surfaces corresponding exactly to the equation

$$C_1^{\nu_1} C_2^{\nu_2} \cdots\cdots = \text{const.}$$

will rarely be met with in actual cases. The foregoing considerations may, however, be of some value as establishing the normal types. On the other hand the straight line and the plane of solubility corresponding to the equation

$$C_1 = K$$

will be often met with.

(*b*) *The Relation between the Temperature of Fusion and the Composition of the Solution.*

That no sharp distinction can be made between fusion and dissolution of solids was pointed out long ago by GUTHRIE (Phil. Mag., V, **18**, 118; 1884), who exemplified his view by the system potassium nitrate—water, and it has now become a current opinion. Hence in speaking of a binary system the terms fusion curve and solubility curve have identical meanings. Yet it is more convenient to have one term which denotes isothermal relations and another which denotes the relation between the temperature and the composition of the solution which is in equilibrium with a solid phase. The terms solubility curve and solubility surface have been employed to denote isothermal relations in the foregoing passages. The terms fusion curve and fusion surface will be employed to denote the relation between temperature and composition.

The ideal fusion curve of a binary system has already been repeatedly a subject of study. LE CHATELIER and SCHROEDER chose the RAOULT-VAN T'HOFF equation for vapour pressure as the starting point of their investigation, while DAHMS and VAN LAAR employed the method of thermodynamic potential. The result arrived at is the same and is represented by the equation:

$$ln\,C_1 = \frac{Q_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right), \text{......................}(17)$$

in which Q_1 is the molecular heat of the fusion of the component $\mathfrak{S}_1$, and T_1 is the temperature of the fusion of the same. The form is identical with that of equation (12), the only difference being caused by the different signs of q_1 and Q_1. Detailed discussion is given by ROOZEBOOM in his standard work (Heterogene Gleichgewichte, II, 274). The three conditions stipulated for the validity of the equation are:

I. The concentration C_1 shall be the so called thermodynamical one, i.e. the molar fraction.
II. The solid component shall separate out pure.
III. Q_1 shall be independent of temperature.

The necessity of the second condition is evident. The cases in which this is not fulfilled will be treated in the next section.

The third condition is an assumption which does not stand in any necessary connection with the conception of the ideal solution developed in the present study. TAMMANN has observed that the heat of fusion is nearly constant along the fusion curve of one component system (the temperature-pressure curve). And as the heat of mixing is nil in the case of ideal solutions the assumption seems to be quite plausible. But the specific heats of the same component as solid and liquid are in general not equal. Hence the condition will rarely be fulfilled exactly. Still for the cases in which the temperature range is somewhat limited the assumption may be admitted as a convenient approximation. Two conditions out of the three being thus extraneous to the conception of an ideal solution, there remains only the first condition to be examined. Excepting the cases in which the gas pressure or the osmotic pressure are avowedly taken into consideration, the idea of molecular weight is generally rather vague in thermodynamical discussions, and the molecular weights employed in calculating C_1 may well be those in the gaseous state and not those in the liquid state. This is often explicitely stated in the deduction of the laws of dilute solutions. Hence the first condition does not coincide with condition (1) or (2), and it is doubtful whether the three conditions given by ROOZEBOOM suffice to establish equation (17). On the other hand DAHMS mentions conditions (1) and (2) explicitely.

The relation between the temperature and the composition of an ideal solution which is in equilibrium with a solid phase, either a component or a compound, can be deduced in the following manner. The equation (see page 7),

$$\begin{aligned} Z'' &= \nu_1 \mu_1 + \nu_2 \mu_2 + \cdots\cdots \\ &= \nu_1 z_1 + \nu_2 z_2 + \cdots\cdots + RT(\nu_1 \, ln \, C_1 + \nu_2 \, ln \, C_2 + \cdots\cdots), \end{aligned}$$

is of course valid for any temperature. On differentiating with respect to T we get:

$$\frac{\partial Z''}{\partial T} = \nu_1 \frac{\partial z_1}{\partial T} + \nu_2 \frac{\partial z_2}{\partial T} + \cdots\cdots + RT \frac{\partial \, ln \, K}{\partial T} + R \, ln \, K,$$

where K has the meaning defined by equation (14), but is no longer constant as the temperature is considered variable. From the definition of Z'', z_1, z_2,········ it follows:

$$\frac{\partial Z''}{\partial T} = -S'', \qquad \frac{\partial z_1}{\partial T} = -S_1, \qquad \frac{\partial z_2}{\partial T} = -S_2, \quad \text{etc.}$$

where S'' is the molecular entropy of the solid compound $\mathfrak{S}_{1\nu_1}\mathfrak{S}_{2\nu_2}$········, and S_1, S_2,········ are the molecular entropies of the components in the liquid state. We have therefore,

$$RT \frac{\partial \, ln \, K}{\partial T} = \nu_1 S_1 + \nu_2 S_2 + \cdots\cdots - S'' - R \, ln \, K.$$

But as $-RT \, ln \, K$ is nothing but the maximum work obtainable by mixing the liquid components in the proportion necessary for the formation of one mol of the compound, we have the following relation:

$$\nu_1 S_1 + \nu_2 S_2 + \cdots\cdots - S'' - R \, ln \, K = \frac{Q}{T},$$

where Q is the molecular heat of fusion of the compound. The foregoing differential equation reduces therefore to:

$$\frac{\partial \, ln \, K}{\partial T} = \frac{Q}{RT^2}, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (18)$$

a form which is identical to the reaction isochor of VAN T'HOFF.

This equation can be integrated when Q is given as function of temperature. Let us assume as an approximation, that Q is independent of temperature. Then

$$ln \frac{K}{\varkappa} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right), \ldots (19)$$

where $\varkappa$ stands for the value of K in the melt of the pure compound, according to equation (16), and T_1 stands for the melting point of the compound.

When the solid is a component, then

$$\varkappa = 1$$

and $$K = C_1,$$

and equation (19) assumes the form (17), which is applicable to systems of any number of components.

Several cases in which equation (17) represents the actual course of fusion curves in binary systems have been

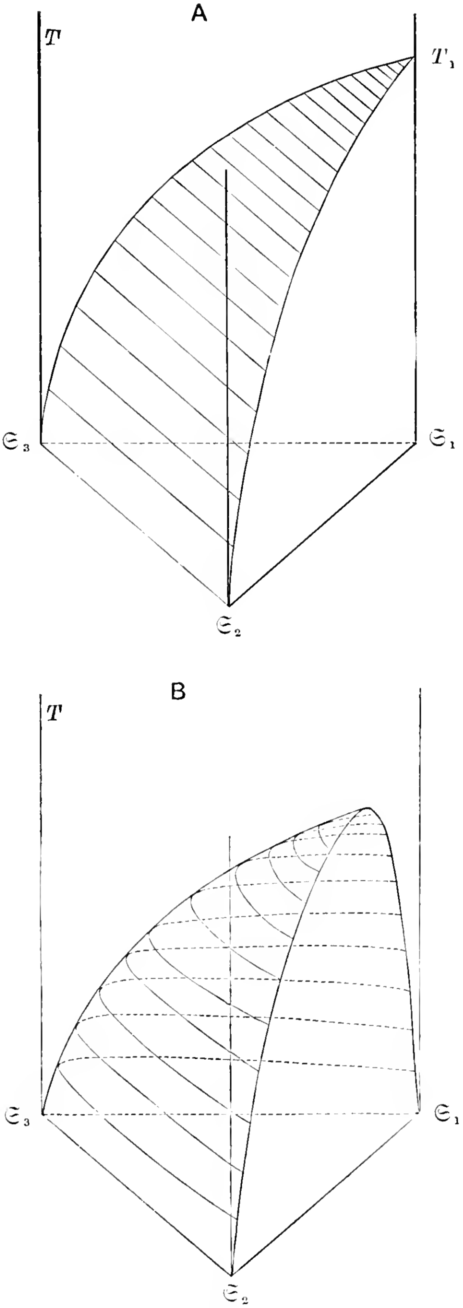

Fig. 9.

studied by the authors mentioned above. The form of the curve has been discussed by van Laar in detail. On the other hand graphical representations of the general features of the fusion curves and surfaces may be of some interest although they do not bring out anything new.

Fig. 9, A represents the fusion surface of a component in a ternary system, while Fig. 9, B and C represent the fusion surfaces of a binary and a ternary compound.

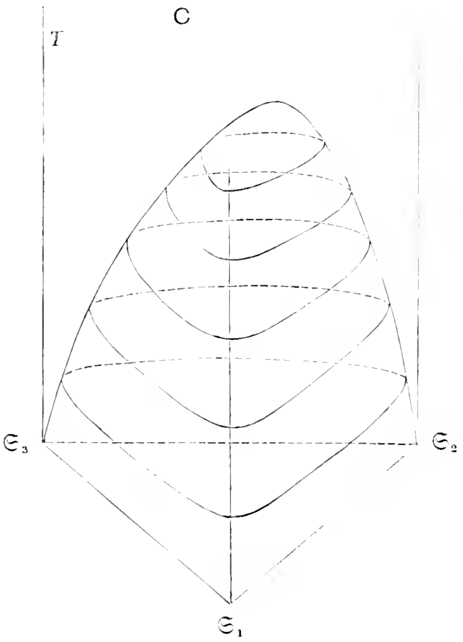

Fig. 9.

§ 4. The Equilibrium between an Ideal Liquid and an Ideal Solid Solution.

It is probable that, in some cases, at least, conditions (1) and (2) are satisfied by solid solutions. For example, Retger observed in several cases of isomorphous mixtures, that the volume was equal to the sum of the volumes of their components. And if these conditions are fulfilled, we may apply equation (3) in the discussion of equilibria into which such solid solutions enter. In the present section the equilibrium between an ideal solid and an ideal liquid solution will be considered. As the solid phase is supposed by the very conditions not to contain any compound, the problem is so far simplified. The equilibrium between a solid component or a solid compound and an ideal solid solution may be treated just in the same manner as in the foregoing section.

(*a*) *Isothermal Relations.*

The relation between the compositions of an ideal liquid and an ideal solid solution at a constant temperature can be found in the following manner. Let μ_1 and μ_2'' be the molecular chemical potential of the first component in the liquid and the solid phase respectively. Then we have by equation (3)

$$\mu_1 = z_1 + RT\,ln\,C_1$$

and

$$\mu_1'' = z_1'' + RT\,ln\,C_1''$$

where z_1'' and C_1'' denote the corresponding quantities for the solid solution, as z_1 and C_1 for the liquid phase. In the case of equilibrium

$$\mu_1 = \mu_1'' ;$$

hence

$$ln\,\frac{C_1}{C_1''} = \frac{z_1''-z_1}{RT}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(20)$$

The supposition that z_1'' as well as z_1 is independent of pressure may be looked upon as a close approximation as long as the variation of pressure is not very considerable. Under this assumption we have

$$\frac{C_1}{C_1''} = r_1 = \text{const.} \quad \ldots\ldots\ldots\ldots\ldots\ldots(21)$$

for a constant temperature. Similarly

$$\frac{C_2}{C_2''} = r_2 = \text{const.}$$

....

....

$r_1, r_2, \cdots\cdots$ are all positive numbers greater or less than unity; but they can not all be greater or less than unity, because this would lead to incompatibilities. For example, in a binary system

$$\frac{C_1}{C_1''} = r_1 \quad \text{..............................(A)}$$

and

$$\frac{1-C_1}{1-C_1''} = \frac{1-r_1 C_1''}{1-C_1''} = r_2 \text{..................(B)}$$

Hence if r_1 be greater than unity then r_2 must be less than unity. These two equations (A) and (B) determine the values of C_1 and C_1''. In other words, the composition of the two phases must have fixed values, which is in accordance with the phase rule.

For a ternary system we have

$$\frac{C_1}{C_1''} = r_1, \qquad \frac{C_2}{C_2''} = r_2, \qquad \frac{1-C_1-C_2}{1-C_1''-C_2''} = r_3,$$

from which we get

$$\left.\begin{aligned} C_2'' &= \frac{r_3-1}{r_3-r_2} + \frac{r_1-r_3}{r_3-r_2}\,C_1'' \\ C_2 &= \frac{r_2(r_3-1)}{r_3-r_2} + \frac{r_2(r_1-r_3)}{r_1(r_3-r_2)}\,C_1 \end{aligned}\right\} \quad \text{...........(22)}$$

The former of these two equations represents the solubility curves with respect to the composition of the solid phase, and the latter with respect to that of the liquid. These curves are straight lines, and the angle which one of them makes with the axis of C_1 must have the same sense as the angle which the other line makes with the same axis. Fig. 10 represents these lines, with the conjugated points connected by straight lines.

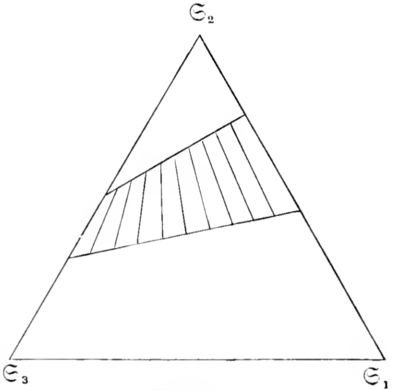

Fig. 10.

(*b*) *The Relation between the Temperature and the Composition of the two Phases.*

Differentiating equation (20) with respect to T,

$$RT\frac{\partial\, ln\dfrac{C_1}{C_1''}}{\partial T}=(S_1-S_1'')-R\,ln\frac{C_1}{C_1''},$$

$$RT\frac{\partial\, ln\dfrac{C_2}{C_2''}}{\partial T}=(S_2-S_2'')-R\,ln\frac{C_2}{C_2''},$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

where S_1'', S_2'', etc. are the molecular entropies of the solid components. The right sides of the equations represent the increase of entropy when one mol of each component passes from the solid to the liquid phase. When r_1, r_2,......... are not very large or very small the heat absorbed when one mol of $\mathfrak{S}_1$, $\mathfrak{S}_2$,......... passes from the solid to the liquid solution is very nearly equal to the heat of fusion q_1, q_2,........., and we have

$$\frac{\partial\, ln \frac{C_1}{C_1''}}{\partial T} = \frac{q_1}{RT^2}$$

$$\frac{\partial\, ln \frac{C_2}{C_2''}}{\partial T} = \frac{q_2}{RT^2}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

Assuming q_1, q_2,........ to be independent of temperature and integrating, we get:

$$C_1 = C_1'' \, e^{\frac{q_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)}$$

$$C_2 = C_2'' \, e^{\frac{q_2}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

But as

$$C_1 + C_2 + \cdots\cdots = 1,$$

and

$$C_1'' + C_2'' + \cdots\cdots = 1,$$

we have

$$\left.\begin{aligned} C_1'' e^{\frac{q_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)} + C_2'' e^{\frac{q_2}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)} + \cdots\cdots &= 1, \\ C_1\, e^{\frac{q_1}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)} + C_2\, e^{\frac{q_2}{R}\left(\frac{1}{T} - \frac{1}{T_2}\right)} + \cdots\cdots &= 1, \end{aligned}\right\} \ldots(23)$$

relations quite analogous to that represented by equation (11). Equations (23) represent the fusion curves, surfaces, etc. according to the number of the components.

CHAPTER II.

QUASI-IDEAL SOLUTIONS WITH ONE ASSOCIATED COMPONENT.

In the systems, which we have been considering in the preceding chapter, it has been assumed that chemical changes do not take place in the homogeneous phases; because if the state of isomeric or polymeric equilibrium of the independent components be disturbed on mixing them, or if they enter into combination with one another, energy- and volume-change must necessarily occur and conditions (1) and (2) will not be satisfied. Yet, that the chemical species[1] could be mixed without such changes is not excluded, provided the chemical reactions were checked. In order to make the matter more readily conceivable we may suppose with LUTHER (Zeits. Electrochem., **12**, 87; 1906) that a negative catalyser has been added to the chemical species before mixing. This does not of course affect the chemical potentials. Hence if the chemical species are miscible without volume- and energy-change, the chemical potentials have the values given by equation (3). Such a solution, in which reversible chemical reactions take place but whose volume and energy are equal to the sums of the respective quantities of the component chemical species, we propose to call a quasi-ideal solution. It can be readily imagined that actual solutions which approximate more or less closely to the quasi-ideal solution will be far more numerous than those which approximate to the ideal

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[1] The term "chemical species," which has been employed by some older writers but has lately almost gone out of use, may be employed to denote distinct chemical entities real or imaginary. It is preferable to the term "molecular species."

solution. Of all sorts of quasi-ideal solutions, the one with only one associated component is the simplest, and such we undertake to study in the present chapter. When there are two or more associated components, the formation of compounds between them is quite probable and the subject threatens to become rather intricate, and the theoretical discussion runs the risk of losing itself in a labyrinth of hypotheses unless there is a goodly store of exact experimental materials. This will explain the singular limitation imposed on the subject of the present chapter. The subject will be treated in the order of complexity, i.e. according to the number of components in the system.

§ 1. Associated Liquids.

(*a*) *Homogeneous Equilibrium.*

The chemical reactions in a one component system can be represented generally by the equation

$$\nu_\alpha \mathfrak{S}_\alpha \rightleftarrows \nu_\beta \mathfrak{S}_\beta.$$

When $\nu_\alpha = \nu_\beta$ the reaction is an isomeric change, when $\nu_\alpha \gtrless \nu_\beta$ it is a polymeric change, and when $\nu_\beta = 1$ the reaction is called association. Such a system has been called by ROOZEBOOM pseudounary.

In an associated liquid any number of reactions of the type

$$\nu \mathfrak{S}_\alpha \rightleftarrows \mathfrak{S}_\beta$$

may take place. But in order to simplify the discussion we will suppose that there is only one such reaction.

When an associated liquid is a quasi-ideal solution, then

$$\left.\begin{aligned} \mu_\alpha &= z_\alpha + RT\,ln\,C_\alpha, \\ \mu_\beta &= z_\beta + RT\,ln\,C_\beta. \end{aligned}\right\} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (24)$$

As long as the variation of pressure is not very large we may assume z_α and z_β to be functions of temperature alone.

In the case of equilibrium

$$\nu \mu_\alpha = \mu_\beta$$

so that for a constant temperature

$$\frac{C_\alpha^{\nu}}{C_\beta} = \frac{C_\alpha^{\nu}}{1-C_\alpha} = e^{\frac{z_\beta - \nu z_\alpha}{RT}} = \mathfrak{K} = \text{const.} \quad \text{.........(25)}$$

$\mathfrak{K}$ in this equation is what is called the equilibrium coefficient.

The ratio between the mean molecular weight of the liquid and the molecular weight of $\mathfrak{S}_\alpha$ has been called by Ramsay and Shields the degree of association. If we express this ratio by ξ, then

$$\xi = \nu-(\nu-1)\,C_\alpha = 1+(\nu-1)\,C_\beta \quad \text{..............(26)}$$

The experimental determination of ξ presents considerable difficulties. Ramsay and Shields attempted to evaluate it from the temperature coefficient of the molecular surface energy, but with only partial success. Ramsay afterward modified the mode of calculation and his results are widely accepted. But there is a serious doubt about the entire method, because it is based upon the assumption that the composition of the surface film is the same as that of the liquid mass. For mixtures of chemical species of nearly equal volatility the assumption may hold. But in the case of an associated liquid the component chemical species must have a very different volatility. The more volatile species will tend to accumulate in the surface film, because its molecular surface energy will be considerably less than that of the less volatile species, whose critical temperature must be assumed to be much higher than that of the other.

Even in the cases where ξ is given $\mathfrak{K}$ can not be determined at once, because ν is generally unknown. But ν is in general a small integer, and we are often able to deduce or infer its value from various experimental data.

The variation of $\mathfrak{K}$ with the temperature is expressed by the equation

$$\frac{\partial \, ln \, \mathfrak{K}}{\partial T} = \frac{\mathfrak{Q}}{RT^2}$$

where $\mathfrak{Q}$ is the heat of reaction for ν mols of $\mathfrak{S}_\alpha$. As it is quite probable that the heat capacity of $\mathfrak{S}_\beta$ is not very different from that of $\nu \mathfrak{S}_\alpha$, we may as an approximation, assume $\mathfrak{Q}$ to be independent of temperature, then

$$ln \, \mathfrak{K} = \frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}} - \frac{1}{T}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(27)$$

where $\mathfrak{T}$ is the temperature at which $\mathfrak{K}$ becomes unity. This temperature may be called the *equipoise point* of the reaction and is characteristic of the homogeneous equilibrium just as the boiling point, melting point, or eutectic point is characteristic of the respective heterogeneous equlibrium. For such reactions as $2\,O_3 \rightleftarrows 3\,O_2$ or $2\,H_2O \rightleftarrows 2\,H_2 + O_2$ the equipoise point is very high, while for such reactions as $2\,SCl_2 \rightleftarrows S_2Cl_2 + Cl_2$ it is relatively low. When the given temperature is far from the equipoise point we may say that the chemical species on the right or the left side of the equation are stable against the species on the other side according as $\mathfrak{Q}$, the heat of reaction, is positive or negative.

(*b*) *Vapour Tension of an Associated Liquid.*

If we assume that the chemical species $\mathfrak{S}_\alpha$ and $\mathfrak{S}_\beta$ taken separately present the vapour pressures π_α and π_β respectively at the given temperature, the vapour pressure of the associated liquid will be

$$P = C_\alpha \pi_\alpha + (1-C_\alpha)\pi_\beta. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(28)$$

C_α can be determined as a function of temperature from equation (27), when ν, $\mathfrak{Q}$, and $\mathfrak{T}$ are given. We may also put as an approximation

$$\pi_\alpha = \mathfrak{P}\, e^{b\left(1-\frac{T_\alpha}{T}\right)}$$

$$\pi_\beta = \mathfrak{P}\, e^{b\left(1-\frac{T_\beta}{T}\right)}$$

where T_α and T_β are the temperatures at which the vapour pressures of $\mathfrak{S}_\alpha$ and $\mathfrak{S}_\beta$ are equal to $\mathfrak{P}$. The value of b depends on the chosen value of $\mathfrak{P}$ as we have seen in the preceding chapter.

Now it is possible to determine the constants $\mathfrak{Q}$, $\mathfrak{T}$, T_α, and T_β by means of equation (5), when the specific volumes and the pressures of the saturated vapours at two different temperatures are given, provided we can hit upon the proper value of ν. This can certainly be done after a few trials. In this case we have the following sets of equations

$$\left.\begin{aligned} C'_{\alpha 1} P_1 &= C_{\alpha 1}\, \mathfrak{P}\, e^{b\left(1-\frac{T_\alpha}{T_1}\right)} \\ (1-C'_{\alpha 1}) P_1 &= (1-C_{\alpha 1})\, \mathfrak{P}\, e^{b\left(1-\frac{T_\beta}{T_1}\right)} \end{aligned}\right\}$$

$$\left.\begin{aligned} C'_{\alpha 2} P_2 &= C_{\alpha 2}\, \mathfrak{P}\, e^{b\left(1-\frac{T_\alpha}{T_2}\right)} \\ (1-C'_{\alpha 2}) P_2 &= (1-C_{\alpha 2})\, \mathfrak{P}\, e^{b\left(1-\frac{T_\beta}{T_2}\right)} \end{aligned}\right\}$$

where C'_α is the molar fraction of $\mathfrak{S}_\alpha$ in the gas phase, and the suffixes denote the relation to the chosen temperatures T_1 and T_2. C'_α can be calculated from the specific volume of the vapour. If we make $\mathfrak{P}$ = one atmosphere, the value of b is known, and T_α and T_β are the respective boiling points. By equation (27) we can express $C_{\alpha 1}$ and $C_{\alpha 2}$ in terms of $\mathfrak{Q}$ and $\mathfrak{T}$. There being thus four equations to evaluate four unknown constants, the problem can be solved, and the correctness of the values so obtained can be tested by means of the vapour pressures at other temperatures. In this way it will be possible to determine the degree of association of liquids with tolerable accuracy. But the calculation will be somewhat tedious.

It has been frequently observed that the vapour is not polymerised to any noticeable degree, while the liquid must be looked upon as highly associated. In such cases π_β is very small in comparison with π_α, and equation (27) is reduced to

$$P = C'_\alpha \pi_\beta \qquad \text{(29)}$$

In order to evaluate $\mathfrak{Q}$, $\mathfrak{T}$, and T_α in such cases the vapour pressures at three different temperatures must be given besides the value of ν.

Differentiating both sides of equation (29) with respect to T, we get

$$\frac{\partial P}{\partial T} = C'_\alpha \frac{\partial \pi_\alpha}{\partial T} + \pi_\alpha \frac{\partial C'_\alpha}{\partial T} = \left(\frac{1 - C'_\alpha}{\nu - (\nu - 1) C'_\alpha} \mathfrak{Q} + q_\alpha \right) \frac{P}{RT^2},$$

where $\frac{1 - C'_\alpha}{\nu - (\nu - 1) C'_\alpha} \mathfrak{Q} + q_\alpha$ is the quantity of heat absorbed during the production of one mol of the vapour. Now if TROUTON's law be valid for all normal liquids under all pressures below a certain value, as indicated in the foregoing chapter, DÜHRING's relation must hold, and the temperatures at which the liquids have an equal vapour pressure must be proportional to the absolute temperature of the boiling points. This has been found to be the case approximately for a great many unassociated liquids. Hence the vapour pressure curves of these liquids do not intersect one another, at least at pressures below 1000 m.m. of mercury. On the other hand the vapour pressure curves of associated liquids mostly intersect those of the normal liquids, and indeed they are at the points of intersection generally steeper than the normal curves. If the heat of evaporation of a normal liquid under the pressure P be q, then in most cases

$$q_\alpha + \frac{1 - C_\alpha}{\nu - (\nu - 1)\, C_\alpha}\, \mathfrak{Q} > q.$$

But as a consequence of TROUTON's law

$$q_\alpha < q.$$

Hence in many cases $\frac{1 - C'_\alpha}{\nu - (\nu - 1)\, C'_\alpha}\, \mathfrak{Q}$ must have considerable value. In other words, the heat of dissociation must be considerable.

As an illustration of what has been said in the foregoing paragraphs we may adduce the vapour tension of acetone. As will be shown in § 2 (*b*) it is possible to determine the value of ν and $\mathfrak{K}$ from the vapour pressure of binary mixtures which consist of a normal liquid and the associated liquid under consideration. From the data of CUNAEUS at 0°C, it has been concluded that $\nu = 3$ and $\pi_\alpha = 162$ m.m. As the vapour density of acetone is normal π_β must be very small, so that equation (29) may be applied. The vapour pressure of acetone at 0° is $P = 69.6$ m.m. from which we get $\mathfrak{K} = 0.1495$. The hypothetical vapour pressure of pure simple acetone at various temperatures can be represented by

$$\pi_{\chi} = e^{10.9\left(1-\frac{311.71}{T}\right)}$$

where the unit of pressure is one atomosphere and 311.71 is the hypothetical absolute boiling point. 10.9 is the general constant according to the law of TROUTON and the constant 311.71 is determined from the data at 0°. Now if a second point on the vapour pressure curve be given, $\mathfrak{Q}$ and $\mathfrak{T}$ can be determined. ZAWIDZKI found the vapour pressure of acetone at 35.17° to be 344.2, from which we get

$$\mathfrak{Q} = 3290 \text{ calories}$$
$$\mathfrak{T} = 404.43.$$

With these constants the vapour pressure of acetone at various temperatures has been calculated as shown in the following table.

TABLE 1.[1]

t	C_{χ}	ξ	P (calculated)	P (observed)
0°	0.4296	2.1408	69.6 m.m.	(69.6 m.m.)
5°	0.4422	2.1156	89.6 ,,	—
10°	0.4546	2.0908	114.4 ,,	—
15°	0.4668	2.0664	144.6 ,,	—
20°	0.4787	2.0426	181.4 ,,	182.5 ,,
25°	0.4904	2.0192	225.7 ,,	229. ,,
30°	0.5018	1.9964	278.8 ,,	281. ,,
35°	0.5130	1.9740	341.9 ,,	343. ,,
35.17°	0.5132	1.9736	344.2 ,,	(344.2 ,,)
40°	0.5239	1.9522	416.5 ,,	416. ,,
45°	0.5346	1.9308	504.1 ,,	505. ,,
50°	0.5450	1.9100	606.3 ,,	607. ,,
55°	0.5552	1.8896	725.1 ,,	721. ,,
60°	0.5652	1.8696	862.1 ,,	860. ,,

---

[1] This table has been calculated by Y. YAMASAKI, a student of chemistry.

In the table the result of calculation is compared with the observation of A. E. TAYLOR (Journ. physic. Chem., 4, 336; 1900). The agreement is quite satisfactory. The degree of association ξ has been calculated by equation (26).

The heat of evaporation for one mol of vapour at the boiling point 56.2° has been calculated to be

$$\frac{1-C_x}{\xi}\mathfrak{Q}+q_x = 7520 \text{ calories.}$$

[q_x is set $10.9\times 311.71\times 1.985 = 6744$ calories]. The calculation according to the well known equation,

$$\text{Molecular heat of evaporation} = \frac{R\,(ln\,P_1 - ln\,P_2)}{\frac{1}{T_2}-\frac{1}{T_1}},$$

from TAYLOR's data gives 7640 calories, while WIRTZ (Landolt-Börnstein-Meyerhofer's Tabellen) has determined it to 7300 calories. Were acetone a normal liquid the molecular heat of evaporation would amount to only 6960 calories.

(c) *Acetaldehyde and Paraldehyde.*

The equilibrium between acetaldehyde and paraldehyde has been studied by HOLLMANN (Zeits. physik. Chem., 43, 129; 1903) under the guidance of ROOZEBOOM. The peculiarity of the system is that the reaction

$$3\,C_2H_4O \rightleftarrows C_6H_{12}O_3$$

proceeds so very slowly at lower temperatures, that the chemical species can be treated as independent components, while at higher temperatures or in the presence of catalysers the reaction takes place so rapidly that the state of equilibrium is reached in a very short time. From HOLLMANN's data we may conclude that the mixture of the two chemical species behaves approximately as an ideal solution, the fusion curve having nearly the form represented by equation (17)

$$ln\, C_1 = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right),$$

as is to be seen from the following table.

TABLE 2.

Fusion curve of the system paraldehyde and acetaldehyde.

$T-273$	C_β	C_β (calculated)	Q
12.55°	1.000	1.000	—
8.90°	0.928	0.921	3279
6.60°	0.879	0.874	3441
3.70°	0.821	0.816	3502
0.93°	0.767	0.764	3549
−1.02°	0.727	0.726	3585
−4.00°	0.676	0.677	3612
−6.65°	0.633	0.633	3600
−9.10°	0.584	0.594	3722
−11.1°	0.545	0.564	3818
−12.2°	0.525	0.548	3855
−13.0°	0.513	0.536	3855
−14.1°	0.493	0.521	3900
−16.4°	0.460	0.489	3907
−17.7°	0.444	0.463	3798
−23.0°	0.381	0.406	3852
−26.5°	0.345	0.366	3814
−29.8°	0.313	0.331	3786
−33.0°	0.284	0.299	3759
−33.7°	0.279	0.294	3749

$-38.0°$	0.245	0.256	3712
$-42.6°$	0.217	0.219	3623
$-46.8°$	0.192	0.189	3570
$-52.5°$	0.167	0.154	3444
$-58.2°$	0.144	0.124	3340
$-62.0°$	0.130	0.106	3277
$-65.8°$	0.117	0.091	3221
$-68.0°$	0.109	0.083	3201
$-68.5°$	0.106	0.081	3214
$-71.5°$	0.098	0.071	3162
$-77.5°$	0.086	0.054	3023
$-91.76°$	0.044	0.026	3081
$-113.51°$	0.033	0.007	3085
$-119.18°$	0.016	0.004	2742

C_β is the molar fraction of paraldehyde. Q, the molecular heat of fusion of this substance, has been calculated from the fusion points by equation (17). The values of Q for lower temperatures are not reliable, because the composition of the solution must have suffered considerable change on account of the separation of the paraldehyde as the solid phase; and this source of error is the more considerable as the molar fraction of paraldehyde is the smaller. The notable decrease in the value of Q for $C_\beta < 0.2$ is doubtless due to this cause. On the whole it appears as if Q increases with a lowering temperature. If we assume

$$Q = 3600 \text{ calories}$$

and recalculate the molar fraction C_β for observed fusion points, the agreement with experimental data is tolerably good, the maximum difference being less than 0.03.

Hollmann has also measured the boiling points of various mixtures of the two chemical species. The following calculation is based on the data given in his second table. The temperatures have been corrected for a pressure of 760 m.m. This could be done without difficulty because the differences do not exceed 6 m.m. The compositions of the mixtures corresponding to the boiling points have been calculated by means of equation (11)

$$C_\beta \, e^{b\left(1-\frac{T_\beta}{T}\right)} + (1-C_\beta)\, e^{b\left(1-\frac{T_\alpha}{T}\right)} = 1,$$

where C_β is the molar fraction of paraldehyde as before, and T_α and T_β are the boiling points of the two chemical species. For b the approximate value, 11, has been used. In the following table the results of calculation are compared with observed values.

TABLE 3.

The boiling points of the system paraldehyde and acetaldehyde.

$T-273$	C_β	C_β (calculated)
21.0°	0	0
27.1°	0.201	0.205
32.7°	0.349	0.353
39.8°	0.501	0.497
40.8°	0.523	0.514
43.1°	0.561	0.551
56.9°	0.703	0.721
72.7°	0.798	0.838
103.0°	0.916	0.963
123.9°	1.000	1.000

Up to the molar fraction 0.7 the agreement between the values observed and calculated is tolerably good. That the differences for larger values of C_β are so great is doubtless due to the fact that a comparatively large amount of acetaldehyde was volatilized and was present partly in the gaseous phase and partly in the reverse condenser as liquid. This source of error must be the more serious, the greater the molar fraction of paraldehyde. It is therefore to be regretted that the author determined the composition of the solution from the quantities of the substances put into the boiling vessel and not in a manner more direct. Moreover the boiling point of paraldehyde is more than a hundred degrees higher than that of the other component, a difference certainly too large for the exact applicability of equation (11).

It is not improbable that the chemical species of an associated liquid as a rule behave towards each other as the components of ideal solutions.

According to HOLLMANN the freezing point of the system acetaldehyde ⇄ paraldehyde in the presence of a catalyser lies at

$$T-273^\circ = 6.75^\circ$$

This temperature he calls the natural freezing point of the system, and corresponds to the freezing point of an associated liquids as it is usually observed. The composition of the system at this point is

$$C_\beta = 0.883.$$

The natural boiling point of the system has been determined to be

$$T-273^\circ = 41.6^\circ,$$

with the composition

$$C_\beta = 0.534.$$

From these two sets of values we obtain for the constants of equation (27)

$$\mathfrak{T} = 329.4$$

$$\mathfrak{Q} = 23340 \text{ calories.}$$

The heat of polymerisation $\mathfrak{Q}$ can also be calculated from the thermochemical data. Berthelot and Delepine found the heat of combustion of acetaldehyde C_2H_4O to be 279150 calories, while the heat of combustion of paraldehyde $C_6H_{12}O_3$ amounts to 813200 calories according to Louguinine. Hence

$$\mathfrak{Q} = (3 \times 279150 - 813200) \text{ cal.} = 24250 \text{ cal.}$$

The agreement must be looked upon as quite satisfactory, when we take the errors of thermochemical measurements into consideration.

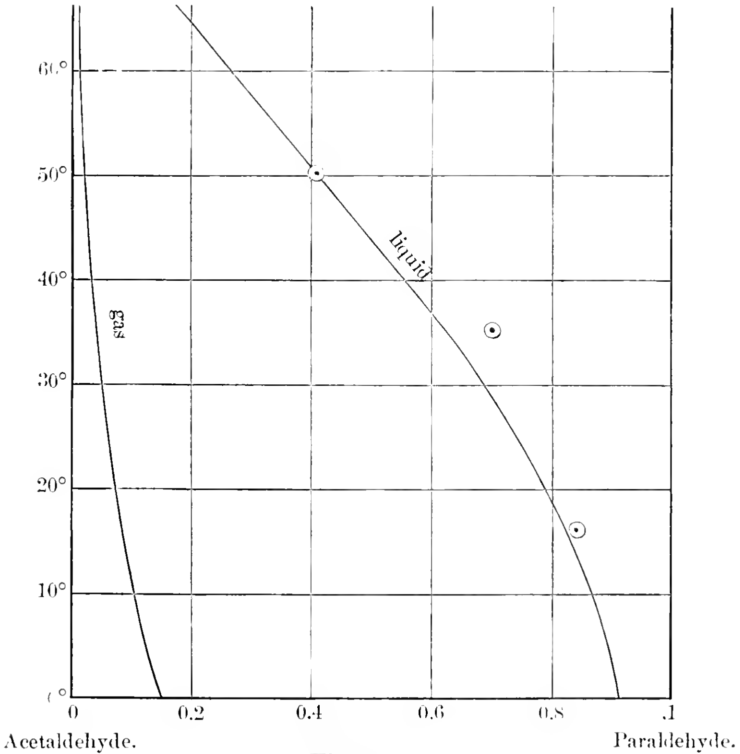

Fig. 11.

For the calculation of the natural vapour pressure curve of the system according to equation (28) we have the following relations :

$$\frac{(1-C_\beta)^3}{C'_\beta} = \mathfrak{K} = e^{\frac{23340}{1.985}\left(\frac{1}{329.4}-\frac{1}{T}\right)}$$

$$\pi_\alpha = e^{11\left(1-\frac{294}{T}\right)}$$

$$\pi_\beta = e^{11\left(1-\frac{396.9}{T}\right)}$$

where the unit of pressure is one atmosphere. The results of the calculation are given in the following table.

TABLE 4.

The natural vapour tension curve of the system acetaldehyde ⇄ paraldehyde.

$T-273°$	$\mathfrak{K}$	C_β	C_β'	π_α	π_β	P
0°	0.000635	0.9165	0.1483	0.429	0.00679	0.0421
10°	0.00289	0.8642	0.1044	0.652	0.01195	0.0989
20°	0.01197	0.789	0.0727	0.963	0.02024	0.2192
30°	0.0445	0.687	0.0496	1.386	0.03310	0.4565
40°	0.1546	0.558	0.0359	1.949	0.05242	0.8150
50°	0.4943	0.412	0.0203	2.684	0.08074	1.611
60°	1.473	0.267	0.0121	3.626	0.1211	2.690

TURBABA found at 50.5° $C_\beta = 0.405$ and $P = 1.5-2$, while the calculation gives $C_\beta = 0.394$ and $P = 1.65$.

The temperature-composition diagram shown in Fig. 11 is constructed from the preceding table. The data found by TURBABA are marked with circlets. These are but rough estimations with the exception of the datum for 50.5° which, being the mean of a large number of tolerably concordant determinations, must be considered accurate.

(*d*) *Physical Properties of Associated Liquids.*

The classical researches of Kopp and Landolt have called forth a great many investigations on the relations existing between physical properties and chemical composition, particularly of liquids. But the work in this field slackened after a time, partly owing to the rapid development of physical chemistry which put forth so many interesting problems for solution, and partly owing to the fact that the regularities found were mostly imperfect and could not be brought into well defined simple schemes. This is no doubt to a great extent due to the fact that the investigators did not distinguish between normal and associated liquids. It is self-evident that no good result can be obtained when, for example, the system acetaldehyde $\rightleftarrows$ paraldehyde is treated as if it consisted of acetaldehyde alone. Such irrational procedure has hitherto been quite general. But if the molecular formulæ and the relative amounts of the chemical species constituting associated liquids be determined by any reliable method, then we shall be in a position to estimate the physical properties of individual species. The comparison of various chemical species will then no doubt show greater regularities.

§ 2. Quasi-ideal Solutions with a Normal and an Associated Component.

(*a*) *Homogeneas Equilibrium.*

In the present case we have

$$C'_\alpha + C'_\beta + C' = 1, \qquad \ldots\ldots\ldots\ldots\ldots\ldots (30)$$

when we assume as in the foregoing section the associated component to consist of two chemical species $\mathfrak{S}_\alpha$ end $\mathfrak{S}_\beta$, and express the molar fraction of the normal component $\mathfrak{S}$ by C. But these molar fractions are mostly unknown. The molar fractions usually given are calculated on the supposstion that the associated component consists of the simpler chemical species $\mathfrak{S}_\alpha$ alone. These we propose to call *empirical* molar fractions. Now let x be the empirical molar fraction of the associated component, then $1-x$ is the empirical molar fraction of the normal substance. The relation between these two sorts of molar fractions is expressed by the following equation :

$$x = \frac{C'_\alpha + \nu C'_\beta}{C'_\alpha + \nu C'_\beta + C'} = \frac{C_\alpha + \nu C_\beta}{1+(\nu-1)\,C_\beta} \quad \text{...........(31)}$$

As the solution is supposed to be quasi-ideal, equation (25) must hold, which may be written

$$\frac{C'^{\,\nu}_\alpha}{C'_\beta} = \mathfrak{K} = e^{\frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}} - \frac{1}{T}\right)} \text{.....................(32)}$$

At a constant temperature $\mathfrak{K}$ is constant and we have

$$x = \frac{C'_\alpha + \nu \dfrac{C'^{\,\nu}_\alpha}{\mathfrak{K}}}{1+(\nu-1)\dfrac{C^{\nu}_\alpha}{\mathfrak{K}}} \text{........................(33)}$$

or

$$x = \frac{\mathfrak{K}^{\frac{1}{\nu}}\, C'^{\,\frac{1}{\nu}}_\beta + \nu C'_\beta}{1+(\nu-1)\,C'_\beta}, \text{........................(34)}$$

while for the molar fraction of the normal component we get from equations (30) and (31)

$$C' = \{1+(\nu-1)\,C_\beta\}\,(1-x). \text{..................(35)}$$

These relations may be made more conspicuous by means of graphical representations in which x is taken as the abscissa and the molare fractions as the ordinate. From equation (33) we get by differentiation

$$\frac{dC_\alpha}{dx} = \frac{\left(1+\frac{\nu-1}{\mathfrak{K}}C_\alpha{}^\nu\right)^2}{1-\frac{(\nu-1)^2}{\mathfrak{K}}C_\alpha{}^\nu+\frac{\nu^2}{\mathfrak{K}}C_\alpha{}^{\nu-1}} = \frac{\{1+(\nu-1)C_\beta\}^2}{1-(\nu-1)^2C_\beta+\frac{\nu^2C_\beta}{C_\alpha}} \quad \ldots(36)$$

$$\frac{d^2C_\alpha}{dx^2} = \frac{\left\{(\nu+1)C_\alpha-\frac{(\nu-1)^2}{\mathfrak{K}}C_\alpha{}^{\nu+1}+\frac{\nu(\nu-1)}{\mathfrak{K}}C_\alpha{}^\nu\right\}\frac{\nu(\nu-1)}{\mathfrak{K}}C_\alpha{}^{\nu-1}\left(1+\frac{\nu-1}{\mathfrak{K}}C_\alpha{}^\nu\right)^3}{\left\{1-\frac{(\nu-1)^2}{\mathfrak{K}}C_\alpha{}^\nu+\frac{\nu^2}{\mathfrak{K}}C_\alpha{}^{\nu-1}\right\}^3}$$

$$=\Big[(\nu+1)C_\alpha+\nu(\nu+1)C_\beta-(\nu-1)^2C_\alpha C_\beta-\nu\Big]\frac{\nu(\nu-1)}{\mathfrak{K}}C_\alpha{}^{\nu-1}\left\{\frac{1+\frac{\nu-1}{\mathfrak{K}}C_\alpha{}^\nu}{1-\frac{(\nu-1)^2}{\mathfrak{K}}C_\alpha{}^\nu+\frac{\nu^2}{\mathfrak{K}}C_\alpha{}^{\nu-1}}\right\}^3$$

because $\frac{C_\alpha{}^\nu}{\mathfrak{K}} = C_\beta$ by equation (32).

$\frac{dC_\alpha}{dx}$ is positive for all values of x because C_α is less than unity. At $x = 0$ we have

$$\left(\frac{dC_\alpha}{dx}\right)_0 = 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(37)$$

because C_β vanishes as x approaches zero, while at $x = 1$ $C_\alpha + C_\beta = 1$ and the differential coefficient becomes

$$\left(\frac{dC_\alpha}{dx}\right)_1 = (C_\alpha)_1, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(38)$$

where $(C_\alpha)_1$ denotes the molar fraction of $\mathfrak{S}_\alpha$ in the associated component in the pure state.

The sign of the second differential coefficient $\frac{d^2C_\alpha}{dx^2}$ is determined by that of the factors in the rectangular brackets, because the other factors are necessarily positive. For small values of x

both C_α and C_β are small and $\frac{d^2C_\alpha}{dx^2}$ is negative. But for large values of x it becomes positive, and at $x = 1$ we have

$$\left(\frac{d^2C_\alpha}{dx^2}\right)_1 = (\nu C_\beta + C_\alpha)^2$$

which is of course positive.

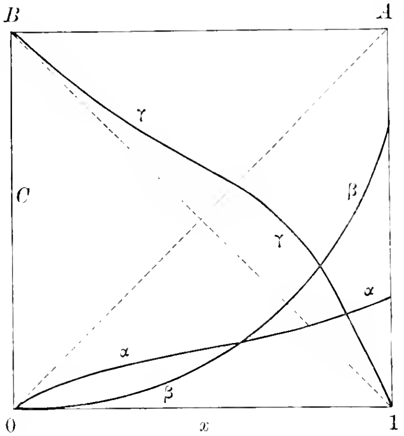

Fig. 12.

Hence, when we represent the relation between C_α and x in a diagram, we get a curve like α in Fig. 12. The curve has for its tangent at $x = 0$ the diagonal $0A$ which lies completely above it. The curve is concave towards the axis of x for small values of x, and turns convex as x approaches unity. The tangent at $x = 1$ is a straight line which passes through the origin 0.

From equation (34) we get by differentiation

$$\frac{dC_\beta}{dx} = \frac{\{1+(\nu-1)\,C_\beta\}^2}{\nu + \frac{1}{\nu}\,\mathfrak{K}^{\frac{1}{\nu}}\,C_\beta^{\frac{1}{\nu}-1} - \frac{(\nu-1)^2}{\nu}\,\mathfrak{K}^{\frac{1}{\nu}}\,C_\beta^{\frac{1}{\nu}}}$$

$$= \frac{\{1+(\nu-1)\,C_\beta\}^2}{\nu + \frac{1}{\nu}\,\frac{C_\alpha}{C_\beta} - \frac{(\nu-1)^2}{\nu}\,C_\alpha} \quad \text{.................. .....(39)}$$

and

$$\frac{d^2C_\beta}{dx^2} = (\nu-1)\left\{2\,\nu + \frac{1}{\nu^2}\,\mathfrak{K}^{\frac{1}{\nu}}\,C_\beta^{\frac{1}{\nu}-2} + \frac{2}{\nu^2}\,\mathfrak{K}^{\frac{1}{\nu}}\,C_\beta^{\frac{1}{\nu}-1}\right.$$
$$\left. - \left(\frac{\nu-1}{\nu}\right)^2 (2\,\nu-1)\,\mathfrak{K}^{\frac{1}{\nu}}\,C_\beta^{\frac{1}{\nu}}\right\}\left\{\frac{1+(\nu-1)\,C_\beta}{\nu + \frac{1}{\nu}\,\frac{C_\alpha}{C_\beta} - \frac{(\nu-1)^2}{\nu}\,C_\alpha}\right\}^3$$

or as $\mathfrak{K}^{\frac{1}{\nu}} C_\beta^{\frac{1}{\nu}} = C_\alpha$ from equation (32)

$$\frac{d^2C_\beta}{dx^2} = (\nu-1)\left\{2\nu+\frac{1}{\nu_2}\frac{C_\alpha}{C_\beta^2}+\frac{2}{\nu^2}\frac{C_\alpha}{C_\beta}\right.$$
$$\left.-\left(\frac{\nu-1}{\nu}\right)^2(2\nu-1)\,C_\alpha\right\}\left\{\frac{1+(\nu-1)\,C_\beta}{\nu+\frac{1}{\nu}\frac{C_\alpha}{C_\beta}-\frac{(\nu-1)^2}{\nu}C_\alpha}\right\}^2$$

As both C_α and C_β are necessarily less than unity, $\frac{dC_\beta}{dx}$ as well as $\frac{d^2C_\beta}{dx^2}$ must be positive throughout. We see further from equation (32) that C_β approaches zero far more rapidly than C_α when x approaches zero. Hence at $x = 0$

$$\left(\frac{dC_\beta}{dx}\right)_0 = 0 \quad \text{........................(40)}$$

and $\frac{d^2C_\beta}{dx^2}$ is also zero. On the other hand at $x = 1$ we have

$$\left(\frac{dC_\beta}{dx}\right)_1 = \nu\,(C_\beta)_1 \quad \text{......................(41)}$$

where $(C_\beta)_1$ denotes the molar fractton of $\mathfrak{S}_\beta$ in the associated component in the pure state. From these considerations it is clear that the curve showing the relation between x and C_β must have a form like β in Fig. 12.

As to the curve representing the molar fraction of the normal component as a function of x, we see from equation (35) that it must throughout lie above the diagonal $B1$ (Fig. 12). Its shape can be further elucidated from the following considerations. From equation (30) we have

$$\frac{dC}{dx} = -\frac{dC_\alpha}{dx}-\frac{dC_\beta}{dx},$$

and as both $\frac{dC_\alpha}{dx}$ and $\frac{dC_\beta}{dx}$ are positive, $\frac{dC}{dx}$ must be negative throughout. Hence C decreases continuously with increasing values of x. At $x=0$ C is equal to unity, while at $x=1$ it is reduced to zero. Again in the equation

$$\frac{d^2C}{dx^2} = -\frac{d^2C_\alpha}{dx^2} - \frac{d^2C_\beta}{dx^2}$$

$\frac{d^2C_\alpha}{dx^2}$ is negative for smaller values of x, while $\frac{d^2C_\beta}{dx^2}$, though positive, is very small. Hence $\frac{d^2C}{dx^2}$ must be positive for small values of x and the curve is convex towards the axis of x. With increasing values of x $\frac{d^2C_\alpha}{dx^2}$ becomes positive too, while $\frac{d^2C_\beta}{dx^2}$ remains positive and increases in amount, so that $\frac{d^2C}{dx^2}$ must turn negative at a certain value of x and from this point the curve becomes concave. The form of the curve must therefore be like that of γ in Fig. 12.

Again from equation (35) we have by differentiation

$$\frac{dC}{dx} = (\nu-1)(1-x)\frac{dC_\beta}{dx} - \{1+(\nu-1)\,C_\beta\}.$$

Hence at $x=0$,

$$\left(\frac{dC}{dx}\right) = -1, \quad \text{.........................(42)}$$

that is to say the tangent to the curve at $x=0$ is the diagonal $B1$. At $x=1$ we have

$$\left(\frac{dC}{dx}\right)_1 = -\{1+(\nu-1)\,C_\beta\}, \quad \text{.................(43)}$$

which says that the tangent at $x=1$ is equal to the degree of association of the pure associated component taken negative.

Thus we see that the state of homogeneous equilibrium at a constant temperature in a system consisting of an associated and a normal component and in which the reversible reaction

$$\nu \mathfrak{S}_\alpha \rightleftarrows \mathfrak{S}_\beta$$

takes place, can be completely represented by a diagram like that shown in Fig. 12.

(b) *The Equlibrium between a Gaseous and a Liquid Phase.*

(1) *Vapour Pressure at a Constant Temperature.*

Let p_α, p_β, and p be the partial pressures of $\mathfrak{S}_\alpha$, $\mathfrak{S}_\beta$, and $\mathfrak{S}$ respectively in the gas phase which is in equilibrium with the solution consisting of these chemical species, and let P be the vapour tension of the pure $\mathfrak{S}$. Then we have by equation (5)

$$p_\alpha = C_\alpha \pi_\alpha,$$

$$p_\beta = C_\beta \pi_\beta,$$

$$p = C P_0,$$

and

$$P = C_\alpha \pi_\alpha + C_\beta \pi_\beta + C P_0, \ldots\ldots\ldots\ldots\ldots\ldots\ldots (44)$$

where P is the total pressure.

The curves representing the relation between these partial pressures and the empirical molar fractions must have forms resembling those given in Fig. 12. As a rule π_α will be far larger than π_β, so that the curve for p_β will often lie far below that for p_α.

When these curves of partial pressures are given, we can evaluate the characteristic magnitudes of the system such as π_α, π_β, and $\mathfrak{K}$. According to equations (5) and (37) π_α can be found by producing the tangent at $x = 0$ to the curve of p_α so as to meet the pressure axis at $x = 1$. The height of the point of intersection is equal to π_α.

From the value of p_α at $x = 1$ the molar fraction of $\mathfrak{S}_\alpha$ in the pure associated component can be determined, and then π_β can be calculated from p_β at $x = 1$.

ν can also be determined from the tangent of the angle, which the curve of p makes with the x axis at $x = 1$. From equation (5) and (43) we have

$$\left(\frac{dp}{dx}\right)_1 = P_0\left(\frac{dC}{dx}\right)_1 = -\{1+(\nu-1)(C_\beta)_1\}\,P_0$$

Hence ξ, the degree of association of the pure associated component, is given by

$$\xi = 1+(\nu-1)(C_\beta)_1 = -\frac{\left(\frac{dp}{dx}\right)_1}{P_0};$$

and for ν we have

$$\nu = \frac{-\dfrac{\left(\frac{dp}{dx}\right)_1}{P_0}-1}{(C_\beta)_1}+1 \qquad \text{.....................(45)}$$

When ν is thus determined $\mathfrak{K}$ can be calculated from equation (32), and we are now in a position to give a quantitative account not only of the vapour pressures, total and partial, of the whole system, but also of the state of chemical equilibrium in the homogeneous solution, liquid as well as gaseous.

As the measurement of the partial pressures, or molar fractions in the gas phase, is rather troublesome, it often happens that the curve of the total pressure alone is determined. Even in such cases the characteristic magnitudes can be evaluated in the following manner, provided the measurement of pressure and composition at both ends of the curve is sufficiently accurate.

The tangent to the total pressure curve may be expressed as follows:

$$\frac{dP}{dx} = \pi_\alpha \frac{dC_\alpha}{dx} + \pi_\beta \frac{dC_\beta}{dx} + P_0 \frac{dC}{dx}.$$

At the end where $x = 0$ equations (37), (40), and (42) hold. Hence

$$\left(\frac{dP}{dx}\right)_0 = \pi_\alpha - P_0$$

and we get

$$\pi_\alpha = \left(\frac{dP}{dx}\right)_0 + P_0 \quad \text{.....................}(46)$$

In other words the tangent to the total pressure curve at $x = 0$ intersects the pressure axis at $x = 1$ at the height of π_α.

At the other end of the curve we have

$$(P)_1 = \pi_\alpha (C_\alpha)_1 + \pi_\beta \{1 - (C_\alpha)_1\} \text{..................}(47)$$

These two equations, (46) and (47), do not suffice for the determination of the three quantities ν, $(C_\alpha)_1$ and π_β. Another experimental datum is necessary for the purpose. The density of the saturated vapour of the pure associated component at the given temperature may be measured and employed to evaluate $(C_\alpha)_1$. Or a point in the middle portion of the total pressure curve may be taken into calculation; then a few trials will suffice to determine the value of ν.

It has been frequently observed that the vapours of associated liquids have normal densities, that is densities corresponding to the molecular weight of the simple chemical species

$\mathfrak{S}_\alpha$. In such cases π_β must be so small that p_β remains negligible in comparison with other pressures. Then we have

$$(C_\alpha)_1 = \frac{(P)_1}{\pi_\alpha} \quad \text{.......... . ...(48)}$$

and

$$\nu = \frac{\dfrac{(P)_1 - \left(\dfrac{dP}{dx}\right)_1}{P_0} - 1}{1-(C_\alpha)_1} + 1. \quad \text{................(49)}$$

When π_α and π_β are known for one temperature then they are known at least approximately for the range of 30° to 50° above and below that temperature. I mean that it is possible to evaluate T_α and T_β in the equations

$$\pi_\alpha = e^{b\left(1-\frac{T_\alpha}{T}\right)}$$

$$\pi_\beta = e^{b\left(1-\frac{T_\beta}{T}\right)}$$

because b has approximately the value of 10.9 for all chemical species, when the pressure is given in atmospheres, as shown in § 2 (c), of the preceding chapter.

The quantities $\mathfrak{Q}$ and $\mathfrak{T}$, which determine $\mathfrak{K}$ as a function of temperature can be evaluated when the tension and density of the saturated vapour of the pure associated component are given for another temperature. In the cases where the vapours have normal densities, only the knowledge of the vapour tension is required.

When the four characteristic quantities $\mathfrak{Q}$, $\mathfrak{T}$, T_α and T_β are known, the state of chemical equilibrium in the system composed of the associated compound alone or with other normal components, can be described quantitatively for varying temperatures and pressures. We thus see the important service which the study of the vapour tension may render to the solution of chemical problems. In the following is given a concrete example in which the foregoing deductions are completely realised.

(2) *The System Acetone and Ethyl Oxide.*

The total and partial pressures of this system at 0°C. have been studied by Cunaeus (Zeits. physik. Chem., 36, 232; 1901). Unfortunately I have not been able to consult the dissertation in which he has given a detailed account of the measurements. This is the more to be regretted because there seems to be several misprints in the numerical data given in the "Zeitschrift," as has been noticed by Bakhuis Roozeboom (Heterogene Gleichgewichte, II, 27, foot-note). In the following table his data are reproduced.

TABLE 5.[1]

x	x'		P in m.m.
0	0	0	185.6
0.165	(0.139)	0.12	181.2
0.383	(0.272)	0.22	166.8
0.490	(0.330)	0.27	158.0 (150.)
0.636	(0.383)	0.35	142.3
0.808	—	—	117.0
0.844	(0.554)	0.54	110.5 (118.5)
1.000	—	1.00	69.6

---

[1] x in the original paper is the empirical molar fraction of ether, while here it stands for that of acetone.

x' in the brackets is the empirical molar fraction of acetone in the gas phase, determined by means of the index of refraction. Unfortunately the method is not an exact one for gaseous mixtures so readily condensible. The other values are those calculated by CUNAEUS by means of the following equation given by VAN DER WAALS:

$$\frac{1}{P}\frac{dP}{d(1-x)}=\frac{x-x'}{x'(1-x')}$$

As the equation is deduced thermodynamically (see Continuität etc., 2, 137) it must be applicable irrespective of the chemical complexity of the liquid phase. The values so calculated deserve therefore more confidence, and these will be employed in the following calculation.

Two of the data on the total pressure are doubtful. I mean those corresponding to $x = 0.490$ and $x = 0.844$. In the original paper the numbers in the brackets are given. When an xP curve is drawn with the other six data we get quite a regular curve; these two values, however, deviate very far from the curve. Hence they have been replaced by the numbers in the column. I believe I am not making too free with the data given, particularly in view of the remark of ROOZEBOOM.

As is well known, ethyl ether is a substance very nearly normal, while acetone has been demonstrated by RAMSAY and SHIELDS to be associated, though its vapour density corresponds to the simple formula C_3H_6O. Hence in the gas phase of the system there are only two chemical species C_3H_6O and $(C_2H_5)_2O$, while in the liquid phase there are at least three, i.e. C_3H_6O, $(C_3H_6O)_\nu$, and $(C_2H_5)_2O$. Under the supposition that there is only one polymer of acetone the mode of calculation developed above may be applied to this case.

On tracing the curve of partial pressure for acetone and drawing the tangent to the curve at $x = 0$, the following approximate value has been found for the vapour pressure of pure C_3H_6O

$$\pi_\alpha = 160. \text{ m.m.}$$

The tangent of the angle which the curve of partial pressure of ether makes with the x axis has been found to be nearly

$$\left(\frac{dp}{dx}\right)_1 = -400.$$

The molar fraction of C_3H_6O in pure acetone is

$$(C_\alpha)_1 = \frac{69.6}{160} = 0.435$$

and in consequence that of $(C_3H_6O)_\nu$ amounts to

$$(C_\beta)_1 = 0.565$$

ν can now be determined by equation (45)

$$\nu = \frac{\dfrac{-\left(\dfrac{dp}{dx}\right)_1}{P_0} - 1}{(C_\beta)_1} = \frac{\dfrac{400}{185.6} - 1}{0.565} + 1 = 3.04.$$

There is no doubt that $\nu = 3$.

With these data the value of $\mathfrak{K}$ for 0°C. is determined to be

$$\mathfrak{K} = \frac{C_\alpha{}^\nu}{C_\beta} = \frac{0.435^3}{0.565} = 0.1456.$$

From the total pressure curve we get values but slightly different.

$$\pi_\alpha = 162 \qquad \text{and} \qquad (C_\alpha)_1 = 0.430$$

and

$$\nu = \frac{\dfrac{(P)_1 - \left(\dfrac{dP}{dx}\right)_1}{P_0} - 1}{1-(C_\alpha)_1} + 1 = \frac{\dfrac{69.6-(-325)}{185.6} - 1}{0.570} + 1 = 2.97.$$

We are now in a position to give the equations of the curves of the molar fractions of the three chemical species and of the total and partial pressures. These are

$$C_\beta = \left\{\left[\frac{x}{6-4x} + \sqrt{\left(\frac{x}{6-4x}\right)^2 + \frac{0.1456}{(9-6x)^3}}\right]^{\frac{1}{3}} + \left[\frac{x}{6-4x} - \sqrt{\left(\frac{x}{6-4x}\right)^2 + \frac{0.1456}{(9-6x)^3}}\right]^{\frac{1}{3}}\right\}^3$$

$$C = (1+2\,C_\beta)\,(1-x)$$

$$C_\alpha = 1 - C_\beta - C$$

$$p_\alpha = 160\,C_\alpha$$

$$p = 185.6\,C$$

$$P = p_\alpha + p.$$

The curves calculated by means of these equations are reproduced in Figs. 13 and 14. The data found by Cunaeus are marked with circlets. The agreement must be considered to be satisfactory, in as much as we have employed as the basis of calculation only the vapour pressures of pure acetone and ether and the tangents of the partial pressure curves at the ends.

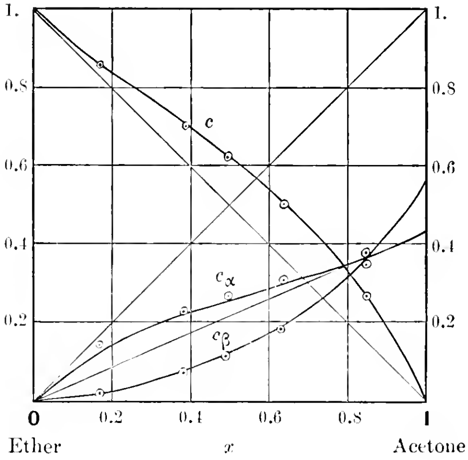

Fig. 13.

In order to make possible a more exact comparison the calculated values of molar fractions and pressures are given in the following tables together with the data obtained by Cunaeus.

TABLE 6.

Molar fractions of the three chemical species.

x	C		C'_{α}		C'_{β}		x'	
	Direct	Calc.	Direct	Calc.	Direct	Calc.	Waals	Calc.
0	1.000	1.000	0	0	0	0	0	0
0.165	0.859	0.859	0.136	0.127	0.015	0.014	0.12	0.113
0.383	0.701	0.707	0.231	0.221	0.068	0.073	0.22	0.212
0.490	0.622	0.629	0.268	0.255	0.110	0.117	0.27	0.258
0.636	0.498	0.504	0.317	0.303	0.185	0.193	0.35	0.341
0.808	—	0.316	—	0.362	—	0.322	—	0.497
0.844	0.273	0.269	0.352	0.371	0.375	0.360	0.54	0.544
1.000	0	0	—	0.435	—	0.565	1.00	1.000

TABLE 7.

Total and partial pressures.

x	p		p_{α}		P	
	Cunaeus	Calc.	Cunaeus	Calc.	Found	Calc.
0	185.6	185.6	0	0	185.6	185.6
0.165	159.5	154.9	21.7	20.3	181.2	179.7
0.383	130.1	131.2	36.7	35.3	166.8	166.5
0.490	115.3	116.7	42.7	40.7	158.0	157.4
0.636	92.5	93.6	49.8	48.5	142.3	142.1
0.808	—	58.6	—	57.9	117.0	116.5
0.844	50.8	49.8	59.7	59.4	110.5	109.2
1.000	0	0	69.6	69.6	69.6	69.6

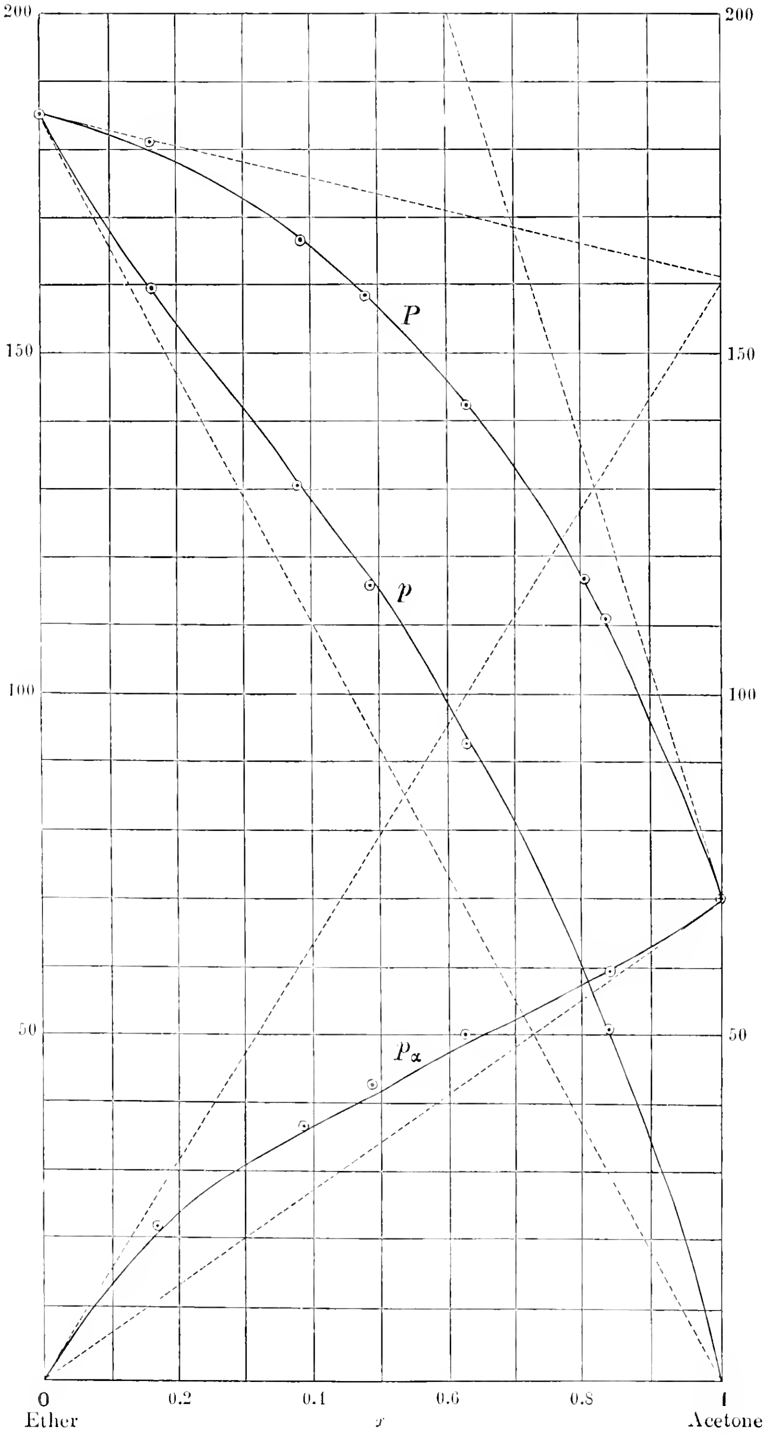
200
200
P
150
150
p
100
100
50
50
p_α
0
0.2
0.4
0.6
0.8
1
Ether
x
Acetone

Fig. 14.

The molar fractions of the three chemical species under the heading "direct" have been calculated more directly from the data of Cunaeus by means of the following equations,

$$C = \frac{(1-x')\,P}{185.6}$$

$$C_\alpha = \frac{x'\,P}{160}$$

$$C_\beta = 1 - C_\alpha - C.$$

The empirical molar fraction of the gas phase has been calculated as follows:

$$x' = \frac{p_\alpha}{p_\alpha + p}$$

the calculated partial pressures being employed.

It is quite probable that the other value for the vapour pressure of the pure chemical species C_3H_6O, that is $\pi_\alpha = 162$, is more in accordance with the facts. But the exact determination of tangents from curves being very difficult, better agreement could hardly be expected. At any rate the foregoing is quite enough to demonstrate that our theory is not a purely hypothetical construction which corresponds to no reality.

(3) *Boiling Point under Constant Pressure.*

Here we may proceed as in § 2 (*c*) of the preceding chapter. In equation (44)

$$C_\alpha\,\pi_\alpha + C_\beta\,\pi_\beta + C\,P_0 = P$$

we have now to consider P as constant, and the molar fractions as well as the vapour tensions of the pure chemical species as functions of temperature. C_α etc. can be expressed as explicit functions of T and x by solving equations (33), (34), and (35), in which $\mathfrak{K}$ is to be put, as in equation (32),

$$\mathfrak{K} = e^{\frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}} - \frac{1}{T}\right)}.$$

Now denote the given pressure by $\mathfrak{P}$, and remembering that

$$\frac{C_\alpha \pi_\alpha}{\mathfrak{P}} = C'_\alpha$$

$$\frac{C_\beta \pi_\beta}{\mathfrak{P}} = C'_\beta$$

$$\frac{C P_0}{\mathfrak{P}} = C'$$

where C'_α etc. are the molar fractions in the gas phase, and that

$$\pi_\alpha = \mathfrak{P}\, e^{b\left(1 - \frac{T_\alpha}{T}\right)}$$

$$\pi_\beta = \mathfrak{P}\, e^{b\left(1 - \frac{T_\beta}{T}\right)}$$

$$P_0 = \mathfrak{P}\, e^{b\left(1 - \frac{T_\gamma}{T}\right)}$$

in which T_α etc. are the boiling points of the pure chemical species under the given pressure, and b is a constant determined by the same, we have

$$\varphi_\alpha(x, T, \mathfrak{Q}, \mathfrak{T})\, e^{b\left(1 - \frac{T_\alpha}{T}\right)} + \varphi_\beta(x, T, \mathfrak{Q}, \mathfrak{T})\, e^{b\left(1 - \frac{T_\beta}{T}\right)}$$
$$+ \varphi_\gamma(x, T, \mathfrak{Q}, \mathfrak{T})\, e^{b\left(1 - \frac{T_\gamma}{T}\right)} = 1 \ldots\ldots (50)$$

for the equation representing the relation between the boiling point and the composition. This equation can indeed be employed for the calculation of the boiling point, but it is too complex for general discussion. Hence the study of the boiling point is not so well fitted for elucidating the chemical conditions of the solution, as the study of vapour pressure at a constant temperature.

(c) *The Equilibrium between Liquid and Solid Phases.*

It has been shown by **Beckmann** in his well known cryoscopic studies that the depression of the freezing point caused by associated substances such as alcohol in solutions in normal liquids, as for instance benzene, is sometimes far less than might be expected. This has been further confirmed by the investigations of various savants and particularly by those of **Auwers** and his pupils. J. **Schroeder** (Zeits. physik. Chem., **11**, 449; 1893) has shown that the fusion curve of a normal substance deviates considerably from the ideal course, when the other component is associated, and indeed in the sense expected.

In the cases in which the conditions of quasi-ideal solutions are satisfied, the equations of the fusion curves can be readily obtained as shown in the sequel.

(1) *The Solid is the Normal Component.*

Since equation (7) must hold in this case, we have by (35)

$$C = \{1+(\nu-1)\,C_\beta\}\,(1-x) = e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)} \quad \text{.........(51)}$$

or

$$1-x = \frac{e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{1+(\nu-1)\,C_\beta} \quad \text{.....................(52)}$$

where T_0 is the melting point of the normal substance. Were both components normal,

$$1-x = e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)};$$

hence the fusion point T for the equal values of x must be higher in the present case than in the ideal solution.

Since

$$C = 1-C_\alpha-C_\beta = 1-\mathfrak{R}^{\frac{1}{\nu}}C_\beta^{\frac{1}{\nu}}-C_\beta$$

we get from equation (51)

$$\mathfrak{R}^{\frac{1}{\nu}}C_\beta^{\frac{1}{\nu}}+C_\beta = 1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}.$$

Solving this equation and substituting for $\mathfrak{R}$ its equivalent in equation (32), we get C_β in terms of $T, \mathfrak{Q}, \mathfrak{T}, Q$, and T_0. Let this be

$$C_\beta = F(T, \mathfrak{T}, T_0, \mathfrak{Q}, Q),$$

then

$$1-x = \frac{e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{1+(\nu-1)\,F(T, \mathfrak{T}, T_0, \mathfrak{Q}, Q)}.$$

For example, when $\nu = 3$

$$1-x = \frac{e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{1+2\left\{\sqrt[3]{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{2}+\sqrt{\frac{\left\{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}\right\}^2}{4}+\frac{e^{\frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}}-\frac{1}{T}\right)}}{27}}}+\sqrt[3]{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{2}+\sqrt{\frac{\left\{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}\right\}^2}{4}-\frac{e^{\frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}}-\frac{1}{T}\right)}}{27}}}\right\}^3}$$

This equation has been tested by YAMAMOTO,[1] and has been found to represent the fusion curve of naphthalene in the system naphthalene and phenol with a very close approximation.

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[1] See Art. 11 of this volume, where x denotes the empirical molar fraction of naphthalene and not that of phenol, as is implied in the foregoing deductions.

The fusion point of the normal substance can, therefore, be profitably employed to elucidate the state of chemical equilibrium in the solution. For this purpose the determination of C_β by the equation

$$C_\beta = \frac{e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{(\nu-1)(1-x)} - \frac{1}{\nu-1} \text{...... ....} (53)$$

seems to be the most convenient. That ν must be found by trial is the weak point in this method. But when its value is once determined, C_α and $\mathfrak{K}$ can readily be found. For the determination of the characteristic quantities ν, $\mathfrak{Q}$, and $\mathfrak{T}$ three fusion points are necessary.

(2) *The Solid is the Associated Component.*

Of which chemical species the solid phase of the associated substance consists is a matter of indifference, because the heat of dissociation or association will be included in the heat of fusion as it is observed or calculated. But it is otherwise when the solid phase consists of the mixture of the two chemical species $\mathfrak{S}_\alpha$ and $\mathfrak{S}_\beta$. In this case the heat of fusion must vary with the temperature on account of the variation of the degree of association in the solid phase. As this consideration leads to a tolerably complicated result, we shall not discuss it in this place.

In the following we shall consider the solid phase to be in immediate relation to the chemical species $\mathfrak{S}_\beta$ in the solution. Then we have by equation (17)

$$C'_\beta = e^{\frac{Q'}{R}\left(\frac{1}{T_0'}-\frac{1}{T}\right)} \text{........................} (54)$$

where Q' is the molecular heat of fusion of the solid to a liquid consisting of pure $\mathfrak{S}_\beta$, and T_0' is the hypothetical fusion point. From equations (32), and (54) we get

$$C'_\alpha = e^{\frac{\mathfrak{Q}}{\nu R}\left(\frac{1}{\mathfrak{T}}-\frac{1}{T}\right)+\frac{Q'}{\nu R}\left(\frac{1}{T_0'}-\frac{1}{T}\right)}.$$

But as

$$x = \frac{1-C_\alpha-C_\beta}{1+(\nu-1)\,C_\beta}$$

we have

$$x = \frac{1-e^{\frac{\mathfrak{Q}}{\nu R}\left(\frac{1}{\mathfrak{T}}-\frac{1}{T}\right)+\frac{Q'}{\nu R}\left(\frac{1}{T_0'}-\frac{1}{T}\right)}-e^{\frac{Q'}{R}\left(\frac{1}{T_0'}-\frac{1}{T}\right)}}{1+(\nu-1)\,e^{\frac{Q'}{R}\left(\frac{1}{T_0'}-\frac{1}{T}\right)}}\text{......(55)}$$

This is the equation of the fusion curve of the associated component under the supposition made. This equation has also been tested by YAMAMOTO for the fusion curve of phenol in the above mentioned system, but it has not been found in satisfactory agreement with observations. Whether solid phenol is a mixture of two or more chemical species, or whether the data employed in the calculation are at fault can not be determined. The subject evidently requires more thorough study.

§ 3. Systems with one Associated and two Normal Components.

(a) *Homogeneous Equilibrium.*

In the present case we have four chemical species $\mathfrak{S}_\alpha$, $\mathfrak{S}_\beta$, $\mathfrak{S}_1$, and $\mathfrak{S}_2$, the last two of which are normal substances. Their molar fractions must satisfy the following equation :

$$C_\alpha+C_\beta+C_1+C_2 = 1\text{........................(56)}$$

It is quite clear that the chemical species $\mathfrak{S}_1$ and $\mathfrak{S}_2$ are symmetrically related to the other chemical species. If we put

$$C_1 + C_2 = C,$$

we get quite the same equations as in the foregoing section, and the relations found there must apply to the present case without any alterations.

Now let the empirical molar fraction of the associated component be x, and those of the normal components, y and z; then we have

$$x = \frac{C'_\alpha + \nu C'_\beta}{C'_\alpha + \nu C'_\beta + C'_1 + C'_2} = \frac{C'_\alpha + \nu C'_\beta}{1 + (\nu - 1) C'_\beta} \quad \text{.........(57)}$$

$$y = \frac{C'_1}{1 + (\nu - 1) C'_\beta} \quad \text{.....................................(58)}$$

$$z = \frac{C'_2}{1 + (\nu - 1) C'_\beta} \quad \text{.....................................(59)}$$

and $\qquad x + y + z = 1.$

These equations together with (30) enable us to determine C_α, C'_β, C'_1, and C'_2 as functions of the empirical molar fractions. As C'_β must have a constant value for $C'_1 + C'_2 = C'$ = constant, it follows from (58) and (59) that $y + z$ = constant. But this is equivalent to x = constant. The surfaces of C_α and C_β must therefore have the forms represented in Figs. 15 and 16. The locii of the points

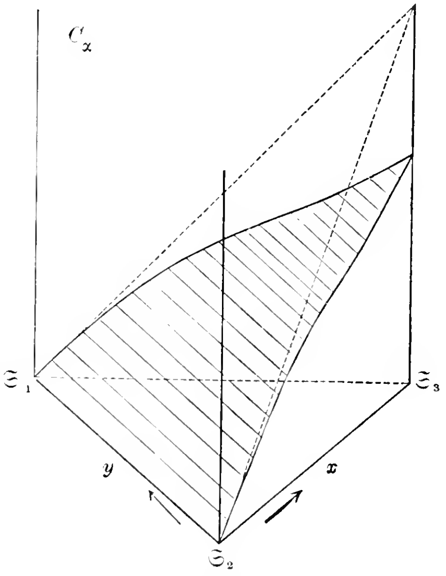

Fig. 15.

on the surfaces having equal values must be straight lines parallel to the axis of y. The projections of these locii upon the plane of composition may be called equifractional curves. In the present case they may also be called equipotential curves, because they are the locii of points at which the chemical potential has equal values. These are of course straight lines parallel to the axis of y.

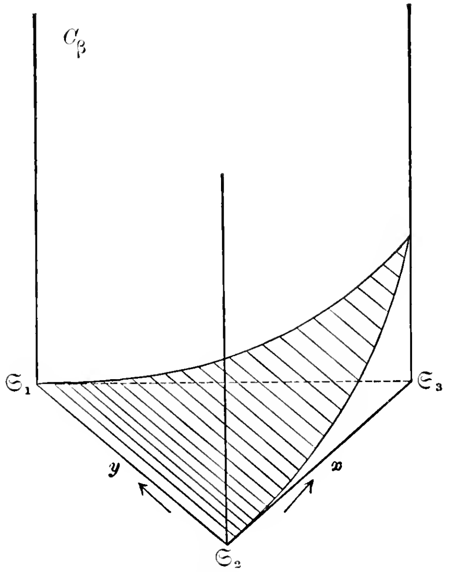

Fig. 16.

The surfaces of C_1 and C_2 are perfectly similar, hence we need consider but one of them. The surface is bounded on one side by the binary curve Fig. 12 γ, and on the other by a straight line as shown in the annexed diagram. On solving equation (57) C_β can be obtained as an explicit function of $\mathfrak{Q}$, $\mathfrak{T}$, T, and x; and the equation for the surface of C_1 has the following form

$$C_1 = y\{1+(\nu-1)\varphi(\mathfrak{Q},\mathfrak{T},T,x)\}\ldots(60)$$

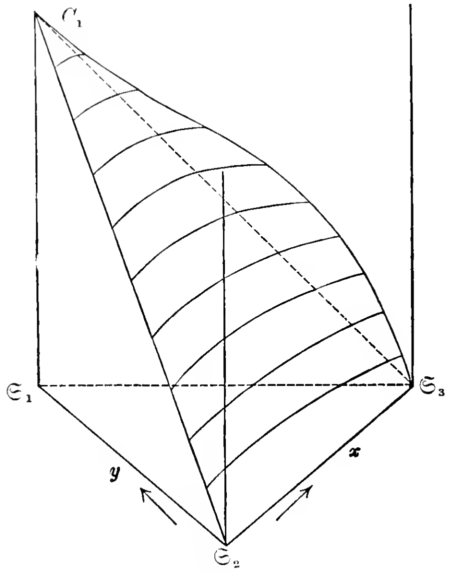

Fig. 17.

As C_β is independent of y we have for constant C_1

$$\frac{dy}{dx} = -\frac{(\nu-1)\,C'_1\,\dfrac{\partial C'_\beta}{\partial x}}{\{1+(\nu-1)\,C'_\beta\}^2}. \qquad\text{..................(61)}$$

We have seen by equation (39) that $\frac{\partial C'_\beta}{\partial x}$ is always positive, hence

$$\frac{dy}{dx} < 0.$$

Only at $x = 0$, $\frac{\partial C'_\beta}{\partial x} = 0$, hence

$$\left(\frac{dy}{dx}\right)_0 = 0,$$

while at the other end where $z = 0$,

$$\frac{dy}{dx} = -\frac{(\nu-1)\,C'_1}{\nu+\dfrac{C'_\alpha}{\nu C'_\beta}-\dfrac{(\nu-1)^2}{\nu}\,C'_\alpha} < 0.$$

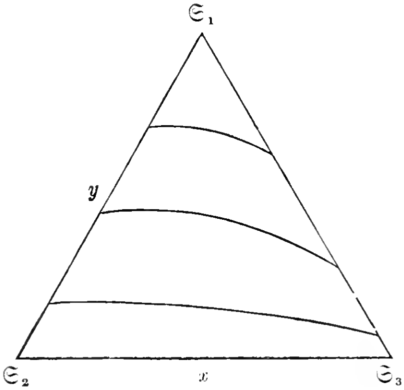

Fig. 18.

The equifractional curve for C'_1 must, therefore, have a form shown in Fig. 18, being concave to the axis of x at least for the smaller values of x.

(*b*) *The Equilibrium between Gaseous and Liquid Phases.*

As the form of the surfaces of the partial vapour pressures at a constant temperature can be readily deduced from the surfaces of the molar fractions we need not describe them in this place. As to the surface of the total pressure it is represented by the equation

$$P = \pi_\alpha\,C'_\alpha+\pi_\beta\,C'_\beta+\pi_1\,C'_1+\pi_2\,C'_2,$$

which may be written

$$P = \pi_\alpha C_\alpha + \pi_\beta C_\beta + \{1+(\nu-1)C_\beta\}\{\pi_1 y + \pi_2(1-x-y)\}$$

or $$P = \pi_\alpha C_\alpha + \pi_\beta C_\beta + \{1+(\nu-1)C_\beta\}(1-x)\pi_2 + \{1+(\nu-1)C_\beta\}(\pi_1-\pi_2)y.$$

As C_α and C_β are independent of y, only the last term is variable in the right side of this equation, when x is made constant. Hence planes erected perpendicular to the plane of composition and parallel to the axis of y must cut the surface of the total pressure in straight lines. This surface is therefore a ruled surface as shown in Fig. 19. As $\frac{\partial C_\beta}{\partial x}$ is positive the inclination of the straight lines must increase with increasing x. The system ethyl alcohol—benzene—carbon tetrachloride studied by SCHREINEMAKERS (Zeit. physik. Chem., 47, 445; 1904) appears to be in qualitative agreement with the foregoing result. Yet the mutual relation between the alcohol and the normal components seems to be more complicated, the decrease of the chemical potential on mixing being less than might be expected, were the conditions of the quasi-ideal solutions fulfilled.

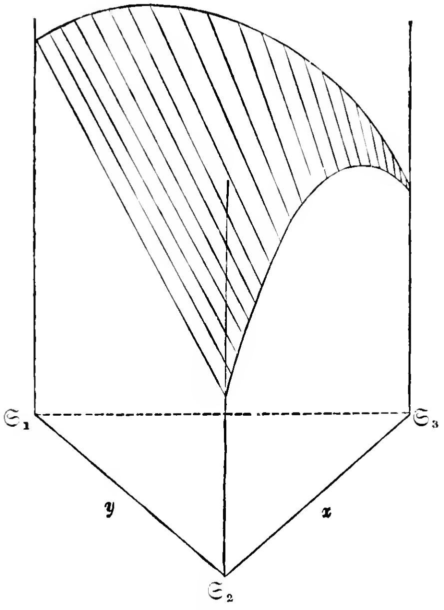

Fig. 19.

The relation between the boiling point and the composition will not be discussed in this place, because it is rather complicated and there seems at present to be but scanty field for application of the results to be obtained.

(*c*) *The Equilibrium between Liquid and Solid Phases.*

(1) *Solubility Curves.*

Let us first take the case in which the solid phase is a normal component; and as the two normal components must show quite similar relations it is enough to consider only one of them. According to equation (17) the molar fraction of $\mathfrak{S}_1$ in a solution, which is in equilibrium with the solid $\mathfrak{S}_1$, must be constant at a constant temperature. The solubility curves of $\mathfrak{S}_1$ must therefore have the same form as the equifractional curve shown in Fig. 18. This has been verified by H. HIROBE[1] in the solubility curves of naphthalene in the system phenol-naphthalene-chlorobenzene. Equation (61) has been found to represent the solubility curves with tolerable approximation, the deviation in the value of x not exceeding 0.015.

When the solid phase is the associated component the solubility curves must be straight lines parallel to the axis of y, as the equifractional curves of C_β as well as those of C_α are such. HIROBE has found that the solubility curves of phenol in the system at various temperatures almost exactly fulfill this requirement.

We have seen in § 3 (*a*) of the preceding chapter that the solubility curves of a component in an ideal solution are straight lines parallel to one of the axes. But we are not justified in concluding from such a course of a solubility curve that the solution is an ideal one, because this is but a consequence of a symmetrical relation between the components. When two components are symmetrically related to a third the solubility curve of the latter must necessarily be such a straight line.

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[1] See Art. 12 of this Volume.

(2) *Fusion Surfaces.*

The equation for the fusion surface of a normal component can be obtained by expressing C_1 in equation (60) as a function of temperature. Hence from (17) we have

$$y\left\{1+(\nu-1)\,\varphi\,(\mathfrak{Q},\,\mathfrak{T},\,T,\,x)\right\}=e^{\frac{Q}{R}\left(\frac{1}{T_1}-\frac{1}{T}\right)}.$$

This equation has been found by HIROBE[1] to represent the fusion aurface of naphthalene with tolerable approximation, the temperature of fusion calculated differing by not more than 1° from the observed values.

The fusion surface of the associated component will be represented by equation (55), because the fusion point is quite independent of y. In the system studied by HIROBE the fusion surface of phenol is nearly a plane, which deviates considerably from the calculated surface.

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[1] Loc. cit.

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The Fusion Curves of the System Naphthalene-Phenol.

By

T. Yamamoto, *Rigakushi.*

(*With 1 plate.*)

1. Introduction.

The investigations on the vapour pressure and solidifying points of concentrated solutions, whose components are avowedly "normal," i.e. unassociated, have made it clear that remarkably simple relations obtain in a great many cases. These are the so-called ideal solutions.[1] They are characterised by the comparative independence of their components, the chemical potential of each being represented by the following simple equation :

$$\mu = z + RT\ln C \text{ ....}(1)$$

where μ is the chemical potential of the component in the solution, z the same in the pure state, and C the molar fraction, or numerical concentration as Haber prefers to call it. R and T have the usual meaning and stand for the universal gas constant and the absolute temperature. The equation applies of course more or less approximately to actual cases, because the conditions upon which it is based are never fulfilled absolutely. These

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[1] See the foregoing article.

conditions are the unchangeability of total volume and total energy on mixing the components at constant temperature and pressure.

In those cases, in which one or more of the components are associated, the relations found are more complicated. But it is quite probable that some of them at least become amenable to theoretical treatment when various chemical species actually present in the solution are taken into consideration. The energy- and volume-changes which occur on mixing the components in such cases may be attributed to chemical changes. Chemical combination may take place between different components, and the degree of association may be decreased by the act of mixing.

Suppose, for the sake of argument, that the solution has reached the state of chemical equilibrium. Let the chemical changes, which the component chemical species may undergo, be arrested by the addition of appropriate negative catalysers. The chemical species can now be separated and again mixed together without causing any appreciable volume- or energy-changes, for no chemical change takes place. The presence or absence of the catalysers will make no difference in the chemical potential of the various chemical species, which must then conform to the equation (1). The removal of the catalysers will not cause any change in the state of equilibrium. When the equation holds strictly, then the mixture is what has been called a quasi-ideal solution by Prof. IKEDA. The present study is undertaken to furnish an instance of such a solution.

The usual methods of chemical analysis do not enable us to distinguish between various chemical species when the velocity of their mutual transformation is not very small. Hence what we call a chemical substance may not be chemically quite uni-form. It is indeed more rational to suppose that all sorts of association and dissociation take place to a greater or less extent. When one of the chemical species so preponderates over the others, that their existence may be neglected in quantitative considerations, then the substance is said to be normal. In other cases the substance is called associated or dissociated according to the circumstances.

It is beyond doubt that naphthalene is a normal substance in the sense above defined, because it is one of the components of several systems, whose fusion curves satisfy fairly well the equation for that of an ideal solution. On the other hand, phenol must be looked upon as a highly associated substance. Even in dilute solutions the depression of the freezing point caused by it is far below the normal value. We have therefore to assume the existence of the following chemical equilibrium in the solution.

$$2\,C_6H_6O \rightleftarrows (C_6H_6O)_2 \quad \dots\dots\dots\dots\dots\dots (a)$$

$$3\,C_6H_6O \rightleftarrows (C_6H_6O)_3 \quad \dots\dots\dots\dots\dots\dots (b)$$

etc., etc.,

When we assume further that each of the chemical species C_6H_6O, $(C_6H_6O)_2$, $(C_6H_6O)_3$, etc., has a chemical potential represented by the equation (1), then the following conditions must be satisfied by the polymers when they are in equilibrium.

$$\frac{C_1^2}{C_2} = K_2 \quad \dots\dots\dots\dots\dots\dots\dots\dots (\alpha)$$

$$\frac{C_1^3}{C_3} = K_3 \quad \dots\dots\dots\dots\dots\dots\dots\dots (\beta)$$

etc., etc.,

in which C_1, C_2, C_3 etc., are the molar fractions of the chemical species C_6H_6O, $(C_6H_6O)_2$, $(C_6H_6O)_3$, etc., respectively, K_2, K_3 etc., are the so-called dissociation constants.

The reversible reactions

$$(C_6H_6O)_2 + C_6H_6O \rightleftarrows (C_6H_6O)_3$$
$$3\,(C_6H_6O)_2 \rightleftarrows 2\,(C_6H_6O)_3$$
$$\text{etc.,} \qquad \text{etc.,}$$

must take place simultaniously with the reactions (a), (b), etc., and the relations

$$\frac{C_1\,C_2}{C_3} = K_{23}$$
$$\frac{C_2^3}{C_3^2} = K'_{23}$$
$$\text{etc.,} \quad \text{etc.,}$$

must also hold. But as these relations can all be deduced from the foregoing (α), (β), etc., we need not take them into consideration.

Careful examination of the experimental data, however, showed that the molar fraction of the chemical species $(C_6H_6O)_2$ can but be small in comparison with those of C_6H_6O and $(C_6H_6O)_3$. The presence of the higher polymers in any great concentration appears also to be improbable. Hence the chief chemical reaction which we have to consider in the study of the system is

$$3\,C_6H_6O \rightleftarrows (C_6H_6O)_3$$

with the corresponding reaction isotherm

$$\frac{C_1^3}{C_3} = \mathfrak{K}.$$

It is interesting to note that the only instance, for which the quantitative relation of the reversible polymerisation in the liquid phase has been established beyond any doubt, belongs to the same class, the reaction[1] being represented by

$$\underset{\text{Acetaldehyde.}}{3\,C_2H_4O} \rightleftarrows \underset{\text{Paraldehyde.}}{C_6H_{12}O_3}$$

Since volume-changes usually accompany polymerisation, pressure must exercise some influence on the equilibrium. But the effect can be considerable only when the variation of pressure amounts to hundreds of atmospheres. We may therefore safely ignore it in the present study, in which the pressure remains practically constant at one atmosphere. Hence $\mathfrak{K}$ is to be considered as a function of temperature alone.

It is a necessary consequence of equation (1), that the equation of VAN T'HOFF

$$\frac{\partial\, ln\, \mathfrak{K}}{\partial T} = \frac{\mathfrak{Q}}{RT^2}$$

applies to the present case. Here $\mathfrak{Q}$ is the heat of dissociation of one gramme-molecule of $(C_6H_6O)_3$ including the heat expended in performing any mechanical work accompanying the chemical change. We may assume, without much hesitation, $\mathfrak{Q}$ to be constant, because the heat capacity of $3\,C_6H_6O$ will be very nearly equal to that of $(C_6H_6O)_3$. The equation can therefore be integrated, when it assumes the following simple form:

$$\mathfrak{K} = e^{\frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}}-\frac{1}{T}\right)}, \qquad \text{.........................(2)}$$

where $\mathfrak{T}$ represents the temperature at which $\mathfrak{K}$ becomes unity.

It is not very probable that naphthalene and phenol should form compounds, and even when they do so, the compounds

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[1] HOLLMANN: Zeits. physik. Chem., **43**, 129 (1903).

would be very unstable. They would be dissociated to such extent, that they might be left out of consideration without affecting the accuracy of the calculation.

2. The Fusion Curve of Naphthalene.

In the graphical representation of the fusion curve the composition of the solution, which is in equilibrium with the solid phase, is taken as the abscissa and the temperature as the ordinate, or vice versa. To express the composition it is usual to employ the molar fraction calculated by using the simplest molecular formula. This may be called the empirical molar fraction in contrast with the actual molar fraction, to calculate which the quantities of all the chemical species must be taken into consideration.

When A stands for the number of gramme molecules of naphthalene $C_{10}H_8$ in the solution, and N for the number of gramme molecules of phenol calculated with the simplest molecular formula C_6H_6O, then the empirical molar fraction of naphthalene is expressed by the following equation:

$$x = \frac{A}{A+N}.$$

This can also be expressed in terms of actual molar fractions. The actual molar fraction of naphthalene is $1-C_1-C_3$, because the sum total of molar fractions is always unity. Hence

$$x = \frac{1-C_1-C_3}{(1-C_1-C_3)+C_1+3\,C_3} = \frac{1-C_1-C_3}{1+2\,C_3}. \quad \text{.........}(4)$$

The actual molar fraction of naphthalene $1-C_1-C_3$ can be represented as a function of temperature. As all the chemical species of the system are supposed to fulfill the conditions of the ideal solution, the following relation must hold:

$$1-C_1-C_3 = e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}, \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

in which Q is the molecular heat of fusion of naphthalene, and T_0 is its melting point. Q is supposed to be independent of temperature, which is not quite exact, but may be assumed as a tolerable approximation.

Writing

$$C_1+C_3 = 1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)} = \mathfrak{C}, \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

and substituting $\sqrt[3]{\mathfrak{K}\,C_3}$ for C_1 by equation (2), we get

$$C_3+\sqrt[3]{\mathfrak{K}\,C_3}-\mathfrak{C} = 0,$$

which on solution gives

$$\sqrt[3]{C_3} = \sqrt[3]{\frac{\mathfrak{C}}{2}+\sqrt{\frac{\mathfrak{C}^2}{4}+\frac{\mathfrak{K}}{27}}}+\sqrt[3]{\frac{\mathfrak{C}}{2}-\sqrt{\frac{\mathfrak{C}^2}{4}+\frac{\mathfrak{K}}{27}}}.$$

Putting this value of C_3 in (4) and substituting for $\mathfrak{K}$ and $\mathfrak{C}$ the expressions given in (3) and (6), we have,

$$x = \frac{e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{1+2\left\{\sqrt[3]{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{2}+\sqrt{\frac{\left\{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}\right\}^2}{4}+\frac{e^{\frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}}-\frac{1}{T}\right)}}{27}}}+\sqrt[3]{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{2}-\sqrt{\frac{\left\{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}\right\}^2}{4}+\frac{e^{\frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}}-\frac{1}{T}\right)}}{27}}}\right\}^3} \ldots(7)$$

This is the equation sought, for it expresses the empirical molar fraction of naphthalene as an explicit function of temperature, and thus represents the fusion curve.

Of the four constants in this equation the two, Q and T_0, have been experimentally determined. The other two, $\mathfrak{Q}$ and $\mathfrak{T}$, may be deduced, when the degree of association of phenol at different temperatures can be determined by any appropriate method. But in default of other reliable data we are forced to evaluate them from the fusion points of the system under consideration. And this can be accomplished in the following manner.

If n_1 and n_3 represent the number of gramme molecules of C_6H_6O and $(C_6H_6O)_3$ respectively, then

$$n_1 + 3\,n_3 = N, \qquad \text{(8)}$$

and if we put

$$n_1 + n_3 = \mathfrak{N}, \qquad \text{(9)}$$

we have

$$C_1 = \frac{n_1}{A + \mathfrak{N}}, \qquad \text{(10)}$$

and

$$C_3 = \frac{n_3}{A + \mathfrak{N}}. \qquad \text{(11)}$$

From (9), (10), (11), and (6)

$$\mathfrak{C} = \frac{\mathfrak{N}}{A + \mathfrak{N}},$$

or

$$\mathfrak{N} = \frac{A\,\mathfrak{C}}{1 - \mathfrak{C}}. \qquad \text{(11 a)}$$

When the fusion point T is determined, $\mathfrak{C}$ is given by (6), and $\mathfrak{N}$ can be calculated.

From (8) and (9)

$$n_1 = \frac{3\,\mathfrak{N} - N}{2},$$

$$n_3 = \frac{N - \mathfrak{N}}{2}.$$

Putting these values in (10) and (11)

$$C_1 = \frac{3\,\mathfrak{N} - N}{2\,(A+\mathfrak{N})},$$

$$C_3 = \frac{N - \mathfrak{N}}{2\,(A+\mathfrak{N})}.$$

Hence the equation (2) can be written

$$\mathfrak{K} = \frac{C_1^3}{C_3} = \frac{(3\,\mathfrak{N} - N)^3}{4\,(N-\mathfrak{N})\,(A+\mathfrak{N})^2}. \quad \ldots\ldots\ldots\ldots\ldots(12)$$

In this way the dissociation constant $\mathfrak{K}$ can be evaluated from experimental data. It has been found to decrease rapidly with a falling temperature. The relation between the dissociation constant deduced in this way and the temperature can be represented tolerably well by an equation of the form

$$\mathfrak{K} = e^{\frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}} - \frac{1}{T}\right)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

in which the constants $\mathfrak{Q}$ and $\mathfrak{T}$ are to be determined empirically.

When the values of $\mathfrak{Q}$ and $\mathfrak{T}$ thus empirically found are inserted in (7), the equation was found to express the fusion curve of naphthalene with tolerably close approximation as will be shown in § 4.

3. The Fusion Curve of Phenol.

As phenol consists essentially of two chemical species, it is necessary to determine to which of them the solid phase stands in immediate relationship. At the melting point of pure phenol, $(C_6H_6O)_3$ preponderates greatly over C_6H_6O; hence it will be more natural to suppose that in the action of melting and solidifying the transformation takes place between the solid phase ond $(C_6H_6O)_3$ in the liquid. The theory of the ideal solution then furnishes the following relation:

$$C_3 = e^{\frac{Q_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

in which T is the fusion point, T_1 the hypothetical temperature at which the solid phenol would be in equilibrium with the liquid phase consisting of $(C_6H_6O)_3$ alone, and Q_1 is the hypothetical molecular heat of fusion for $(C_6H_6O)_3$.

From (2) and (13)

$$C_1 = e^{\frac{\mathfrak{Q}}{3R}\left(\frac{1}{\mathfrak{T}} - \frac{1}{T}\right) + \frac{Q_1}{3R}\left(\frac{1}{T_1} - \frac{1}{T}\right)}; \quad \ldots\ldots\ldots\ldots (14)$$

and as

$$x = \frac{1 - C_1 - C_3}{1 + 2\,C_3},$$

we get for the fusion curve of phenol the expression:

$$x = \frac{1 - e^{\frac{\mathfrak{Q}}{3R}\left(\frac{1}{\mathfrak{T}} - \frac{1}{T}\right) + \frac{Q_1}{3R}\left(\frac{1}{T_1} - \frac{1}{T}\right)} - e^{\frac{Q_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)}}{1 + 2\,e^{\frac{Q_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)}} \quad \ldots (15)$$

Of the four constants contained in this equation $\mathfrak{Q}$ and $\mathfrak{T}$ can be evaluated from the fusion curve of phenol as shown in the foregoing section, and the other two can be found in the following manner.

When C_1' and C_3' express the molar fraction of C_6H_6O and $(C_6H_6O)_3$ in the liquid phase at the melting point of pure phenol, then

$$C_1' + C_3' = 1. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

Hence we have

$$C_1'^3 = (1 - C_1')\,\mathfrak{K}$$

or $$C_1' = \sqrt[3]{\frac{\mathfrak{K}}{2} + \sqrt{\frac{\mathfrak{K}^2}{4} + \frac{\mathfrak{K}^3}{27}}} + \sqrt[3]{\frac{\mathfrak{K}}{2} - \sqrt{\frac{\mathfrak{K}^2}{4} + \frac{\mathfrak{K}^3}{27}}} \quad \text{.........(17)}$$

The value of C_3' can now be found from (16), and the degree of dissociation

$$\alpha = \frac{C_1'}{C_1' + 3\, C_3'}$$

becomes known.

The heat of fusion of phenol as determined in the usual manner, is the sum of the heat of fusion proper and of the heat of dissociation. Q', the ordinary molecular heat of fusion (for the molecular formula C_6H_6O), can be expressed by the following equation :

$$3\, Q' = Q_1 + \alpha\, \mathfrak{Q}. \quad \text{........................(18)}$$

Since Q' as well as α and $\mathfrak{Q}$ are known, Q_1 can be evaluated.

T_1 can now be determined by equation (13)

$$T_1 = \frac{Q_1\, T_0'}{Q_1 + R\, T_0'\, ln\, C_3'} \quad \text{......................(18 a)}$$

where T_0' is the melting point of phenol.

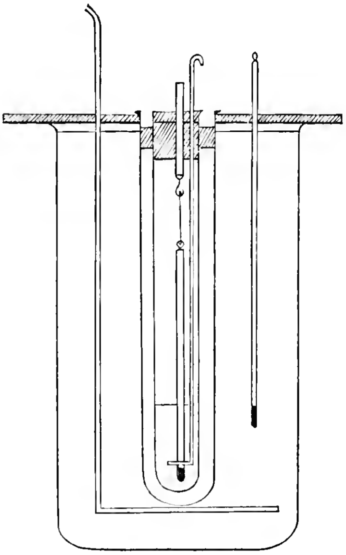
4. Experimental Details.

The method employed in the determination of the fusion points was quite similar to the cryoscopic method of BECKMANN. The outer vessel which served as the bath was a large beaker of about three litre capacity and was nearly filled with water. The temperature of the bath was kept a few degrees below the fusion point to be observed. After some practice this could be managed with tolerable certainty by regulating the height of the flame of a burner placed beneath the vessel.

The inner tube, in which the mixture was placed, was a large test-tube of about 150 c.c. capacity, being some 20 cm. in length and about 3 cm. in internal diameter. The outer tube, which served as the air chamber was considerably wider. The tubes did not emerge much above the cover of the outer vessel, and the cork was deeply inserted into the inner tube. The exposed parts were covered with cotton wool, in order to prevent the loss of heat by radiation. In this way every part of the inner space of the tube was kept at a temperature not much below that of the bath, and the danger of sublimation of the naphthalene was minimised. This evil could not be entirely avoided, but the quantity which sublimed to the upper part of the tube was so small, that no serious error could arise from this source.

To make a series of observations on the fusion curve of naphthalene, about 20 grammes of this substance was placed in the tube, and phenol was added in successive portions, the fusion point being determined after each addition. The mixture was carefully melted by direct application of heat, and then allowed to cool down in the air chamber. For the determination of the fusion curve of phenol about 34 grammes of this component was taken, and naphthalene was added in portions.

For the measurement of temperature two ANSCHUTZ thermometers graduated in 0.2° were employed. One of them had the range of 0°–60°, and the other 50°–100°. They were calibrated by comparison at various temperatures with a normal thermometer standarised at the Reichsanstalt. As the thermometer for higher temperature showed considerable secular change, the determination of certain fixed points was repeated from time to time. The reading was done through a telescope, and was accurate to 0.04°. The solution was stirred mechanically by means of a thin glass rod, whose lower end was bent to form a loop. The whole arrangement is shown in the annexed diagram.



The effect of supercooling, which is quite insignificant in ordinary cryoscopic determinations, is very considerable when the solution is concentrated. In order to apply the correction for this effect, a knowledge of the heat capacity of the solution is necessary. This was measured by the electrical method, the current being passed through a manganin wire of known resistance immersed in the solution. The duration of the current lasted about 200 seconds, and the rise of temperature amounted to 2–3 degrees. The quantity of electricity was measured by means of a copper-voltameter. The determination was made at a temperature slightly above the fusion point. It was not very accurate, single measurements differing by 5% in extreme cases. Five or six determinations were, therefore, made for each solution and the mean was taken. For 20.16 gramme of naphthalene and G grammes of phenol the heat capacity could be expressed with sufficient approximation by the equation:

$$H = 10.77 + 0.592\,G.$$

In this expression the heat capacity of that part of the tube which was in contact with the solution was included. The equation is by no means exact, but it sufficed for the purpose of the correction. As the quantity of naphthalene employed in other series of determinations did not differ by more than one gramme from the above, the expression was employed without alteration.

In the actual measurement of the fusion point the solution was allowed to cool down about half a degree below this temperature, and then stirred vigorously for a few seconds to start the crystallisation. In this way plenty of crystalline flakes separated out. This was favorable to the rapid establishment of equilibrium between the solid and liquid phases. The thermometer rose to a certain point, remained constant for a while and then began to fall again. The amount of naphthalene or phenol which separates out in this way can be readily calculated. When the supercooling amounts to ΔT, the quantity of the solid formed is $\frac{\Delta T H}{Q}$ in gramme molecules. This must be subtracted from the amount of the component originally put into the solution in order to get its actual quantity at the fusion point measured.

For the solutions in which the quantity of phenol was constant and that of naphthalene variable no empirical equation for heat capacity was calculated out, but graphical interpolation was employed instead.

The chief sources of error lay in the sluggishness of the thermometrical indication, and in the impurity of the substances employed. The former source of error was rather serious, because the thermal insulation was not very good and the mixture was losing heat during the measurements.

Naphthalene was purified by recrystallisation from alcohol, dried and distilled. The boiling point was absolutely constant. The melting point was 79.95°C.

Phenol is very difficult to obtain pure. The loose crystals got from Kahlbaum were dried and distilled, and the middle portion of the distillate was collected separately. Its melting point was 40.58°C. The greatest danger lay in the hygroscopic nature of the substance. It was kept melted in a long necked, round bottomed flask, and transferred to the fusion tube by means of a pipette which carried a cork fitting closely to the mouth of the flask. The flask was weighed with the pipette and the content, and in this way the quantity of phenol added to the solution was determined. But as the weather was very wet during the whole period of the experiment, hygroscopic moisture could not be excluded completely. This was particularly troublesome, because one series of measurements extended over more than ten hours. For errors from these sources it is impossible to apply corrections. The fact that the eutectic point arrived at by following up the fusion curve of naphthalene was more than a degree below that found by following up the fusion curve of phenol, is to be explained by the greater amount of moisture absorbed in the former case, because the time which had elapsed from the beginning of the experiment was very much longer, and the manipulations were repeated much oftener.

5. Numerical Data.

The following table gives the experimental data on the fusion curve of naphthalene obtained in one series of determinations.

The first column gives the number of observations. In the second column are the fusion points in absolute temperature, the absolute zero being set at −273.00°C. In the third column, the degree of supercooling is given. In the fourth, the quantities

TABLE 1.

Amount of naphthalene employed 21.205 gramme.

No.	T	ΔT	F	G	A	N	x
1	352.95	—	21.205	—	0.1656	—	1.0000
2	349.81	0.36	21.050	1.062	0.1647	0.0113	0.9359
3	346.33	0.19	21.137	2.607	0.1651	0.0272	0.8562
4	342.70	0.58	20.982	4.866	0.1638	0.0517	0.7599
5	338.43	0.49	20.986	8.338	0.1639	0.0887	0.6490
6	334.94	0.47	20.991	11.869	0.1637	0.1262	0.5647
7	330.16	0.62	20.823	17.909	0.1627	0.1904	0.4607
8	326.93	0.48	20.869	22.522	0.1631	0.2394	0.4052
9	324.19	0.60	20.739	27.045	0.1620	0.2875	0.3604
10	320.92	1.21	20.152	32.814	0.1575	0.3449	0.3136
11	318.51	1.99	13.305	37.124	0.1511	0.3947	0.2769
12	315.60	1.61	19.490	43.449	0.1529	0.4620	0.2482
13	312.26	1.61	19.331	49.129	0.1513	0.5223	0.2246
14	311.42	0	21.205	54.870	0.1656	0.5833	0.2211
15	309.39	0	21.205	61.673	0.1656	0.6557	0.2061
16	305.60	0	21.205	72.176	0.1656	0.7674	0.1774
17	302.61	0	21.205	82.318	0.1656	0.8752	0.1592
18	301.60	Eutectic					

of naphthalene in grammes corrected for the supercooling. This is designated F. In the fifth, are the quantities of phenol added. In the sixth and seventh columns, the number of gramme molecules of naphthalene and phenol. In the last column, the empirical molar fraction of naphthalene.

The curve in the accompanying plate represents the fusion curve; the crosslets are the observed points.

From the values of T, given in the foregoing table, $\mathfrak{C}$ was calculated by equation (6). For Q, R, and T_0 the following values were used:

Q = 4559. calories
R = 1.985 „
$T_0 = 79.95 + 273.00 = 352.95$

$\mathfrak{N}$ was calculated by (11 a), and finally $\mathfrak{K}$ by (12). The results of these calculations are reproduced in Table 2.

TABLE 2.

No.	T	$\mathfrak{C}$	N 1)	$\mathfrak{N}$ 1)	C_1	C_3	log $\mathfrak{K}$	log $\mathfrak{K}$ calc.
1	352.95	0	0	0	0	0	—	—
2	349.81	0.0569	0.0685	0.0603	0.0553	0.00164	$\bar{2}.581$	$\bar{1}.018$
3	346.33	0.1170	0.1678	0.1325	0.1035	0.0135	$\bar{2}.825$	$\bar{2}.914$
4	342.70	0.1770	0.3157	0.2151	0.1369	0.0401	$\bar{2}.780$	$\bar{2}.808$
5	338.43	0.2437	0.5409	0.3223	0.1625	0.0812	$\bar{2}.704$	$\bar{2}.681$
6	334.94	0.2953	0.7709	0.4191	0.1691	0.1262	$\bar{2}.609$	$\bar{2}.575$
7	330.16	0.3620	1.1703	0.5674	0.1722	0.1898	$\bar{2}.405$	$\bar{2}.426$
8	326.93	0.4044	1.4676	0.6789	0.1698	0.2346	$\bar{2}.316$	$\bar{2}.323$
9	324.19	0.4389	1.7750	0.7824	0.1587	0.2802	$\bar{2}.172$	$\bar{2}.163$
10	320.92	0.4777	2.190	0.9147	0.1600	0.3177	$\bar{3}.959$	$\bar{2}.125$
11	318.51	0.5048	2.612	1.0188	0.1651	0.3397	$\bar{3}.527$	$\bar{2}.044$
12	315.60	0.5371	3.029	1.1601	0.1497	0.3874	$\bar{3}.420$	$\bar{3}.945$
13	312.26	0.5717	3.452	1.3348	0.1485	0.4232	$\bar{3}.545$	$\bar{3}.828$
14	311.42	0.5802	3.522	1.3820	0.1400	0.4402	$\bar{3}.699$	$\bar{3}.798$
15	309.39	0.5999	3.959	1.4997	0.1315	0.4684	$\bar{3}.409$	$\bar{3}.725$
16	305.60	0.6352	4.623	1.7414	0.1207	0.5145	$\bar{3}.376$	$\bar{3}.587$
17	302.61	0.6613	5.285	1.9525	0.1243	0.5370	$\bar{3}.209$	$\bar{3}.475$

1) In this table N and $\mathfrak{N}$ are calculated for $A = 1$.

It is interesting to note that C_1 has its maximum value at about 330° absolute, at a lower temperature it diminishes slowly in spite of the increasing x. While at 350° only 8% of phenol is associated to $(C_6H_6O)_3$, at 300° less than 7% remains unassociated. In these regions experimental error has enormous influence on the value of $\mathfrak{K}_3$ as calculated by the equation (12), and it is hardly possible to determine more than the order of the magnitude. Hence for the evaluation of $\mathfrak{Q}$ and $\mathfrak{T}$ in equation (3) only a part of the data is available. These were calculated by combining five of the most trustworthy values of $\mathfrak{K}_3$ and T (No. 4 - No. 8). It was found

$$\mathfrak{Q} = 15762. \text{ calories}$$
$$\mathfrak{T} = 388.74.$$

The value of q, the heat of dissociation of $(C_6H_6O)_3$ appears rather large. Yet it is considerably less than the heat of dissociation of paraldehyde, which was found to be 23300 calories.[1]

$\mathfrak{K}$ corresponding to various temperatures was then calculated by (3) employing these values of $\mathfrak{Q}$ and $\mathfrak{T}$. The values of $\mathfrak{K}$ obtained in this way are given in the last column of the foregoing table. The agreement between the last two columns is on the whole quite satisfactory, although the deviations at the highest and the lowest temperatures may appear at first sight unduly large. But as indicated above a very slight error in determination of temperature or composition affects the value of $\mathfrak{K}$ enormously, and the deviations are not so great but that they can be accounted for by experimental errors. On the whole we may consider the equation (3) well fitted to show how the dissociation varies with temperature.

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1) See the foregoing article.

With these values of $\mathfrak{Q}$ and $\mathfrak{T}$ we proceed to calculate x for various temperatures of fusion employing the equation (7). The values so calculated are compared with the experimental data in the following table.

TABLE 3.

Fusion curve of naphthalene calculated

No.	T	x	x calculated
1	352.95	1.0000	1.0000
2	349.81	0.9359	0.9402
3	346.33	0.8562	0.8598
4	342.70	0.7599	0.7621
5	338.43	0.6490	0.6507
6	334.94	0.5647	0.5627
7	330.16	0.4607	0.4623
8	326.93	0.4052	0.4054
9	324.19	0.3604	0.3597
10	320.92	0.3136	0.3194
11	318.51	0.2769	0.2949
12	315.60	0.2482	0.2608
13	312.26	0.2246	0.2319
14	311.42	0.2211	0.2233
15	309.39	0.2061	0.2066
16	305.60	0.1774	0.1798
17	302.61	0.1592	0.1633

In four cases, Nos. 10, 11, 12, and 13 the difference between the experimental and the calculated values of x exceed 0.5% ; and as is to be seen from Table 1, it was in these cases that the degree of supercooling had been excessively large. In all other cases the difference is much smaller, being on the average only 0.2%. But the deviation is somewhat one-sided.

The experimental data concerning the fusion curve of phenol are given in the following table. The symbols at the head of the table have the same meaning as in Table 1.

TABLE 4.

The fusion curve of phenol.

Amount of phenol employed 34.079 gramme.[1]

No.	T	ΔT	F	G	A	N	x
1	313.39	—	0.000	34.079	0.00000	0.3624	0
2	309.39	0.16	2.698	33.929	0.02155	0.3607	0.0564
3	306.42	0.80	5.009	33.254	0.03911	0.3535	0.0997
4	303.97	0.49	7.279	33.529	0.05683	0.3567	0.1376
5	302.80				eutectic		

From the value of $\mathfrak{K}$ at the melting point of phenol 40.39°C. the degree of dissociation of $(C_6H_6O)_3$ at this temperature was calculated to be

$$\alpha = 0.0615.$$

The available data on the heat of fusion of phenol are not concordant; we employ the value determined by EYKMANN,

$$Q' = 2455 \text{ calories},$$

from which the hypothetical heat of fusion of $(C_6H_6O)_3$ is calculated by equation (18) to

$$Q_1 = 6275 \text{ calories}.$$

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1) The sample of phenol employed in this series of determinations was not the same as in other series. The melting point was somewhat lower.

The hypothetical melting point of $(C_6H_6O)_3$ will then have the value

$$T_1 = 319.74$$

according to equation (18 a).

With these values of $\mathfrak{Q}$ and $\mathfrak{T}$, x was calculated by equation (15). The result of the calculation is given in the following table.

TABLE 5.

The fusion curve of phenol calculated.

No.	T	x	x calculated
1	313.39	0	0
2	309.39	0.0564	0.0524
3	306.42	0.0997	0.0915
4	303.97	0.1376	0.1254

Here the agreement is not so good as in the case of the fusion curve of naphthalene.

The fusion curves of naphthalene and phenol are reproduced in the accompanying plate. The experimental points are distinguished by circles. The calculated curves are drawn in dotted lines.

The coordinates of the eutectic point seem to be about

$$T = 302.7 \qquad x = 0.157.$$

6. Conclusions.

As is to be seen from Table 3 and the plate the fusion curve of naphthalene can be represented with tolerable approximation by equation (7). It may be argued that the whole treatment has too much of a conjectural nature, and that the equation is nothing more than an empirical one. The justness of this objection must indeed be admitted, particularly because the characteristic constants $\mathfrak{Q}$ and $\mathfrak{T}$ were determined from the curve itself, and the agreement between observation and calculation is in general no guarantee for the soundness of a hypothesis. But in the present case the curve is of such peculiar form, that its representation by means of an equation with only two empirical constants through so wide a range may be looked upon as a partial vindication of the hypothesis. Moreover there is nothing improbable in the hypothesis itself. Whether it is right or not must be decided by the study of other chemical as well as physical behaviors of phenol under different conditions.

The discrepancy between the observed and calculated fusion curves of phenol are too large to be accounted for by experimental errors. The specific hypothesis employed may not be appropriate; but it is not impossible that other constants involved in the calculation are inaccurate.

On the whole a certain degree of probability has been established for the existence of the reversible reaction

$$3\,C_6H_6O \rightleftarrows (C_6H_6O)_3$$

in liquid phases, in which phenol is a component.

Resumé.

1. The fusion curve of naphthalene in the system naphthalene-phenol has been experimentally determined.
2. The peculiar form of this curve has been interpreted as due to association of phenol.
3. The equilibrium constant of this association has been expressed as a function of temperature, the heat of association being also determined.
4. The fusion curve of phenol has also been studied experimentally and an attempt has been made to give its theoretical interpretation.

This study has been undertaken and carried out under the guidance of Prof. Ikeda, to whom my best thanks are due.

The Chemical Institute of the Science College,
the Imperial University of Tokyo.

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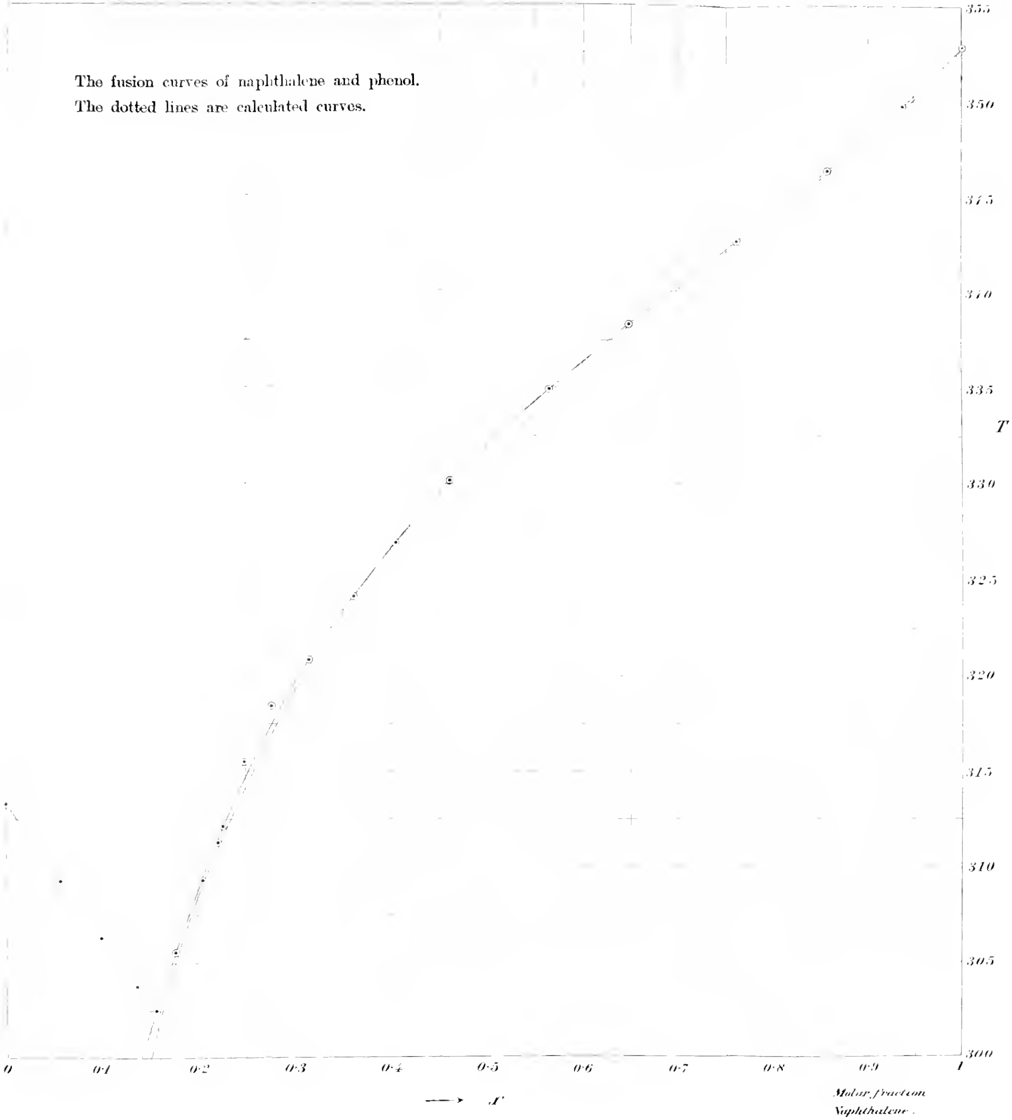

The fusion curves of naphthalene and phenol.
The dotted lines are calculated curves.

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On the Fusion Surfaces of the System Naphthalene-Chlorobenzene-Phenol, and the Molecular Association of Phenol.

By

H. Hirobe, *Rigakushi.*

With 2 plates.

Introduction.

There is a rather large number of ternary systems, whose fusion surfaces have been investigated. But they have been studied mostly in the light of the phase rule, which is avowedly qualitative; and the chief weight has been laid on the determination of the composition and the stability range of the solid phases. The chemical reactions which take place in the liquid phases (excepting dilute solutions) have hitherto been studied only qualitatively, though it is quite clear that more exact knowledge is essential to the elucidation of the quantitative relations of the heterogeneous equilibria. This is doubtless due to the difficulty of getting more precise insight into the state of homogeneous equilibrium in concentrated solutions.

When the liquid phase is a dilute solution, the quantitative relations of the heterogeneous equilibria can be calculated with great precision, provided the chemical reactions in the solution be known. And conversely, when the quantitative relations of the heterogeneous equilibria are given, the state of chemical equilibrium in the solution can be determined. Such in short is the essential feature of the theory of dilute solution in its manifold applications. And this is possible because the chemical potential of each chemical species in the dilute solution is a simple function of the concentration, and its variation with temperature and pressure can be readily calculated. If the chemical potential in a solution of any concentration were as well known, the general quantitative theory of heterogeneous equilibrium could be developed with equal ease. This is at present by no means the case. But in the solutions, whose component chemical species fulfill the conditions of the ideal solution, the chemical potential has the simple form, whatever may be the relative amount of the various substances. *Therefore, when the liquid phase in a ternary system is such a solution, it should be possible to express the fusion surfaces in terms of the heat and the temperature of fusion of the solid phases and the equilibrium constants and the heat of reaction of the reversible chemical changes in the liquid phase. And on the other hand it should be possible to deduce the equilibrium constants etc. of the chemical reaction in the liquid phase from the study of the fusion surfaces.*

In the majority of the ternary systems hitherto investigated, the chemical reactions involved appear to be too complex to lend themselves readily to mathematical treatment. At least it appears premature to attack them without due preparation. Moreover, the temperature has in general not been measured with sufficient accuracy, simply because it has not been necessary for the purpose of the investigators. Hence in order to be able to test the foregoing thesis, I had to study experimentally a comparatively simple case. I chose the system consisting of naphthalene, chlorobenzene, and phenol. The two former components are known to be normal or unassociated substances; and the melting point of naphthalene is such that the temperatures of fusion fall mostly within the range in which exact measurement can be made with comparative ease. Phenol is chosen as the third component as it is known to be highly associated. As all the chemical species of the system are aromatic compounds and hence of allied chemical nature, it is probable that the conditions of ideal solutions are fulfilled with tolerable approximation. Chemical combination between the components appears to be excluded, so that the only chemical reaction which takes place in the solution is the polymerisation and depolymerisation of phenol.

The determination of the molecular complexity of substances in the liquid state is a very important subject, but the methods hitherto employed for the purpose are rather one sided and not very accurate. Of these the method of EÖTVÖS, and RAMSAY and SHIELD alone is applicable to pure liquids. But there is some doubt about the mode of calculation involved. Other methods are applicable only to solutes in dilute solutions; particularly the cryoscopic method and that of the partition coefficient have been employed with success. In cases like the present, these methods of heterogeneous equilibrium can be employed over a very wide range of concentration.

BECKMANN1) demonstrated for the first time by the cryoscopic method that phenol is polymerised in its solutions. NERNST2) arrived at the same conclusion by the method of partition co-

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1) Zeits. f. physik. Chem., 2, (1888), 715.
2) Zeits. f. physik. Chem., 8, (1891), 116.

efficient. T. YAMAMOTO[1] has lately studied the fusion curve of naphthalene in the system naphthalene-phenol, and concluded from his data that the reaction is

$$3\,(C_6H_6O) \rightleftarrows (C_6H_6O)_3.$$

But as there could be only one concentration corresponding to each temperature in the system studied by him, he was unable to study the isothermal relations.

In the present study the fusion surfaces with naphthalene and phenol as solid phases have been determined, necessary precautions being observed in the measurement of the temperatures of equilibrium. From the data so obtained the polymerisation of phenol in the solution has been deduced.

The partition of phenol between water and chlorobenzene in relatively concentrated solution has also been studied, and the results are compared with those obtained in the foregoing investigation.

I. The Fusion Surface of the ternary System, Naphthalene-Chlorobenzene-Phenol.

1. EXPERIMENTAL.

A. The Materials.

Naphthalene was first distilled, and then the portion with a constant boiling point was recrystallised from a large quantity

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1) See the foregoing paper.

of ordinary alcohol. After the alcohol had been removed, it was dried in a vacuum desiccator over concentrated sulphuric acid. Its melting point was 79.88°–79.89°.

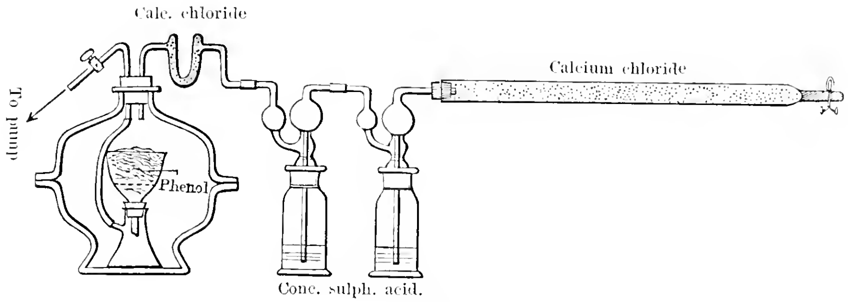


Fig. 1.

Phenol in loose crystals obtained from Kahlbaum, was first distilled, and then crystallised from petroleum-ether (b. p. ca. 60°), from which it separated as fine pure white needles. It was difficult to get rid of the petroleum-ether which adhered to the crystals, because phenol is so hygroscopic that it can not be handled on the suction filter. The apparatus shown in the annexed diagram was therefore set up, and after two days of suction in dry atmosphere with a slow but steady current of air, the sample was placed in a desiccator over phosphoric pentoxide. The melting point was not quite constant but fluctuated between 40.27° and 40.42°, perhaps on account of the different degrees of humidity of the atmosphere and of the vessels at the time of observation.

Chlorobenzene, also from Kahlbaum, was sufficiently pure without further treatment. On distillation the boiling point was quite constant at 132.00°.

B. The Measurement of Temperature.

All temperatures were measured with a thermo-element of iron and nickeline. The fixed temperature was maintained by a thermostat at 25°.

The temperature of a thermostat is subject to irregular local fluctuations, which are not usually indicated by the thermometer placed in it, because an ordinary mercury thermometer reacts too slowly. But this may affect the thermo-element whose indication is much quicker. As the disturbance is due to the current of water it can be easily removed. Fig. 2 *b* is a glass vessel with a cork, through two holes in which the thermometer *d* and one of the junctions *c* of the thermo-element are inserted, *e* is a wide glass tube put around the thermometer. The water of the thermostat is sucked up into it and kept at the proper level by means of a pinch cock. In this way the water circulates by convection, and it may be assumed that the whole mercury thread of the thermometer is at the temperature of the thermostat. The glass vessel dipped in the thermostat hinders the communication of the water with the outside and the small local variation in the temperature of the thermostat has little influence upon the interior of the vessel. Thus

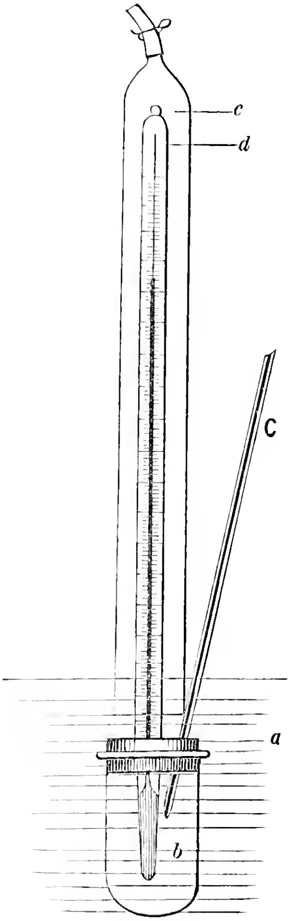


Fig. 2.

the fixed temperature was safely constant up to 0.01° during the whole period of observation. The thermometer in the thermostat was corrected by comparison with a thermometer standardised at the Reichsanstalt.

The electromotive force of the thermo-element was compensated by a Weston standard cell of a very large capacity. The cell-liquid contained no crystal of cadmium sulphate to eliminate temperature influence.

Since the regular compensation apparatus was not at hand, we used the ordinary resistance box, and the mode of compensation was as shown in the diagram (Fig. 3).

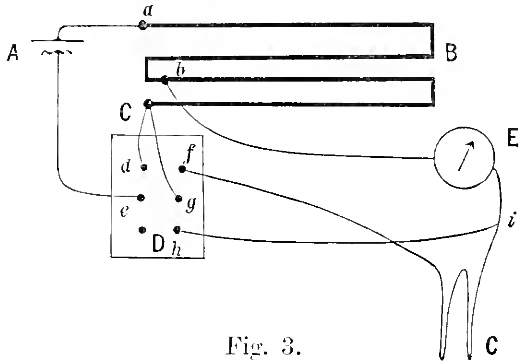


Fig. 3.

A = standard cell. *B* = resistance box.
C = thermo-element. *E* = mirror galvanometer.
D = commutator made of a paraffine block.

Between *a* and *b* 20000 ohms were inserted, while the necessary resistance for compensating the thermo-electricity was put between *b* and *c*. On closing *d*, *e* and *f*, *g* we have the thermo-electricity compensated by the fraction of the electromotive force of the standard cell. On opening them and closing *g*, *h* we have a circuit from which both the thermo-element and the Weston cell are excluded, and we obtain the zero point of the galvanometer, and even if very little thermo-electricity occurs, on account of some inequality in the distribution of temperature in the circuit, it may be thus eliminated by reading the zero point after every observation. The smallest resistance in B was 0.1 ohm, and by means of the deflection of the galvanometer one hundredth of one ohm could easily be read. Since the sensibility of the galvanometer depends upon the resistance in the circuit, we calculated the relation between the resistance between b and c and the deflection of the galvanometer for the excess of one ohm between the same points, by means of the following equation :

$$y = 89 \times \frac{4.70}{89 + 12.5 + x},$$

where y = the deflection for an excess of one ohm.
89 = the resistance of the galvanometer.
12.5 = the resistance of the thermo-element.
x = the resistance between b and c.
4.70 = the deflection for an excess of one ohm between b and c without the thermo-junctions.

The calibration of the thermo-element was done as shown in the "physiko-chemishe Messungen" by Ostwald and Luther (p. 445). For fixed temperatures we selected the freezing points of water, benzene and acetic acid, and the boiling points of carbon bisulphide, chloroform and benzene, compared with the temperature of the thermostat. All the temperatures were measured with the normal thermometer itself or the thermometer corrected by the former, and could be relied upon up to 0.02°. The deviations from the linear equation,

$$\Delta t = \beta r.$$

where Δt = 25.00° − Observed temperature,
r = resistance in b and c,
β = coefficient,

were traced in the curve (Fig. 4).

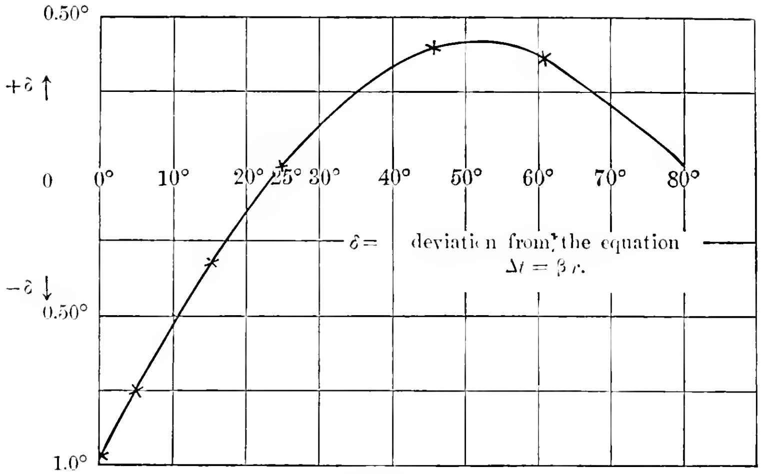


Fig. 4.

C. The Heat Capacity of the Solutions.

In the case of dilute solutions the quantity of crystals which separates out is negligible in the determination of the concentration, but in concentrated solutions this must be taken into account. For this purpose it is necessary to know the heat capacity of the solution, the vessels, etc., and the degree of supercooling. Before proceeding to the observation of the fusion points, the heat capacity was determined in the following manner. Electric energy was converted into heat, and the rise of temperature was read, from which the specific heat could be calculated by the equation,

$$\text{Specific heat} = \frac{R \times \frac{C^2}{t} \times 0.238}{\text{weight of liquid} \times \text{temperature increase}},$$

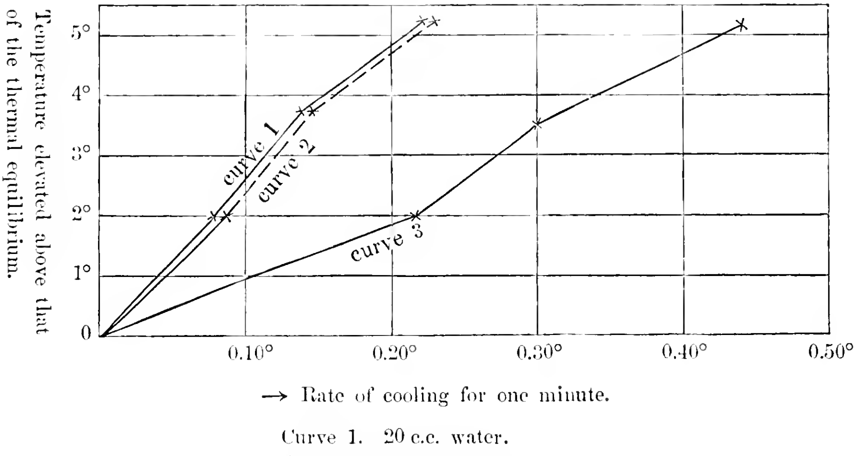
where

R = the resistance of the manganine wire for heating the liquid,

Q = the quantity of electricity passed,
t = the time during which the current was passed,
0.238 = the electric equivalent of the heat.

Q was determined by means of the iodine voltameter,[1] and the time was read to a second with an ordinary watch.

The apparatus employed for the determination was the same as that described later on. In such an arrangement the cooling effect is considerable and must of course be taken into account. In Fig. 5 the relation between the temperature elevation above that of thermal equilibrium and the rate of cooling for one minute is given for water and chlorobenzene. As is to be seen from curves 1 and 2 (Fig. 5) the rapidity of cooling is almost independent of the quantity of the liquid. This is perhaps due to the fact that the greater the amount of the liquid, the greater is the surface exposed. By comparing the curves for chloro-



Curve 1. 20 c.c. water.
Curve 2. 40 c.c. water.
Curve 3. 20 c.c. chlorbenzene.

Fig. 5.

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[1] Phys. Zeit, **6**, 579-581, (1905).

benzene and water we see that the former has a rapidity of cooling twice as great as the latter. The heat capacity of the vessel etc. was 3.5 while the heat capacity of 20 c.c. chlorobenzene was 22×0.33 (see below). Hence the total heat capacity was:

$$22 \times 0.33 + 3.5 = 10.8.$$

The total heat capacity of the vessel with 20 c.c. of water was:

$$20 \times 1 + 3.5 = 23.5.$$

The ratio of these heat capacities is:

$$\frac{23.5}{10.8} = 2.17.$$

As might be expected the heat capacity is inversely proportional to the rate of cooling, other conditions being equal. We therefore calculated the loss of heat during observation according to this conclusion. We determined in the first place the heat capacity of the vessel, the stirrer, etc. The result was as follows:

t	Δt	v	$H. Q$	$h. q$	$H. C$
45°C.	2.77°	19.9	65.4	55.4	3.8
70°C.	1.20°	19.9	27.1	24.0	3.3
45°C.	1.83°	2 × 19.9	83.5	73.2	6.0
45°C.	1.77°	2 × 19.9	81.0	70.8	6.0

where

t = the temperature at which the determination was made,
Δt = the temperature elevation due to the electric current, + the cooling during the observation,
v = the volume of water to be warmed,
$H. Q$ = the heat quantity determined by means of the iodine-voltameter,

$h.\,q$ = the heat quantity necessary to warm the water only, calculated from its volume,

$H.\,C$ = the heat capacity of the vessel etc.

As can be seen from the foregoing table the heat capacity of the vessel, etc. depends upon the volume of the liquid contained in the vessel. We represented graphically the heat capacities of the latter, using those for 20 c.c. and 40 c.c. of the liquid contained in it. In the next place, with the help of the values thus found, we determined the specific heat of naphthalene etc. The results are given in the following table and compared with those of former observers.

t	Substance and its weight.	$s.h$ found.	$s.h$ by former observers.
40°	C_6H_5Cl 21.9 gr.	0.328	0.325 Schiff
60°	,, ,,	0.326	
90°	$C_{10}H_8$ 16.3 gr.	0.381	0.396 Batteli
65°	C_6H_6O 21.1 gr.	0.594	0.561 Schlamp
80°	,, ,,	0.607	

From these values we calculated the heat capacities of various solutions, on the assumption that the heat capacity is an additive quantity.

The heat capacity enters into the calculation as a term of correction in the determination of the fusion point. If it is reliable up to 10% we can in almost all cases calculate the composition of a solution to $1\,^0/_{00}$.

The rate of cooling depends not only on the temperature of the bath, but also on the difference between this temperature and that of the room, for heat may radiate into the space above. Hence we observed the rate of cooling immediately before making observations on the fusion points.

D. The Fusion Surface of Naphthalene.

The arrangement employed is shown in Fig. 6. *B* is a glass tube (17 cm. in height, 4 cm. in diameter), within which

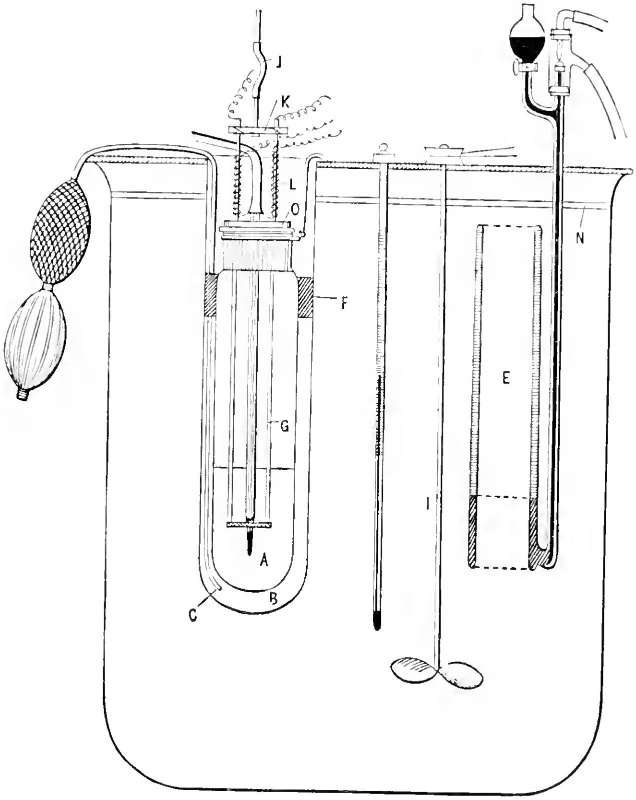

Fig. 6.

a smaller tube *A* (height 13 cm., diameter 3 cm.) is placed. The larger tube is fastened to the wooden cover of the bath. The smaller tube has a hollow glass stopper, the inside of which is filled with a cork. The latter is provided with four holes, two of which serve to admit the stirring rods, the third for the insertion of the thermo-junction, and the fourth for adding phenol or chlorobenzene to the solution. *D* is a hand-bellows which is used to force in air in order to cool the inner tube. *F* is a piece of thick felt and serves to keep the inner tube in position. *L* is thin insulated manganine-wire wound round the stirring rods, through which an electric current is passed to prevent the cooling of the rods from the outside.

When this precaution is not observed, the naphthalene is apt at higher temperatures to sublime round the rods; and moreover it is difficult to maintain the state of superfusion before stirring the liquid, since naphthalene crystalises rapidly round the cold copper rods. *K* is an ebonite piece. *J* is a caoutchouc tubing connecting the stirrer and the rod hanging from an excentric wheel which is kept in motion by an electric motor. The caoutchouc tube proved to be very useful, since by shortening or elongating it we could very easily adjust the height to which the stirrer was to be lifted; so that it might correspond to the amount of liquid contained in the tube. *I* is the stirrer of the bath kept rotating by a hot air engine. *E* is a temperature regulator with a hollow cylindrical reservoir containing toluene in the space between its double walls, so that the surface exposed to the liquid of the thermostat is large in comparison to the capacity of the reservoir. The temperature of the bath must be varied from time to time as the fusion point descends, and it was absolutely necessary to have a sensitive and rapidly adjustable regulator to economise time. The shape given to the regulator was found to answer the purpose very well. It required only two or three minutes before we could be assured that the toluene within it had attained the temperature of the bath, and there was no fear of breaking the thin rubber cover[1] by closing the stop-cock too early. N is the layer of paraffine oil floating upon the water to prevent evaporation.

In order to make observations on the fusion surface of naphthalene, about 10 gramme of it was placed in the inner tube, and phenol or a mixture of phenol and chlorobenzene was added in successive portions by means of the pipette shown in Fig. 7. After each addition the bath was cooled a few degrees below the supposed fusion point, and forcing in cold air by means of the hand-bellows the fusion point was roughly observed. Then the temperature of the bath was raised to just within 0.1°–0.5° of the fusion point. The crystal which had separated out was dissolved by passing an electric current through the ring of wire attached to the stirrer, and on opening the circuit the rate of cooling was observed for one minute. Then cold air was blown in, the temperature in the inner tube fell 0.1°–0.2° below the fusion point. The stirrer was again set in motion, the minimum temperature was observed, and the time was recorded. In a short time crystals made their appearance in abundance, the maximum temperature and the time were noted. The cooling during the observation of the fusion point was calculated from the rate of cooling already observed, assuming it to be proportional to the temperature difference between the solution and the bath. In this way the quantity

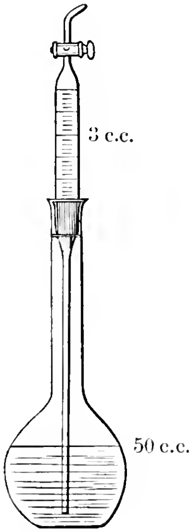

Fig. 7.

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[1] In order to prevent the mercury from coming into direct contact with the gas, a thin rubber cover is stretched over the top of the tube containing the mercury and communicating below with the reservoir. This device, the invention of an English chemist, proved very advantageous when a very exact regulation of temperature was needed.

of the crystals separated out was calculated, and the composition of the solution was corrected accordingly. The maximum temperature was constant for from 20 seconds to 2 minutes according to the rate of cooling.

The results of our determinations are given in the following tables.

TABLE I.

Fusion Curve No. 8.

Naphthalene-chlorobenzene. Solid phase : naphthalene.

No.	t	c	Δt	X	n	C	N	C_A	Q
1	79.88	0.000	—	—	—	—	—	1.0000	(4650)
2	72.88	1.285	0.58	0.13	10.47	.01142	.08179	0.8775	4530
3	65.67	2.815	0.47	0.11	10.49	.02502	.08196	0.7662	4450
4	59.46	4.464	0.80	0.20	10.40	.03968	.08125	0.6720	4535
5	53.66	6.193	0.73	0.20	10.40	.05505	.08125	0.5964	4515
6	47.73	8.209	0.62	0.20	10.40	.07300	.08125	0.5269	4480
7	42.69	10.259	0.63	0.23	10.37	.0913	.08102	0.4700	4490
8	35.01	13.701	0.80	0.20	10.30	.1228	.08047	0.3980	4420
9	25.58	19.142	0.78	0.34	10.26	.1701	.08017	0.3205	4390

t is the fusion temperature in centigrade,

c is the weight of chlorobenzene added,

Δt is the degrees of supercooling + degrees of cooling during observation,

X is the quantity of the crystals separated out, calculated from Δt and the heat capacity of the solution, the vessel, etc.,

n is the weight of naphthalene in the solution at the moment of equilibrium,

C_A is the molar fraction of naphthalene in the same solution,

Q is the value calculated from the equation,

$$ln\, C_A = \frac{Q}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right),$$

where T_0 = the absolute fusion point of pure naphthalene,
T = the absolute fusion point of the solution,
(4650) is the value experimentally obtained by ALLUARD.[1]

The values of Q in No. 2 and No. 3 are not reliable, because $(T_0 - T)$ and $ln\, C_A$ have too small values and an error may effect even the second figure of Q.

At any rate the values decrease regularly with a decreasing temperature, or with an increasing concentration of chlorobenzene. This is doubtless due to the inequality of the specific heats of liquid and solid naphthalene. But it may also be due to the insufficient fulfillment of the conditions of the ideal solution by naphthalene and chlorobenzene. This point will be discussed further on.

TABLE 2.

Fusion Curve No. 1.

Naphthalene-phenol. Solid phase: naphthalene.

No.	t	p	Δt	X	n	P	N	x
1	79.87°	0.000	—	—	—	—	—	1.0000
2	72.87°	1.355	0.81	0.18	9.90	.01441	.07734	0.8433
3	67.98°	2.807	1.16	0.29	9.79	.02986	.07648	0.7190
4	63.58°	4.684	0.68	0.20	9.88	.04983	.07719	0.6083
5	59.11°	7.010	1.35	0.45	9.63	.07458	.07523	0.5002
6	54.64°	9.708	0.33	0.13	9.95	.1033	.07773	0.4294

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[1] Ann. de chim. et de phys. (3), **57**, 471, (1859).

7	51.02°	12.757	0.58	0.26	9.82	.1358	.07672	0.3610
8	45.59°	17.310	0.91	0.48	9.60	.1842	.07500	0.2894
9	40.20°	22.846	0.55	0.35	9.73	.2431	.07602	0.2382
10	34.59°	29.295	0.59	0.45	9.63	.3117	.07524	0.1947
11	29.60°	37.345	0.09	0.09	9.99	.3974	.07805	0.1641
12	29.27°	—	—	—	—	—	—	(0.162)

where

p is the weight of phenol added,
P is the number of phenol molecules calculated as C_6H_6O,
N is the number of naphthalene molecules,
x is the empirical molar fraction of naphthalene calculated with phenol as C_6H_6O,
t, Δt, X, n have the same meaning as table 1.

The fusion curve observed by T. YAMAMOTO[1] coincides fairly with ours except at a few points.

The data in the two foregoing tables give the boundary curves for the fusion surface with naphthalene as the solid phase.

TABLE 3.

Fusion Curve No. 2.

Naphthalene-chlorobenzene-phenol. Solid phase: naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	(79.88°)	—	—	—	—	—	—	1.0000
2	72.49°	1.336	0.18	0.04	9.94	.01400	.07766	0.8472
3	67.76°	2.749	0.83	0.21	9.77	.02880	.07633	0.7263
4	63.97°	4.177	0.48	0.13	9.85	.04376	.07695	0.6375
5	59.55°	6.193	0.52	0.16	9.82	.06488	.07672	0.5418

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1) See the foregoing article.

6	54.76°	8.908	0.62	0.22	9.76	.09333	.07624	0.4496
7	49.32°	12.636	0.40	0.15	9.83	.1324	.07696	0.3675
8	42.38°	18.15	0.49	0.26	9.72	.1902	.07694	0.2854
9	37.31°	23.22	0.34	0.20	9.78	.2433	.07640	0.2390
10	31.55°	29.70	0.60	0.43	9.55	.3112	.07461	0.1943
11	27.02°	36.10	0.78	0.67	9.31	.3782	.07273	0.1613

The fusion point of pure naphthalene was not observed, since the same sample was used as in fusion curves No. 1 and No. 8.

In the above table m is the mixture of phenol and chlorobenzene in the ratio of 40.248 gramme : 4.135 gramme.

$$\frac{P}{P+C} : \frac{C}{P+C} = .9209 : .0791$$

x is the empirical molar fraction of naphthalene calculated with the mean molecular weight of the mixture of phenol and chlorobenzene = 95.45.

TABLE 4.

Fusion Curve No. 3.

Naphthalene-chlorobenzene-phenol. Solid phase: naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	(79.88°)	0.000	—	—	—	—	—	1.0000
2	71.81°	1.474	0.54	0.12	10.02	.01499	.07828	0.8395
3	67.05°	2.710	0.87	0.21	9.93	.02756	.07757	0.7381
4	60.30°	5.036	0.96	0.27	9.87	.05122	.07711	0.6010
5	56.15°	6.807	0.78	0.24	9.90	.06923	.07734	0.5276
6	51.57°	9.136	0.49	0.17	9.97	.09294	.07789	0.4560
7	46.82°	11.84	0.30	0.12	10.02	.1204	.07828	0.3940
8	41.38°	15.59	0.62	0.28	9.86	.1585	.07704	0.3271

9	35.76°	20.12	0.60	0.32	9.82	.2046	.07672	0.2727
10	30.13°	25.64	0.27	0.20	9.94	.2606	.07766	0.2296
11	25.25°	31.42	0.48	0.32	9.82	.3198	.07672	0.1935

where m is the amount of the mixture in the ratio:

24.102 gramme (phenol): 8.967 gramme (chlorobenzene),

i. e. $$\frac{P}{P+C} : \frac{C}{P+C} = .7628 : .2372;$$

the mean molecular weight of the mixture is 98.33.

TABLE 5.

Fusion Curve No. 4.

Naphthalene-chlorobenzene-phenol. Solid phase: naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	79.88°	0.000	—	—	—	—	—	1.0000
2	72.36°	1.326	0.48	0.11	10.10	.01320	.07891	0.8566
3	67.53°	2.485	0.73	0.10	10.11	.02473	.07898	0.7616
4	62.33°	4.018	0.16	0.04	10.17	.03999	.07945	0.6653
5	57.88°	5.536	0.47	0.14	10.07	.05510	.07867	0.5880
6	53.46°	7.364	0.74	0.24	9.97	.07328	.07789	0.5152
7	48.76°	9.623	0.47	0.17	10.04	.09576	.07844	0.4503
8	42.78°	12.90	0.37	0.16	10.05	.1284	.07852	0.3795
9	35.82°	17.60	0.50	0.25	9.96	.1751	.07781	0.3149
10	28.48°	24.13	0.48	0.30	9.91	.2391	.07742	0.2446

Phenol : chlorobenzene = 12.555 gramme : 9.319 gramme,

i. e. $$\frac{P}{P+C} : \frac{C}{P+C} = .6482 : .3518;$$

the mean molecular weight of the mixture is 100.5.

TABLE 6.

Fusion Curve No. 5.

Naphthalene-chlorobenzene-phenol. Solid phase: naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	(79.88°)	—	—	—	—	—	—	1.0000
2	67.01°	2.496	0.44	0.10	10.08	.02428	.07876	0.7644
3	61.92°	3.823	0.35	0.09	10.09	.03718	.07876	0.6795
4	57.13°	5.403	0.45	0.13	10.05	.05254	.07852	0.5990
5	51.98°	7.393	0.34	0.11	10.07	.07190	.07867	0.5224
6	47.52°	9.308	0.58	0.21	9.97	.09055	.07790	0.4626
7	43.43°	11.298	0.44	0.17	10.01	.1099	.07820	0.4157
8	39.88°	13.31	0.18	0.07	10.10	.1295	0.7891	0.3786
9	35.22°	16.23	0.21	0.10	10.08	.1578	.07876	0.3329
10	30.58°	19.76	0.21	0.11	10.07	.1922	.07867	0.2904
11	24.70°	24.58	0.34	0.17	10.01	.2390	.07820	0.2466

Phenol : chlorobenzene 16.47 gramme : 18.07 gramme,

i. e. $$\frac{P}{P+C} : \frac{C}{P+C} = .5218 : .4782\,;$$

the mean molecular weight of mixture is 102.8.

TABLE 7.

Fusion Curve No. 6.

Naphthalene-chlorobenzene-phenol. Solid phase: naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	(79.88°)	—	—	—	—	—	—	1.0000
2	73.01°	1.243	0.24	0.06	10.54	.01179	.08234	0.8748
3	67.35°	2.486	0.56	0.14	10.46	.02357	.08171	0.7761
4	62.54°	3.710	0.33	0.09	10.51	.03517	.08211	0.7000

5	57.67°	5.181	0.33	0.12	10.48	.04911	.08188	0.6250
6	52.88°	6.791	0.30	0.09	10.50	.06437	.08203	0.5604
7	48.03°	8.645	0.50	0.17	10.43	.08196	.08149	0.4985
8	42.89°	10.94	0.36	0.17	10.43	.1037	.08149	0.4401
9	37.37°	13.78	0.56	0.23	10.36	.1306	.08095	0.3827
10	31.56°	17.31	0.50	0.23	10.36	.1641	.08095	0.3304
11	25.23°	21.92	0.50	0.27	10.33	.2078	.08071	0.2798

Phenol : chlorobenzene = 8.073 gramme : 15.785 gramme,

i. e. $$\frac{P}{P+C} : \frac{C}{P+C} = .3796 : .6204 ;$$

the mean molecular weight of the mixture is 105.5.

TABLE 8.

Fusion Curve No. 7.

Naphthalene-chlorobenzene-phenol. Solid phase : naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	(79.88°)	—	—	—	—	—	—	1.0000
2	73.71°	1.061	0.42	0.09	9.96	.00991	.07782	0.8870
3	68.21°	2.114	0.26	0.06	9.99	.01975	.07805	0.7982
4	63.31°	3.241	0.58	0.14	9.91	.03028	.07743	0.7190
5	58.53°	4.503	0.41	0.11	9.94	.04207	.07766	0.6488
6	53.69°	5.959	0.44	0.13	9.92	.05568	.07750	0.5815
7	49.42°	7.410	0.60	0.18	9.87	.06923	.07711	0.5269
8	44.71°	9.160	0.57	0.19	9.86	.08560	.07704	0.4738
9	40.29°	11.09	0.57	0.20	9.85	.1036	.07695	0.4261
10	36.12°	13.14	0.51	0.19	9.86	.1228	.07704	0.3856
11	31.58°	15.70	0.44	0.18	9.87	.1467	.07711	0.3445
12	23.41°	21.34	0.35	0.16	9.89	.1994	.07727	.02792

Phenol : chlorobenzene = 7.000 gramme : 10.052 gramme,

i. e. $$\frac{P}{P+C} : \frac{C}{P+C} = .2940 : .7058\,;$$

the mean molecular weight of the mixture is 107.0.

These eight curves are reproduced in Plate I, with the empirical molar fraction of naphthalene x as abscissa and the temperature t as ordinate. $1-x$ is the sum of the molar fractions of phenol and chlorobenzene, which have a fixed ratio in each curve. It is advantageous to represent the relative amount of these two components again in the form of the molar fraction:

$$Y = \frac{P}{P+C}.$$

Curve 8, in which $Y = 0$, has a form approximating to that of the ideal fusion curve, while in Curve 1, in which $Y = 1$, the deviation is enormous. All the other curves find their positions between these two boundary curves according to the value of Y. The curves with Y larger than 0.5 have inflexion points, while the other curves are concave throughout. These curves should properly be erected on the triangular diagram representing the composition, and the curved surface passing through these eight curves is the fusion surface of naphthalene.

The isothermal curves in the triangular diagram (Plate II) are obtained in the following manner. In this diagram N stands for naphthalene, C for chlorobenzene, and P for phenol. The points corresponding to the different values of Y are taken on the line PC, and these points are united with the apex N by straight lines. These straight lines are the projection of the fusion curves on the plane of composition. Drawing straight lines parallel to the axis of x in Plate I, the points of intersection give the values of x on the fusion curves at constant temperatures. In the next place the points having these values of x (the empirical molar fraction of naphthalene) are taken on the corresponding straight lines in the triangular diagram of Plate II, and connecting all the points of the same temperatures we get the isotherms.

These are shown in the figure and are all convex towards N. The diagram thus obtained is the horizontal projection of the fusion surface. Suppose these isothermal curves to be elevated to proper heights according to the temperature, and imagine a surface passing through all these isothermal curves, then we get the fusion surface under consideration. The surface on the whole has a negative curvature, only a small portion near the apex and next the line NP has a positive curvature being convex towards the corner N.

E. The Fusion Surface of Phenol.

The fusion surface of phenol was determined in a similar manner, and the experimental data are given in the following five tables.

TABLE 9.

Fusion Curve A.

Naphthalene-phenol. Solid phase : phenol.

No.	t	n	Δt	X	p	N	P	x'
1	40.29°	—	—	—	—	—	—	1.0000
2	35.79°	1.004	0.41	0.13	10.74	.00784	.1143	0.9357
3	32.26°	1.957	0.68	0.23	10.64	.01529	.1132	0.8809
4	30.05°	2.577	0.87	0.31	10.56	.02014	.1123	0.8485
5	29.42°	—	—	—	—	—	—	(0.838)

x' is the empirical molar fraction of phenol calculated as C_6H_6O.

All the other symbols in this table have the same meanings as those in the foregoing tables. Naphthalene was added in the pressed form. The curve coincides fairly well with that observed by T. YAMAMOTO.[1]

The eutectic point is 0.15° higher than that in the curve with naphthalene as the solid phase, this is due to the moisture absorbed, since in the former case the observations took two days, while in the present case they were completed in only a few hours.

TABLE 10.

Fusion Curve B.

Naphthalene-chlorobenzene-phenol. Solid phase: phenol.

No.	t	Δt	X	p	n	c	N	C	P	x'
1	40.42°	—	—	—	—	—	—	—	—	1.0000
2	37.27°	0.32	0.09	12.54	0.698	0.084	.00545	.00075	.1334	0.9556
3	32.15°	0.26	0.07	12.56	1.736	0.507	.01356	.00451	.1336	0.8808
4	28.24°	0.34	0.11	12.52	2.817	0.797	.02201	.00709	.1332	0.8207

Since naphthalene and chlorobenzene in such proportions as are given in Table 10 do not form solutions at ordinary temperatures, naphthalene was first added in compressed form and then a corresponding quantity of chlorobenzene by means of a thin graduated pipette.

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[1] See the foregoing article.

TABLE 11.

Fusion Curve C.

Naphthalene-chlorobenzene-phenol. Solid phase : phenol.

No.	t	Δt	X	p	n	c	N	C	P	x'
1	40.37°	—	—	—	—	—	—	—	—	1.0000
2	38.32°	0.49	0.18	12.87	0.279	0.241	.00218	.00214	.1358	0.9692
3	34.18°	0.69	0.27	12.78	0.938	0.716	.00735	.00637	.1360	0.9083
4	29.83°	0.58	0.23	12.82	1.661	1.392	.01298	.01237	.1364	0.8433
5	24.64°	0.69	0.30	12.65	2.526	2.577	.01970	.02290	.1346	0.7595
6	20.39°	0.51	0.24	12.81	3.621	3.662	.02830	.03260	.1363	0.6911

TABLE 12.

Fusion Curve D.

Naphthalene-chlorobenzene-phenol. Solid phase : phenol.

No.	t	m	Δt	X	p	$N+C$	P	x'
1	40.33°	—	—	—	—	—	—	1.0000
2	38.49°	0.459	0.16	0.06	13.64	.00396	.1451	0.9732
3	35.75°	1.178	0.44	0.18	13.53	.01015	.1439	0.9338
4	32.20°	2.239	0.27	0.11	13.59	.01929	.1446	0.8822
5	28.05°	3.697	0.47	0.21	13.50	.03185	.1436	0.8182
6	24.02°	5.813	0.23	0.11	14.13	.05009	.1503	0.7501
7	19.93°	8.044	0.35	0.18	14.06	.06931	.1496	0.6834
8	16.59°	10.418	0.42	0.23	14.01	.08977	.1490	0.6242
9	12.83°	13.817	0.93	0.57	13.67	.11905	.1454	0.5499
10	9.38°	17.18	0.35	0.23	14.01	.1480	.1490	0.5017
11	6.50°	20.48	0.23	0.16	14.08	.1765	.1498	0.4591

where

m is the mixture of naphthalene and chlorobenzene in the proportion :

1.473 gramme (naphthalene) : 4.322 gramme (chlorobenzene)

i. e. $$\frac{N}{N+C} : \frac{C}{N+C} = .2305 : 7695$$

the mean molecular weight of the mixture is 116.1.

TABLE 13.

Fusion Curve E.

Chlorobenzene-phenol. Solid phase: phenol.

No.	t	c	Δt	X	p	C	P	x'
1	40.24°	—	—	—	—	—	—	1.0000
2	38.46°	0.477	0.29	0.12	14.25	.00424	.1516	0.9730
3	34.69°	1.509	0.36	0.15	14.22	.01340	.1513	0.9185
4	30.87°	2.723	0.55	0.24	14.13	.02421	.1503	0.8614
5	27.54°	3.986	0.34	0.16	14.21	.03542	.1512	0.8101
6	21.76°	6.231	0.54	0.25	13.18	.05539	.1402	0.7168
7	18.89°	7.982	0.49	0.24	13.19	.07095	.1403	0.6642
8	14.88°	10.461	0.51	0.11	13.32	.09298	.1417	0.6038
9	11.09°	13.60	0.42	0.24	13.19	.1209	.1403	0.5372
10	6.12°	18.94	0.40	0.26	13.17	.1684	.1401	0.4542

In the fusion curves D and E the different temperatures below 20°C. were maintained by dropping ice-cold water into the bath at different rates of rapidity.

These five curves reproduced on the left side of Plate I coincide almost exactly. But at lower temperatures the deviation between the curves D and E exceeds the limits of experimental error. The curves are nearly straight lines being only very slightly convex towards the axis of temperature. Of some of these curves only short sections have been observed owing to the appearance of the eutectic points. Were the observations extended to lower temperatures, doubtless the curves would become concave.

As the curves (t, x) coincide so closely, the isothermals are nearly straight lines parallel to the line NC. From the deviation between the curves D and E we are led to the conclusion that the isothermal must be slightly concave toward P.

The fusion surface of phenol is therefore almost a plane, having a very small negative curvature, being slightly concave in the horizontal and convex in the vertical direction in the region observed.

As the melting point of chlorobenzene is too low for convenient measurement, its fusion surface has not been determined.

F. The Eutectic Curve.

Of the three eutectic curves of the system only one has been studied, i.e. the line of intersection of the fusion surfaces of naphthalene and phenol. On this curve six points have been determined. The binary eutectic point is already given in Tables 2 and 9. Two other points have been determined by following up the fusion curves of naphthalene, and the other three by following up those of phenol.

In the observation of a point on the eutectic line the temperature of the bath was kept some ten degrees below the fusion point of the solution, which was steadily stirred in order to have the liquid and the crystals in a state of equilibrium. The temperature sank continuously while the crystals separated out more and more. At a certain point $t-\Delta t$ the temperature began to rise owing to the separation of the other component as the solid phase, reached the maximum point t in a short time, and fell again slowly. This maximum temperature was read, and the composition of the liquid phase corresponding to it was calculated in the following manner.

To make the procedure clear let us suppose that the eutectic point, or more properly the point on the eutectic line, had been reached by cooling along the fusion curve of naphthalene. The projection of this curve on the plane of composition is represented by a straight line passing through the apex N and the point

$$Y = \frac{P}{P+C},$$

on the line CP. But the fusion curve was displaced somewhat owing to the separation of a small quantity of phenol as the second solid phase. In order to estimate this amount ΔP it is necessary to know the quantity of heat required to heat the system from $t-\Delta t$ to t, and also the heat lost by radiation during the rise of temperature. The latter can be estimated from the rate of cooling, which for this duration amounted to $\Delta t'$. The former amount of heat is again the sum of two heat quantities, viz., first the heat required simply to elevate the temperature of the system; and second the heat absorbed by the dissolution of a small amount of naphthalene, because with the rise of temperature the concentration of naphthalene in the solution must again increase. Now the quantity so dissolved is

$$\Delta N = (N+P+C)\,\frac{dx}{dt}\,\Delta t,$$

$$= \frac{P+C}{1-x}\,\frac{dx}{dt}\,\Delta t.$$

The value of x and $\frac{dx}{dt}$ at t can be determined from the fusion curve, if necessary by exterpolation; hence ΔN can be estimated in this way. If we express the heat capacity of the system by H, and the molecular heat of fusion of naphthalene and phenol by Q_N and Q_P respectively, then the quantity of phenol crystalised out is :

$$\Delta P = \frac{\Delta N \cdot Q_N + (\Delta t + \Delta t')\, H}{Q_P},$$

and

$$Y = \frac{P - \Delta P}{P - \Delta P + C}.$$

The composition of the eutectic point is to be found in the diagram of Plate II at the intersection of the projection of the fusion curve so displaced and the isothermal curve of the fusion surface of phenol for the temperature t. As both these curves are straight lines the composition is found readily by this graphical method.

Quite the same method of calculation applies to the cases in which the fusion curves of phenol were followed up, where

$$\Delta N = \frac{\Delta P\, Q_P + (\Delta t + \Delta t')\, H}{Q_N},$$

and

$$Z = \frac{N - \Delta N}{N - \Delta N + C}.$$

On following up the fusion curves of phenol were observed,

t	Δt	$\Delta t'$	n	Δn	c	Z
26.21°	.13	.06	2.77	.06	.802	.748
19.47°	.08	.14	2.74	.24	2.54	.465
12.26°	.04	.12	2.74	.22	4.63	.323

On following up the fusion curves of naphthalene,

t	Δt	$\Delta t'$	p	Δp	c	Y
25.18°	.02	.16	32.74	.23	3.36	.915
17.00°	.13	.26	22.93	.56	8.51	.745

n, *c*, *p* are the weights of naphthalene, chlorobenzene and phenol in grammes.

The coordinates of the points are,

	Molar fraction of		
t	naphthalene	chlorobenzene	phenol.
29.00°	.162	.000	.838
26.21°	.160	.057	.783
25.18°	.159	.073	.768
19.47°	.150	.177	.673
17.00°	.150	.217	.633
12.26°	.141	.309	.550

The projection of the eutectic curve on the plane of composition is nearly a straight line; and as the fusion surface of phenol is almost a plane, the curve itself must be nearly a straight line, so far as it has been observed. This does not hold for lower temperatures, but the projection must have the course indicated by the dotted line.

2. THEORETICAL.

In order to facilitate a general survey, the fusion surfaces (in projection on the plane of composition) are reproduced with their isothermal curves. The parts which have not been experimentally determined are supplemented from analogical considerations. This can be done in this case without much danger of falling into gross errors, because the relations of symmetry are so simple and clear.

As we have seen the isotherms of the fusion surface of phenol are nearly straight lines parallel to the line *NC*. This means that phenol stands to chlorobenzene in exactly the same relation as to naphthalene. Naphthalene can be replaced in the solution mol for mol by chlorobenzene without causing any change in the concentration of the phenol which is in equilibrium with the solid phase.

The isotherms of the fusion furface of naphthalene are concave towards the line CP, and the empiricial molar fraction of naphthalene decreases with the increasing proportion of phenol. The fusion surface of chlorobenzene lies of course much lower than the other two, but it must have a form quite similar to that of naphthalene, and the isotherms must lie as shown in the figure.

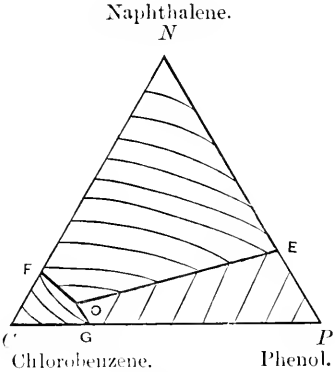

Fig. 8.

The eutectic curve E O must be the longest of the three, being the line of intersection of the fusion surfaces of the two components with the highest melting points. The other two eutectic curves F O and GO would be relatively undeveloped.

So much can be supplemented from the symmetry relations of the three components. These relations can be readily comprehended, when we consider that naphthalene and chlorobenzene are normal, undissociated substances fulfilling the conditions of the ideal solution with respect to each other, while phenol is an associated substance. That the isotherms of the fusion surface of naphthalene are concave to the axis CP at least in the region where the molar fraction of phenol is not very large, is also to be expected.[1] But in order to account quantitatively for the

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[1] See Art. 10 of this volume.

special form assumed by the fusion surface, we must have more detailed knowledge about the association of phenol.

Nothing certain is as yet known about the polymerisation of phenol in solution. NERNST has concluded from the study of the partition coefficient, that phenol dissolved in benzene is associated to double molecule.[1] But it can not be ascertained whether all of the phenol is associated to such a degree, since in the more dilute solutions it must be considered to be dissociated to a great extent.[2] On the other hand YAMAMOTO[3] has concluded from his study on the fusion curve of naphthalene and phenol, which has also been confirmed in the course of the present investigation, that phenol must be considered to contain more complex molecules, at least $(C_6H_6O)_3$. It is plain that the degree of association depends upon the concentration, as well as on the temperature. The following two equations may be assumed to represent these relations:

$$\mathfrak{K} = \frac{c_1^{\,n}}{c_n},$$

$$ln\,\mathfrak{K} = \frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}} - \frac{1}{T}\right).$$

Where

c_1 = the molar fraction of the simple molecule C_6H_6O,
c_n = the molar fraction of $(C_6H_6O)_n$,
$\mathfrak{Q}$ = the heat of dissociation,
$\mathfrak{T}$ = the temperature at which $ln\,\mathfrak{K}$ vanishes,
T = the temperature under consideration.

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1) Zeit. phys. Chem., **8**, p. 116, (1891).
2) BECKMANN: Zeit. phys. Chem., **2**, 715, (1888).
AUWERS: Zeit. phys. Chem., **18**, 599, (1895).
3) Loc. cit.

Here n is quite unknown. Moreover various sorts of associated molecules may exist simultaneously in a solution, and the reactions between them take place freely. Hence the actual relation may be so complex that to make a reliable deduction from the data obtained is impossible. Yet we have ventured to make some calculations on the basis of a simple hypothesis. We have assumed that in the temperature range of 80°–20°, only $(C_6H_6O)_3$ and (C_6H_6O) exist, and other molecular associations may be neglected. It is not excluded that in the higher temperature $(C_6H_6O)_2$ may exist also and in the lower $(C_6H_6O)_4$, and even in the temperature range under consideration molecular associations other than $3(C_6H_6O) \rightleftarrows (C_6H_6O)_3$ may take place as a side reaction. But we have ignored these to avoid too great a complexity in the calculation.

From the data given in Tables 2–8 $\mathfrak{K}$ has been calculated for each observation, in order to see whether it remains constant for different concentrations at a constant temperature. The calculation was done in the following manner.

For the ideal or quasi-ideal solutions we have:

$$ln\, C_A = \frac{Q}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right).$$

Where the symbols are the same as in the equation in page 17. In the next place put

$\mathfrak{N}$ = the actual number of molecules of phenol,

N = the empirical number of molecules of phenol calculated as (C_6H_6O),

A = the number of molecules of naphthalene,

B = the number of molecules of chlorobenzene,

n_1 = the number of simple molecules of phenol,

n_3 = the number of triple molecules of phenol,

then we have

$$C_A = \frac{A}{A+B+\mathfrak{N}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(a)$$

$$\mathfrak{N} = n_1 + n_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(b)$$

$$N = n_1 + 3\,n_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(c)$$

$$c_1 = \frac{n_1}{A+B+\mathfrak{N}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(d)$$

$$c_3 = \frac{n_3}{A+B+\mathfrak{N}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(e)$$

$$\therefore \quad \mathfrak{K} = \frac{c_1^3}{c_3} = \frac{(3\,\mathfrak{N}-N)^3}{4\,(N-\mathfrak{N})\,(A+B+\mathfrak{N})^2} \ldots\ldots\ldots\ldots(f)$$

Where $\mathfrak{N}$ may be obtained from (a) and the equation

$$ln\, C_A = \frac{Q}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right).$$

In the following table are shown the values of $-\log \mathfrak{K}$ at different temperatures for every fusion curve.

TABLE 14.

Values of $-\log \mathfrak{K}$.

	Numbers of the fusion curves.						
Temperature.	1	2	3	4	5	6	7
65°	1.30	1.39	1.29	1.20	1.17	1.17	1.18
60°	1.59	1.50	1.35	1.30	1.30	1.20	1.20
55°	1.75	1.69	1.54	1.49	1.35	1.29	1.29
50°	1.93	1.99	1.70	1.58	1.49	1.31	1.30
45°	2.22	2.18	1.91	1.68	1.56	1.37	1.29
40°	2.45	2.41	2.12	1.85	1.55	1.47	1.32
35°	2.75	2.77	2.49	2.07	1.75	1.52	1.36
30°	3.70	3.45	2.74	2.51	2.12	1.65	1.56

The terms $(3\mathfrak{N}-N)^3$ and $(N-\mathfrak{N})$ are highly sensitive to experimental errors, and the effects are moreover magnified in the calculation according to (f). Hence exact determination of this magnitude is impossible particularly when the concentration of phenol is small. At a constant temperature $\mathfrak{K}$ ought to be independent of the concentration of phenol. This holds true only for curves 1 and 2. For all others $\mathfrak{K}$ diminishes with the decreasing amount of phenol. The deviation is too regular and one-sided to be accounted for by accidental experimental errors. Therefore we must conclude that either this simple hypothesis does not correspond closely enough to the actual state of things; or that the conditions of the ideal solution are not fulfilled with sufficient approximation; or that there is some constant source of error in our measurements.

But in order to test the equation

$$\frac{c_1^3}{c_3} = \mathfrak{K},$$

the values of $\mathfrak{K}$ as determined above are not accurate enough. Hence it would be more rational to represent $\mathfrak{K}$ as a function of temperature, and then calculate x by means of $\mathfrak{K}$. The value of x so found can then be compared with observation.

The constants in the equation

$$ln\,\mathfrak{K} = \frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}} - \frac{1}{T}\right),$$

have been calculated from the values of $\log \mathfrak{K}$ for fusion curve No. 1 and found to be:

$$q = 20940 \text{ calories}, \qquad T_3 = 373.2.^{1)}$$

---

1) These values do not agree very well with those found by YAMAMOTO; for he has calculated $\mathfrak{K}$ under the assumption that the heat of fusion of naphthalene Q is constant for all temperatures. Moreover a very slight discrepancy in the measurement of the fusion curve may give rise to such deviations.

Inversely $\mathfrak{K}$ has been calculated with these constants.

No.	2	3	4	6	7	8	9	10	11
t	72.87°	67.98°	63.58°	54.64°	51.02°	45.59°	40.20°	34.59°	29.60°
log $\mathfrak{K}$ (obs.)	1.25	1.23	1.33	1.64	1.87	2.22	2.44	2.78	3.97
log $\mathfrak{K}$ (calc.)	1.01	1.21	1.40	1.59	1.95	2.20	2.46	2.74	3.00

The numbers refer to the points in Table 2. The agreement is tolerable, and it may be said that $\mathfrak{K}$ can be expressed by the logarithmic equation.

We may now proceed to calculate x. Since

$$\mathfrak{K} = \frac{c_1^3}{c_3},$$

$$c_1 = \sqrt[3]{\mathfrak{K}\, c_3};$$

and as the sum of all the molar fractions is unity,

$$c_3 + \sqrt[3]{\mathfrak{K}\, c_3} + C'_B + C'_A = 1,$$

where C_A = the actual molar fraction of naphthalene,
C_B = the actual molar fraction of chlorobenzene.

Put

$$\frac{C'_B}{c_1 + 3\, c_3} = a,$$

i.e. a = the ratio of the number of molecules of chlorobenzene and phenol in the fusion curve.

Hence

$$c_3 + \sqrt[3]{\mathfrak{K}\, c_3} + a\,(c_1 + 3\, c_3) + C'_A = 1,$$

$$\therefore \quad (1+3\,a)\, c_3 + (1+a)\, \sqrt[3]{\mathfrak{K}\, c_3} - (1 - C'_A) = 0,$$

or

$$c_3 + \frac{(1+a)\sqrt[3]{\mathfrak{K}}}{1+3\,a} \sqrt[3]{c_3} - \frac{(1-C'_A)}{1+3\,a} = 0.$$

$$\therefore \quad \sqrt[3]{c_3} = \sqrt[3]{\frac{(1-C_A)}{2\,(1+3\,\alpha)} - \sqrt{\frac{(1-C_A)^2}{4\,(1+3\,\alpha)^2} + \frac{(1+\alpha)^3\,\mathfrak{R}}{27\,(1+3\,\alpha)^3}}}$$

$$+\sqrt[3]{\frac{(1-C_A)}{2\,(1+3\,\alpha)} + \sqrt{\frac{(1-C_A)}{4\,(1+3\,\alpha)^2} + \frac{(1+\alpha)^3\,\mathfrak{R}}{27\,(1+3\,\alpha)^3}}}.$$

But as

$$x = \frac{C_A}{C_A + C_B + c_1 + 3\,c_3} = \frac{C_A}{1+2\,c_3},$$

if we substitute for $\mathfrak{R}$ and C_A in these equations the functions of temperature given above we get the expression for the fusion surface of naphthalene :

$$x = \frac{e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{1+2\left\{\sqrt[3]{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{2\,(1+3\,\alpha)} + \sqrt{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{4\,(1+3\,\alpha)^2} + \frac{(1+\alpha)^3\,e^{\frac{q}{R_0}\left(\frac{1}{T_3}-\frac{1}{T_0}\right)}}{27\,(1+\alpha)^3}}} + \sqrt[3]{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{2\,(1+3\,\alpha)} - \sqrt{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{4\,(1+3\,\alpha)^2} + \frac{(1+\alpha)^3\,e^{\frac{q}{R}\left(\frac{1}{T_3}-\frac{1}{T}\right)}}{27\,(1+3\,\alpha)^3}}}\right\}^3}.$$

In the above expression Q is not a constant factor, and as we could not find any rational expression for it, we have traced graphically the relation between the temperature and the values of Q, and obtained the value of Q for given temperatures by interpolation. To compare the values of x calculated from the above equation with those experimentally obtained, we selected the fusion curve No. 5 and the isothermal curve at the temperature 51.04°, because they lie at about the middle of the fusion surface.

Fusion Curve No. 5.

t	67.01°	61.92°	57.13°	51.98°	47.52°
x (calc.)	.7802	.6691	.5872	.5091	.4490
x (obs.)	.7644	.6795	.5990	.5224	.4626
Δx	−.0158	+.0104	+.0118	+.0133	+.0136

t	43.43°	39.88°	35.22°	30.58°	24.70°
x (calc.)	.4004	.3626	.3191	.2813	.2391
x (obs.)	.4157	.3786	.3329	.2904	.2466
Δx	+.0153	+.0160	+.0134	+.0091	+.0075

Isotherm 51.04°.

No. of fus. curve.	1	2	3	4	5	6	7
x (calc.)	.3585	.3875	.4344	.4663	.4981	.5220	.5364
x (obs.)	.359	.391	.448	.482	.509	.536	.547
Δx	.000	+.004	+.014	+.016	+.011	+.014	+.011

In the foregoing table the values of x observed were obtained by graphical interpolation from their respective curves in Plate I and accordingly they are given with only three figures.

On the whole the deviations are one-sided, and seems to be greatest at about the middle of the surface. The limit of error, considering the effects of heat capacity, surpercooling and temperature reading, seems to be 2 or 3 units in the third decimal of x, while the error from vaporisation of the mixture which reached 0.1–0.2 grammes out of 30–40 grammes of the total solution will cause an error of 5–6 units in the third decimal at the lower temperatures, yet this error is constant and common to all the curves including curve No. 1, from which N has been calculated, and will have little influence upon the values of x as compared above. Hence the deviations in the above two tables are too large as well as too regular to be referred to experimental error, and seem to show that our starting supposition is not quite correct, perhaps other molecular associations are not strictly excluded in the temperature range studied.

We have not extended the comparison over other fusion curves and isotherms, because it is almost certain that the deviations would not be so great as along the two curves we have chosen.

Yet it is of considerable interest to observe that the fusion surface is expressed within the maximum error of 1.5% in composition and of 1° of temperature over the tempereture range of 50° by the equation thermodynamically deduced starting from only the two boundary curves. Hence it may not be too bold to affirm that within the temperature range given the following reaction mainly takes place in the solutions

$$(C_6H_6O)_3 \rightleftarrows 3\ (C_6H_6O).$$

The next question is "What side reaction can take place besides the above?" The above calculation as well as the values of $\mathfrak{K}$ in Table 13, shows that the convexity of the fusion surface towards the edge of the naphthalene is too large to be explained by our simple hypothesis (see Plates I and II). Suppose that there exist double molecules besides triple molecules of phenol and let n_2 represent the number of these double molecules. Then

$$N = n_1 + 2\,n_2 + 3\,n_3$$
$$\mathfrak{N} = n_1 + n_2 + n_3$$

$$\therefore\quad 3\,\mathfrak{N} - N = 2\,n_1 + n_2$$
$$2\,\mathfrak{N} - N = n_1 + n_3.$$

Put $$(3\,\mathfrak{N} - N) = \alpha, \qquad (2\,\mathfrak{N} - N) = \beta$$

then

$$n_2 = \alpha - 2\,n_1$$

$$n_3 = n_1 - \beta$$

$$\therefore \quad \frac{n_1^3}{n_1'^3} = \frac{(n_1 - \beta)\,(A + B + \mathfrak{R})^2}{(n_1' - \beta')\,(A' + B' + \mathfrak{R}')^2} \quad \text{..............}(1)$$

$$\frac{n_1^2}{n_1'^2} = \frac{(\alpha - 2\,n_1)\,(A + B + \mathfrak{R})}{(\alpha' - 2\,n_1')\,(A' + B' + \mathfrak{R}')} \quad \text{............}(2)$$

Where dashed terms refer to a second point of the isothermal under question. We have to solve n_1 and n_1' from the two equations by inspection, but there is the condition that $n_2 > 0$ that is $\alpha > 2\,n_1$. We tried to apply the equations to an isothermal curve in order to obtain n_1 and n_1', but found that they were impossible under condition $n_2 > 0$. Hence it is clear that the deviation can not be explained in that way. In the next place suppose there exist quadleple molecules whose number is n_4, then we have the analogous simultaneous equations for n_1, n_1', and they were found not to be impossible under the condition $n_4 > 0$. But as the simultaneous equations contain the fourth power of n_1 the experimental error is extraordinarily magnified and no conclusive result can be arrived at.

II. Partition Coefficient of Phenol between Water and Chlorobenzene.

The theory of the constant partition coefficient has been developed by NERNST from the theory of the dilute solution, and since that time it has been customary to apply this law only to the study of dilute solutions. But the field of its legitimate application is much wider. The only condition to be fulfilled is the sufficient immiscibility of the two solvents, and the calculability of the chemical potential as a fuction of the composition in one of the solutions. The last condition is fulfilled when the solution is either dilute or approximates sufficiently to the ideal solution.

When one of the solutions is dilute and the other is an ideal or quasi-ideal solution, the relation is particularly simple. Let the spatial concentration of the common chemical species in the dilute solution be c, and the molar fraction of the same in the ideal solution be C. Then the potential of the chemical species is given by

$$\mu = \zeta' + RT\, ln\, c$$

and

$$\mu = \zeta + RT\, ln\, C,$$

in which ζ' and ζ are functions of temperature and pressure. Hence at a constant temperature and pressure, we have

$$\frac{c}{C} = \text{constant}.$$

This relation can be employed for the elucidation of the problem of the molecular association of phenol in solution.

Nernst has concluded that phenol in benzene is associated to double molecule, from the partition coefficient of this substance between water and benzene. But his observations were made on dilute solutions, and the concentrations were determined by the depression of the freezing point. Hence the result seems not to be quite reliable. We tried to determine the partition coefficient of phenol between water and chlorobenzene up to a concentration of about 50% in the oily phase, expecting some verification for the conclusion arrived at from the study of the fusion surface. When the concentration of phenol is so large water goes to the chlorobenzene phase in no small quantities, and moreover phenol in the watery phase becomes too large to be treated as a dilute solution. To avoid these difficulties we took the aqueous solution almost saturated with both Na Cl and Na_2SO_4. The salt solution contained

8.24% Na Cl
18.57% Na_2SO_4

by weight. It is well known that in such solutions the solubility of the phenol is much less than in pure water.

The concentration of phenol in the aqueous solution was determined by the bromine-water method,[1] and that in chlorobenzene was calculated by difference. The method of determination of phenol has hitherto been worked out chiefly for commercial purposes, and is not very exact. It was therefore found necessary to modify the method somewhat. The chief difficulties lie in the fact, that bromine vaporises during the manupilation and that the precipitation of tribromophenol makes the end reaction very indistinct. These difficulties have been overcome in the following manner. We took a bottle of about 10 litre capacity which was filled with a 0.03 normal solution of bromine (Fig. 9). The reason for using such a capacious bottle was to keep the concentration

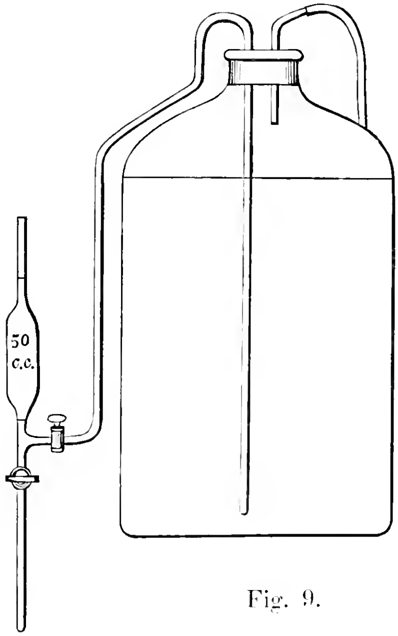

Fig. 9.

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[1] ALLEN's: Commercial Organic Analysis. Vol. II. Part II, p. 244, (1900).

of bromine-water as constant as possible, yet we tested it for the sake of control before and after each observation. It was constant up to about 0.02 c.c. of the sodium thiosulphate solution, of which 40 c.c. was used in each titration. The lower end of the pipette connected with the syphon tube was dipped in the solution containing phenol, while bromine-water was allowed to run into it. This hindered the bromine from evaporating, and consequently made the titration more constant.

The aqueous solution of phenol was first separated by sucking it from under the chlorobenzene, since the salt solution was heavier than the chlorobenzene. 2 c.c. or 5 c.c. of the aqueous solution was taken by means of a pipitte with a cotton wool filter at the end, and put into a bottle of 300 c.c. capacity with a well fitting glass stopper, and 50 c.c. of pure water and 2 c.c. of chlorobenzene or chloroform were added. On admitting bromine-water into the bottle, a white flocky precipitate was produced, which on shaking vigorously dissolved completely in the oil, the greater part of the remaining bromine went to it and there was little fear of losing it by evaporation. After about 15 minutes the necessary quantity of potassium iodide solution was added and well shaken, then the iodine set free was titrated with 0.03 normal solution of sodium thiosulphate, chloroform or chlorobenzene functionating as an indicator. The partition coefficient was observed at three different temperatures 25°, 45°, 65°, the temperatures were maintained in a thermostat and were constant to 0.1° during observation. The most concentrated solution in chlorobenzene contained 50% of phenol. This was made by taking equal quantities by weight. The mixture was diluted with various proportions of chlorobenzene, seven solutions in all being prepared with percentages of phenol varying between 5% and 50%.

20 c.c. of each solution was put into a 50 c.c. bottle with a closely fitting glass stopper, and then 20 c.c. of the salt solution was added. All the seven bottles were placed in the thermostat. After 30 minutes the bottles were shaken until the liquids had become perfectly milky. This was repeated several times at regular intervals. One or two hours after the last shaking, when the liquids had cleared one after another, the aqueous solutions, were sucked out and titrated in the manner described above. In the following tables c is the spatial concentration of phenol in the salt solution, C' is the empirical molar fraction of phenol in the oil phase, which was calculated from the quantity of phenol added and that taken up by the water phase. C'_1 is the molar fraction of simple phenol molecules (C_6H_6O) in the colorobenzene phase, calculated in the following manner.

$$C' = \frac{C'_1 + 3\,C'_3}{1 + 2\,C'_3},$$

$$\mathfrak{K} = \frac{C'^3_1}{C'_3},$$

$$\therefore \quad C' = \frac{\mathfrak{K}_3\,C'_1 + 3\,C'^3_1}{\mathfrak{K}_3 + 2\,C'^3_1},$$

or

$$C'^3_1 + \frac{\mathfrak{K}_3}{3-2\,C'}\,C'_1 + \frac{\mathfrak{K}\,C'}{3-2C'} = 0$$

$$\therefore \quad C'_1 = \sqrt[3]{\frac{\mathfrak{K}\,C'}{2\,(3-2\,C')} + \sqrt{\frac{\mathfrak{K}\,C'}{4\,(3-2\,C')^2} + \frac{\mathfrak{K}^3}{27\,(3-2\,C')^3}}}$$
$$+ \sqrt[3]{\frac{\mathfrak{K}\,C'}{2\,(3-2\,C')} - \sqrt{\frac{\mathfrak{K}\,C'}{4\,(3-2\,C')^2} + \frac{\mathfrak{K}^3}{27\,(3-2\,C')^3}}}.$$

In more concentrated solutions or at lower temperatures where $\mathfrak{K}$ is small the value of C'_1 is almost equal to

$$\sqrt[3]{\frac{\mathfrak{K}\,C'}{3-2\,C'}}.$$

Phenol in water is dissociated to simple molecules at least in the more dilute solutions.[1] Hence if phenol in chlorobenzene is all associated to $(C_6H_6O)_3$, then $\frac{c^3}{C}$ must be constant and if $(C_6H_6O)_2$ alone exists in the solution, then $\frac{c^2}{C}$ must be constant. If it be completely dissociated $\frac{c}{C}$ must be constant, while if it be partially dissociated according to the chemical equation

$$(C_6H_6O)_3 \rightleftarrows 3\,C_6H_6O$$

the ratio $\frac{c}{C_1}$ must be unchangeable.

TABLE 15.

Temperature 25.41°.

No.	c	C	C_1	$\frac{c}{C}$	$\frac{c^2}{C}$	$\frac{c^3}{C}$	$\frac{c}{C_1}$
1	.0489	.537	.0548	.091	.00445	.000217	.89
2	.0457	.440	.0497	.104	.00377	.000217	.92
3	.0443	.349	.0447	.127	.00446	.000249	.99
4	.0404	.299	.0416	.147	.00592	.000240	.97
5	.0377	.213	.0366	.177	.00666	.000251	1.03
6	.0305	.103	.0279	.302	.00899	.000272	1.09
7	.0209	.0485	.0208	.451	.00942	.000197	1.00

TABLE 16.

Temperature 44.93°.

No.	c	C	C_1	$\frac{c}{C}$	$\frac{c^2}{C}$	$\frac{c^3}{C}$	$\frac{c}{C_1}$
1	.0574	.502	.114	.1143	.00656	.000376	.502
2	.0535	.418	.104	.1280	.00686	.000366	.515

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[1] ARRHENIUS: Zeit. physik. Chem., **2**, 491, (1888).

3	.0492	.324	.0931	.1516	.00746	.000367	.529
4	.0454	·256	.0843	.1768	.00803	.000364	.538
5	.0405	.195	.0759	.2070	.00838	.000339	.534
6	.0317	.098	.0588	.3238	.01025	.000325	.539
7	.0185	.0385	.0277	.4820	.00893	.000166	.669

TABLE 17.

Temperature 64.30°.

No.	c	C	C_1	$\frac{c}{C}$	$\frac{c^2}{C}$	$\frac{c^3}{C}$	$\frac{c}{C_1}$
1	.0781	.511	.191	.153	.0119	.000931	.410
2	.0672	.378	.160	.178	.0120	.000805	.419
3	.0620	.342	.154	.182	.0113	.000698	.403
4	.0554	.263	.134	.211	.0117	.000647	.413
5	.0496	.196	.111	.253	.0125	.000621	.446
6	.0358	.099	.0769	.364	.0130	.000466	.466
7	.0213	.0428	.0388	.498	.0106	.000226	.548

On the whole the results obtained accord well with our hypothesis. At lower temperatures where dissociation is small $\frac{c^3}{C}$ is nearly constant, demonstrating that most of the phenol is in the form of $(C_6H_6O)_3$. At 64.30° $\frac{c^3}{C}$ is no longer constant, but decreases with the decreasing concentration of phenol. $\mathfrak{K}$ has a far larger value at this temperature, and the amount of C_6H_6O is not inconsiderable in comparison with that of $(C_6H_6O)_3$. Moreover the degree of dissociation must increase with the decreasing concentration, so that the variation of $\frac{c^3}{C}$ in the sense observed is to be expected.

But the best criterion is the ratio of the concentration of phenol in the aqueous solution and the molar fraction of the chemical species C_6H_6O. If our hypothesis be correct $\frac{c}{C_1}$ must be constant at each temperature. This is approximately the case shown in the last columns of the foregoing tables.

The ratio has indeed the tendency to increase with the decrease of the concentration. In the calculation of C_1 the value of $\mathfrak{K}$ from fusion curve No. 1 was employed and as may be seen from Table 14, $\mathfrak{K}$ increases with the decreasing concentration, so this result corresponds to that deduced from the fusion surface.

The ratio $\frac{c}{C}$ increases rapidly with the decreasing concentration at all temperatures. That the ratio $\frac{c^2}{C}$ is nearly constant at 64.30° must be looked upon as accidental. This demonstrates how dangerous it is to draw theoretical conclusions from observations at a single temperature.

In the foregoing calculations the amount of water taken up by the oily phase has been left out of consideration. In the solutions in which the concentration of phenol is small, this can have no significance; but in the other cases the effect may not be altogether negligible. In order to be able to estimate this disturbing effect, the quantity of water absorbed by the 50% solution of phenol in chlorobenzene was determined in the following manner. A very thin graduated pipette (0.00597 c.c. for 1 division and one drop corresponding to about 2 divisions) was employed to add water to the phenol solution until a slight turbidity occurred. The solution was then shaken with 20 c.c. of the salt solution in the thermostat at 45°. The clear oil was sucked from the bottle and after being cooled, water was again added until turbidity occurred again. The difference of the quantity of water in these two titrations gives the quantity of water absorbed from the salt solution at 45°. 19.90 c.c. of phenol and chlorobenzene mixture was employed and the water absorbed was 0.962 grammes. To apply the proper correction for the quantity of water absorbed is a very difficult matter. On one hand water has a considerable power of dissociating complex molecules, as may be seen from the depression of the freezing point of the aqueous solution of phenol. On the other hand the degree of association of water molecule itself is not known even in dilute solutions. The addition of water decreases the value of C and consequently that of C_1. But since the presence of water promotes the dissociation of phenol, that is increases C_1, the resulting effect can not be very large.

In more dilute solutions the absorption of water must have been much less and the effect must accordingly have been much smaller.

Summary.

1. The fusion surfaces of naphthalene and phenol of the system naphthalene-chlorobenzene-phenol have been determined.

2. The eutectic line between the two fusion surfaces has also been observed.

3. The general forms of the fusion surfaces have been found to be such as would be furnished by two unassociated components and an associated one.

4. An attempt has been made to account quantitatively for the special form of the fusion surface of naphthalene by the hypothesis that in the solution phenol is more or less associated

to triple molecules. It has been found possible to represent the fusion surface approximately by an equation based on this hypothesis and derived from the fusion curves of naphthalene in the binary systems, naphthalene-chlorobenzene and naphthalene-phenol.

5. The partition of phenol between chlorobenzene and an aqueous solution of common salt and sodium sulphate at three different temperatures has been studied, the concentration of phenol in chlorobenzene being in some cases very considerable.

6. The results obtained support on the whole the hypothesis that phenol is associated to triple molecules.

The present study has been undertaken and prosecuted under the kind guidance of Prof. Ikeda to whom my best thanks are due.

August 1907.

Chemical Institute of the Science College,
the Imperial University of Tokyo.

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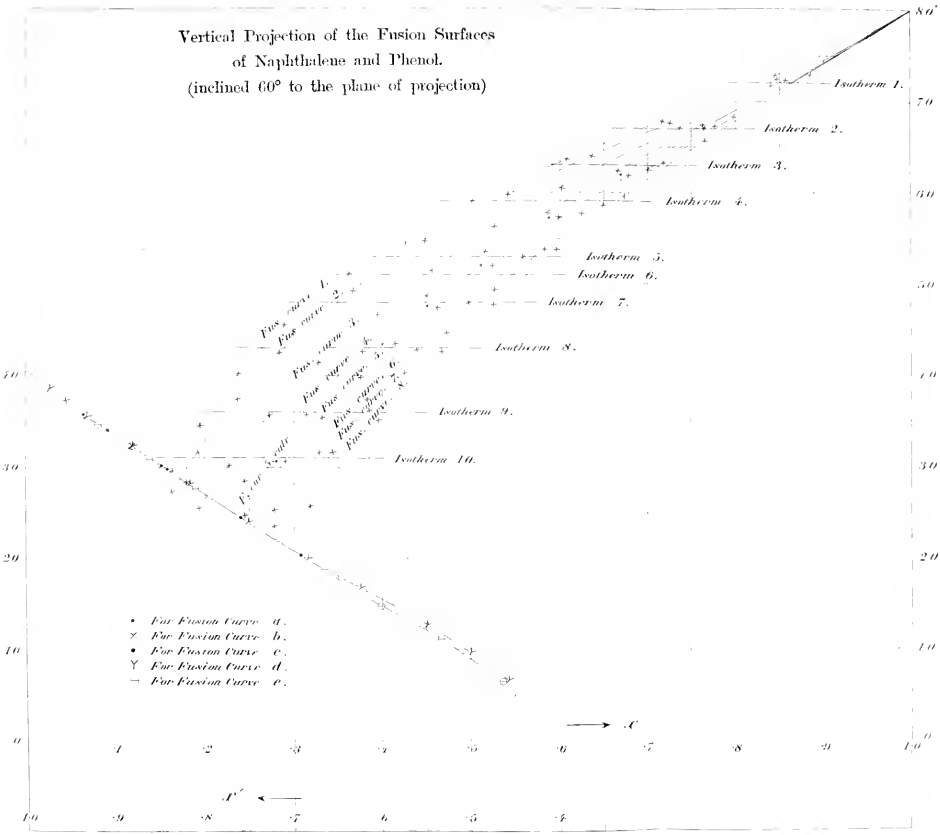

Vertical Projection of the Fusion Surfaces
of Naphthalene and Phenol.
(inclined 60° to the plane of projection)

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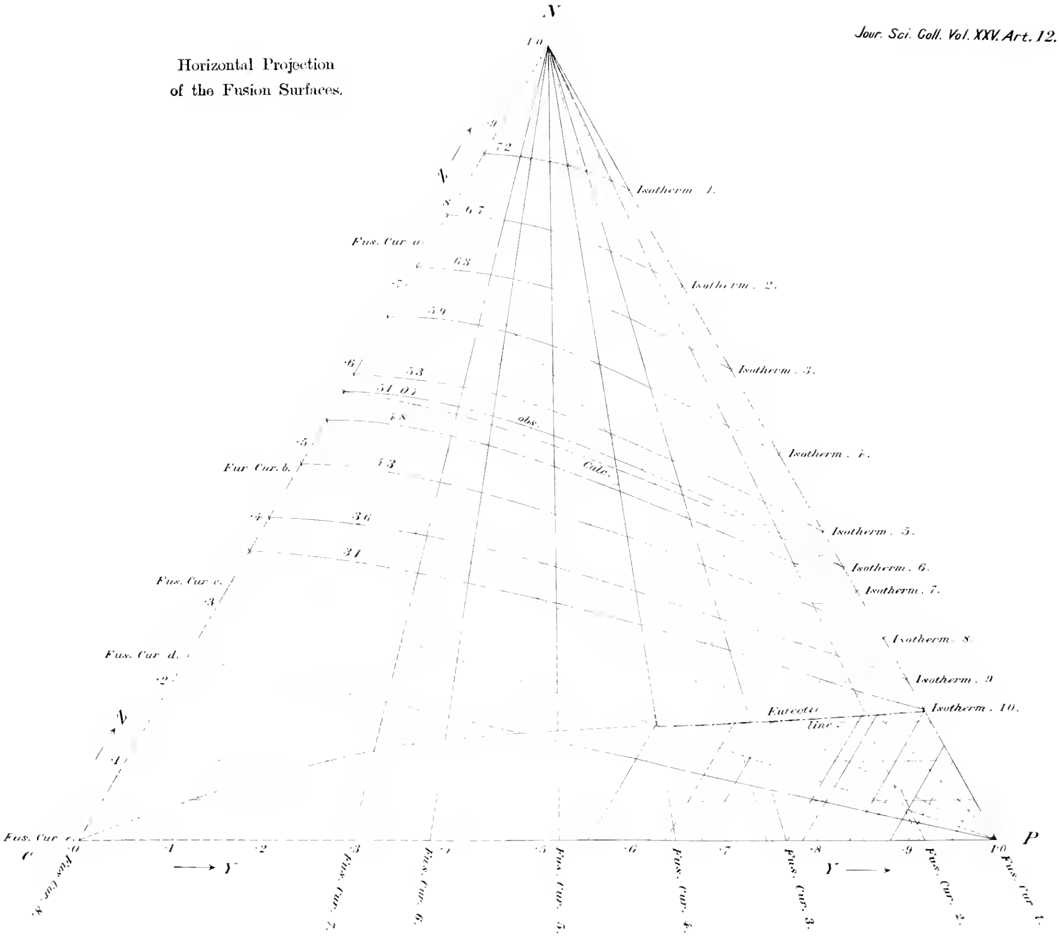
Horizontal Projection
of the Fusion Surfaces.



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A Simple Method of Preparing the Imides of the Aromatic Sulphonic Acids.

By

Tamemasa Haga, *Rigakuhakushi.*

While aromatic sulphamides are quite well known substances, we have only a very scanty knowledge of the corresponding sulphimides. No mention is made of them even in BEILSTEIN's Handbuch. The only work that notices them is the second supplement to RICHTER's Lexikon, which refers to the Chemisches Central-Blatt, 1901, II, 1185, in which an abstract is given of a patent by the FARBWERKE VORM. MEISTER, LUCIUS, UND BRÜNING, Höchst am Main. According to it, these imides are prepared by heating alkali derivatives of aromatic sulphamides with aromatic sulphochlorides at high temperatures, and this is the only method hitherto known of preparing them. The accounts given of these compounds are, moreover, very incomplete, not even their melting points being given, and some of them had, apparently, been obtained only in an impure state.

The author finds that these sulphimides can be easily prepared by reducing aromatic sulphohydroxylamines, sulphur dioxide being the most suitable reducing agent for the purpose. The aromatic sulphohydroxylamines are readily obtainable by treating aromatic sulphinic acids with nitrous acid (W.

KÖNIGS: Ber., 1878, **11**, 615); and aromatic sulphinic acids can now be easily obtained from aromatic amines through their diazo-compounds (GATTERMANN: Ber., 1899, **32**, 1136). It is thus possible to prepare aromatic sulphimides from the corresponding amines with a very good yield, and without going through the rather unsatisfactory process of preparing sulphochlorides and then heating these at high temperatures with the alkali derivatives of sulphamides. The new method, therefore, not only forms a good alternative process to that patented by the firm of MEISTER, LUCIUS, UND BRÜNING, but also offers some considerable advantage over it.

Reduction of Dibenzenesulphohydroxylamine by Sulphur Dioxide.

Yield of Dibenzenesulphimide from Dibenzenesulphohydroxylamine:—Sixty and a half grammes of dibenzenesulphohydroxylamine were dissolved in three hundred and fifty cubic centimetres of about ninety one per cent alcohol and treated with a current of sulphur dioxide, until the increase in weight was about forty nine grammes. After leaving the mixture in a well stoppered bottle for five days, the excess of sulphur dioxide was completely removed by passing a long continued current of air through the liquid. A known fraction of the liquid was taken and, after determining its acidity by titration with sodium hydroxide (p. 9), it was treated with a solution of mercuric nitrate. From the weight of the mercuric dibenzenesulphimide obtained, the yield of dibenzenesulphimide was calculated to be 78.6 per cent of the theoretical amount required by the equation :—

$$(C_6H_5SO_2)_2NOH + SO_2 + H_2O = (C_6H_5SO_2)_2NH + H_2SO_4 \ldots\ldots(1).$$

Another known fraction of the solution was neutralised with barium hydroxide and the crystals of barium dibenzenesulphimide were, as much and as pure as possible, obtained by repeated evaporation and crystallisation. From the weight of the barium dibenzenesulphimide thus obtained, the yield of the imide was calculated to be 73.8 per cent of the theoretical amount. Two more similar experiments, made with sixty and twenty grammes of dibenzenesulphohydroxylamine dissolved in common alcohol and treated with a quantity of sulphur dioxide equal to about five-sixths of the weight of dibenzenesulphohydroxylamine taken, gave 74 and 83 per cent, respectively, of the theoretical amount of dibenzenesulphimide. As the yields of dibenzenesulphimide were in these experiments somewhat below the theoretical, it appeared probable that alcohol entered into the reaction and, in some way, more or less interfered with the formation of the imide. With view to ascertaining if this was really the case, the following experiment was made.

About eight grammes of dibenzenesulphohydroxylamine in the finely powdered state were suspended in about two hundred and seventy cubic centimetres of water and treated with sulphur dioxide, until the increase in weight was about thirteen grammes, and then left in a tightly stoppered bottle, with occasional stirring, until the substance had completely disappeared, which required about five days. The excess of sulphur dioxide was then blown off by a current of air. The whole was neutralised with barium hydroxide and concentrated after filtering off the barium sulphate. By crystallising out as much of the barium dibenzenesulphimide as possible, by repeated concentration and crystallisation, a yield of 71.1 per cent of the theoretical amount was obtained, which is even smaller than the yield in the previous experiments when alcohol was used. The barium sulphate above obtained was purified and weighed, and from its weight the amount of the sulphate sulphur was calculated to be 96.3 per cent of the quantity calculated on the theory, that one molecule of sulphuric acid is formed along with one molecule of the imide.

From this experiment it has become clear, that the low yields of dibenzenesulphimide were not due to the presence of alcohol in the reacting mixture. Experiments were then made, in which an alcoholic solution of dibenzenesulphohydroxylamine was treated with a rapid current of sulphur dioxide, until the solution was nearly saturated with it, and then left closed for forty eight hours in an atmosphere of sulphur dioxide. Contact with the atmospheric air was avoided by replacing it with carbon dioxide before the treatment with sulphur dioxide. The results showed that in this manner, a more nearly theoretical yield of dibenzenesulphimide can be obtained. The actual yields of dibenzenesulphimide, in the form of its barium salt, were 91.9 and 97.7 per cent of the theoretical amount. The yield would, probably, have been the full theoretical quantity, if it had been determined as the less soluble mercury dibenzenesulphimide.

Sulphates formed by the Reaction between Dibenzenesulphohydroxylamine and Sulphur Dioxide :—As was to be expected, a quantity of sulphuric acid is always produced along with dibenzenesulphimide, but when alcohol was used as the medium of the reaction, its quantity was found to be much less than that corresponding to equation (1), given on p. 2, only 31.4 and 32.9 per cent of the theoretical quantity having been found even when no precaution was taken to prevent the oxidation of sulphur dioxide by the air and as little as 20.05 per cent when special arrangements were made to avoid the oxidation of sulphur dioxide. The calculations were based not upon the quantity of the oxime taken, but upon the quantity of the imide actually found. This deficiency of free sulphuric acid was probably, to a large extent, due to the formation of ethylsulphuric acid, for, as already shown, when water alone was used as the medium of the reaction, much larger quantities of sulphuric acid were found to be formed. Moreover, in the experiments, in which alcohol was used as the medium, it was found that heating the liquid with hydrochloric acid to 150°C. after the removal of dibenzenesulphimide as its mercury derivative, produced a further quantity of free sulphuric acid. The total sulphur precipitable by barium chloride was then found to make up 91 per cent of the theoretical quantity required by the equation already given (p. 2), the quantity of the sulphate sulphur being calculated with reference to the quantity of dibenzenesulphimide actually found, and not with reference to that of the oxime taken.

There is thus still a deficiency in the amount of the total sulphates, and this fact shows that dibenzenesulphimide must be partly formed in some other way, unaccompanied by the formation of sulphuric acid. Examination of an alcoholic solution of dibenzenesulphohydroxylamine has shown that hydrolysis of this compound occurs in the solution and that this constitutes a source of dibenzenesulphimide.

Evidences of the Formation of Ethylsulphuric Acid:—As was shown in the preceding section, the principal product of the action of sulphur dioxide upon an alcoholic solution of dibenzenesulphohydroxylamine is dibenzenesulphimide. This is produced almost quantitatively, when sulphur dioxide is used in great excess and contact of the solution with the atmosphere is avoided (p. 4). By special experiments made for the purpose (p. 12), it was also ascertained that about a molecule of sulphur dioxide becomes fixed during the reduction of a molecule of dibenzenesulphohydroxylamine. Further, the total quantity of free sulphuric acid after hydrolysis at 150°C. corresponds to more than ninety per cent of the quantity required by the equation already given (p. 2). It becomes, therefore, almost certain that sulphur dioxide is oxidised to sulphur trioxide and that this acts on alcohol, producing ethylsulphuric acid. This view has been confirmed by the fact that the alcoholic solution, in which dibenzenesulphohydroxylamine has been treated with sulphur dioxide, after evaporation to dryness, yields alcohol on hydrolysis at 150°C.

The experiment was carried out with about one-tenth of the total quantity of the alcoholic solution resulting from the first experiment (p. 2), in which the quantity of dibenzenesulphimide formed was determined. For this purpose, the alcoholic solution, after removing the excess of sulphur dioxide, was neutralised with potassium hydroxide, evaporated to dryness and, finally, dried in vacuo over concentrated sulphuric acid in order to remove every trace of alcohol. The residue was heated with dilute hydrochloric acid in a sealed tube at 150°C. for several hours. The hydrolysed product was neutralised with potassium hydroxide and distilled, when a liquid was obtained, which had all the properties of dilute alcohol. The amount of alcohol thus produced was estimated approximately by comparing the quantity of iodoform obtained from it with the quantities obtained from equal volumes of pure aqueous alcohol of varying strengths. The result showed that the distillate contained slightly more than one per cent of alcohol, but decidedly less than two per cent.

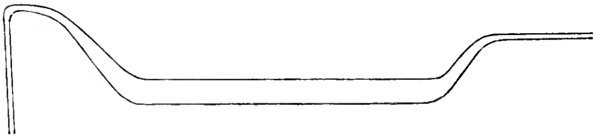
The above determination shows that the amount of alcohol of the same strength to be produced from ethylsulphuric acid, corresponding to the total quantity of mercury dibenzenesulphimide found, viz. 60.14 grammes, is 422 c.c., or, say, 4.4 grammes of real alcohol. If the formation of one molecule of dibenzenesulphimide had been accompanied by that of one molecule of ethylsulphuric acid, then 60.14 grammes of mercury dibenzenesulphimide would correspond to 4.866 grammes of sulphur in the form of ethylsulphuric acid; but in this experiment, 1.36 grammes of sulphur was found in a form directly precipitable by barium chloride. The difference, namely 3.506 grammes, represents the sulphur of ethysulphuric acid, corresponding to 5.036 grammes of alcohol, which quantity is in sufficient agreement with that above found. If, in the same experiment, the portion of sulphur, which became precipitable by barium chloride after hydrolysis at 150°C., namely 3.069 grammes experimentally found, was taken as that of ethylsulphuric acid, then 4.408 grammes of alcohol ought to have been formed, a result, which agrees still better with the quantity found. It was, however, not possible to isolate the ethylsulphuric acid in a form fit for analysis. Attempts to obtain the salts of ethylsulphuric acid in the pure state were only partially successful. The barium, lead, copper, and silver salts were prepared and found to have the properties of the corresponding ethylsulphates, but they could not be obtained pure enough for analysis. Only the potassium salt could be obtained pure. It formed non-deliquescent thin prismatic crystals, quite free from nitrogen, and containing 19.34 per cent of sulphur, while the calculation requires 19.52 per cent. Its solubility in water agreed sufficiently well with that of potassium ethylsulphate. One part of water at 18½°C. dissolved 1.14 parts of the salt, while one part of water at 17°C. dissolves 1.25 parts of potassium ethylsulphate (SCHABUS, quoted in BEILSTEIN's Handbuch from Jahresber., 1854, 560; MARIGNAC, quoted in the same work from Jahresber., 1855, 608). The salt, after hydrolysis at 150°C., gave an abundant iodoform reaction. The free acid was prepared from slightly impure barium salt, and found to be a syrupy liquid, which refused to crystallise in the desiccator.

Benzenesulphonic Acid among the Products of the Action of Sulphur Dioxide upon Dibenzenesulphohydroxylamine.—As may be inferred from what has been stated above, only a portion of the sulphur in the products of the action of sulphur dioxide upon dibenzenesulphohydroxylamine can be converted by hydrolysis into sulphuric acid, the other portion refusing to undergo hydrolysis and being converted into a sulphate only by fusion with potassium hydroxide and nitre. That this is due to the presence of benzenesulphonic acid was proved by isolating the acid in the form of its barium salt. For this purpose, forty grammes of dibenzenesulphohydroxylamine were dissolved in two hundred and thirty cubic centimetres of about ninety per cent alcohol and treated with a current of sulphur dioxide, without any special precaution being taken to avoid contact with air, until the increase in weight was about thirty two grammes. After the mixture had stood for several days in a stoppered bottle, the excess of sulphur dioxide was expelled by a current of air. The liquid was then neutralised with barium hydroxide and evaporated on a water bath. After the removal, by crystallisation, of the sparingly soluble barium dibenzenesulphimide a quantity of a barium salt was obtained in the crystalline state. This was purified by recrystallisation, and was then found to be quite free from nitrogen. On analysis it gave 29.07 per cent of barium and 14.34 per cent of sulphur. The calculation for barium benzenesulphonate requires 30.43 per cent of barium and 14.20 per cent of sulphur. That the substance was barium benzenesulphonate was further confirmed by changing it into the sulphochloride, and this into the amide, which was found to melt at 150°C.

Acidity developed by the Action of Sulphur Dioxide upon Dibenzenesulphohydroxylamine :—This was determined in a portion of the liquid obtained by treating sixty and a half grammes of dibenzenesulphohydroxylamine in three hundred and fifty cubic centimetres of ninety one per cent alcohol with a current of sulphur dioxide (Exp. 1, p. 2). After removing the excess of sulphur dioxide, the alcoholic solution was titrated with sodium hydroxide, using phenolphthalein as the indicator, and it was found that, when calculated for the whole quantity, 396 c.c. of normal sodium hydroxide would be required, while, when calculated according to the equation on p. 2, the quantity would be 193.2 c.c.

The bulk of the alcoholic liquid was then neutralised with barium hydroxide, and, after somewhat concentrating it, the solution was filtered from the traces of barium sulphate and carbonate. Barium was determined in a portion of the filtrate, and its quantity was found to be 161.9 per cent of that calculated for barium dibenzenesulphimide according to equation (1). These experiments show that, by the action of sulphur dioxide upon dibenzenesulphohydroxylamine, some other reaction takes place, besides that indicated by the above equation, and that the products of this reaction must be of a more acidic nature than the imide.

Examination of the Gaseous Product of the Reaction :—2.21 grammes of dibenzenesulphohydroxylamine were dissolved in 7 c.c. of ninety per cent alcohol in a wide horizontal glass tube, with the ends drawn out and bent, first, upwards and, then, horizontally, in the one case, downwards, in the other, as shown in the figure.



After replacing all the air in the tube by means of a current of carbon dioxide, passing in at one end and out at the other, which was kept under mercury, sulphur dioxide was passed in, until it replaced the carbon dioxide and saturated the solution in the tube. The tube was then sealed up near the two ends and the whole was left for two days. It was then connected with the Sprengel pump at the end, which had the downward bend, by means of a thick india-rubber tubing, and the pump was set in action. As soon as the air was exhausted the sealed end of the tube was broken under the india-rubber tubing, and the gas was pumped into a gas measuring tube, which contained a few cubic centimetres of very strong potassium hydroxide. The pump was worked slowly, in order that all the sulphur dioxide might be absorbed by the potassium hydroxide. The residual gas was measured, under a reduced pressure, over a column of mercury plus a column of potassium hydroxide.

From the specific gravity of the original potassium hydroxide solution, the height of the latter was reduced to that of mercury, although the specific gravity must have been considerably altered by the absorption of sulphur dioxide and also the fact that even some quantity of a solid salt had separated out. The gas, which must have been practically dry, measured only 4.98 c.c. at 17°C. under a pressure equal to 565 mm. of mercury. This quantity of the gas would weigh 0.00827 gramme, if it consisted of pure nitrous oxide, and 0.00526 gramme, if it consisted of pure nitrogen. When tested with a glowing wooden splinter, it did not rekindle it into a flame, but the piece of wood glowed decidedly brighter than in the air. It was probably pure nitrous oxide, but, while being tested, it must have been mixed with a comparatively large quantity of the air, so that it became too dilute to rekindle the glowing wood. Moreover, a small fraction of the nitrous oxide must have been dissolved in the potash, especially as a small quantity of alcohol had been carried over into it by the action of the pump. The number above obtained, which can, in any case, be only approximately correct, must, therefore, be regarded as rather too low.

In order to determine the relation of the quantity of the gas to that of the other products of the reaction, the residue left in the tube was diluted with water and treated with an excess of barium nitrate. The barium sulphate formed weighed 0.3055 gramme, equal to 0.04195 gramme of sulphur. Mercuric nitrate solution was then added to the filtrate from the barium sulphate, and the mercury dibenzenesulphimide thus formed was washed and weighed. It was found to weigh 2.5696 grammes, equal to 1.9276 grammes of the free imide.

The filtrate from mercury dibenzenesulphimide was neutralised and, with view to destroying all the nitrates, was treated with an excess of sodium amalgam for several days and, after removing and washing the excess of the amalgam, the liquid and the washings were heated with hydrochloric acid at 150°C., in a sealed tube. The sulphuric acid thus formed was determined as barium sulphate. It weighed 1.0733 grammes, equal to 0.1474 gramme of sulphur, the total sulphate sulphur, therefore, amounting to 0.1893 gramme. The sulphur in the form of sulphonic acid, which resisted hydrolysis at 150°C., was not determined, owing to loss during the analysis. These results will be discussed later (p. 15).

The Quantity of Sulphur Dioxide which enters into Reaction with Dibenzenesulphohydroxylamine :—This was only roughly estimated in two experiments and in the following manner. Dibenzenesulphohydroxylamine was dissolved in about six times its weight of approximatly ninety per cent alcohol and treated with sulphur dioxide, until the increase in weight was about four-fifths of the weight of the oxime taken. After leaving the whole in a well stoppered bottle for two days, the excess of sulphur dioxide was blown off by a current of air passed through the liquid. In the one experiment, the total sulphur in the solution was determined as sulphate by evaporating off the alcohol, oxidising the residue by means of strong nitric acid and fusing the mass with potassium hydroxide and nitre. In the other experiment this was done by neutralising the solution with potassium hydroxide, evaporating the whole to complete dryness, reducing the residue to fine powder, mixing it with about eight times its weight of dry sodium carbonate in a platinum crucible, and roasting it very gradually with a layer of dry sodium carbonate placed over the mixture. In both cases, all the sulphur was converted into the alkali sulphate. This was precipitated as barium sulphate and weighed. The results were practically identical. By subtracting the sulphur of dibenzenesulphohydroxylamine from the total sulphur thus found the quantity of sulphur dioxide fixed by the reaction was estimated. The result showed that, even when the sulphuric acid due to the aerial oxidation of sulphur dioxide was included, its quantity was decidedly less than corresponds to one molecule of it for every molecule of the dibenzenesulphohydroxylamine reduced, it being only 82.6 per cent of the calculated quantity.

There is, apparently, no other substance formed by the reaction between dibenzenesulphohydroxylamine and sulphur dioxide, besides those already mentioned. Neither benzenesulphinic acid nor benzenesulphamide was detected among the products of the reaction. Amidosulphonic acid was also tested for, by adding mercuric nitrate to the solution after dibenzenesulphimide had been removed by means of mercurous nitrate, but it was found to be absent. No ammonia or hyposulphate was detected.

From what has been stated, it is clear that, by the action of sulphur dioxide, the major portion of dibenzenesulphohydroxylamine undergoes reduction to dibenzenesulphimide, the sulphur dioxide being, at the same time, oxidised to sulphuric acid, a portion of which goes to act upon the alcohol to form ethylsulphuric acid. It is also clear that another portion of dibenzenesulphohydroxylamine is converted into an acid substance, which contains sulphur, but which is not sulphuric acid. That the formation of this acid substance is also attended with the production of dibenzenesulphimide is evident from the fact that the yield of dibenzenesulphimide is greater than that corresponding to the total sulphates that are formed (p. 5). We know further that benzenesulphonic acid is formed in a considerable quantity (p. 8) and, probably, also nitrous oxide (p. 10). It appears likely, therefore, that the following change also occurs, besides the main reaction :

$$4HON(SO_2C_6H_5)_2 + H_2O = 2HN(C_6H_5SO_2)_2 + 4C_6H_5SO_3H + N_2O\ldots\ldots(2).$$

That this change, which is independent of the action of sulphur dioxide, actually takes place in aqueous alcoholic solutions of dibenzenesulphohydroxylamine was ascertained from the study of the spontaneous decomposition of the substance in alcohol.

Spontaneous Decomposition of Dibenzenesulphohydroxylamine in dilute Alcohol.

About four grammes of dibenzenesulphohydroxylamine (m.p. 132°C.) were dissolved in ninety per cent alcohol and kept in a stoppered bottle for about a month, when the solution became brownish yellow in colour and deposited a very small quantity of a crystalline product, which was insoluble in sodium hydroxide. After purification, it melted constantly at 98½°C. On analysis it was found to contain 20.72 per cent of nitrogen. The substance was, therefore, tribenzenesulphohydroxylamine, which melts at 98½°C. and contains 21.22 per cent of nitrogen. The mother liquor, from which these crystals have separated, when neutralised with baryta and concentrated, yielded a quantity of thick microscopic prisms almost insoluble in absolute alcohol. Analysis of the purified substance gave 18.85 per cent of barium, 17.21 per cent of sulphur, and 3.80 per cent of nitrogen, showing the substance to be anhydrous barium dibenzenesulphimide.

The mother liquor, from which barium dibenzenesulphimide has separated, yielded, on further concentration, a quantity of crystals, which were found to contain no nitrogen and which agreed in their properties with those of barium benzenesulphonate. On heating at 100–110°C. the substance lost 4.02 per cent in weight. The dehydrated salt, on analysis, gave 30.37 per cent of barium, and 14.68 per cent of sulphur. Anhydrous barium benzenesulphonate contains 30.43 per cent of barium and 14.20 per cent of sulphur. Ordinary crystals of the salt contain one molecule of water, equal to 3.84 per cent. In an aqueous alcoholic solution, therefore, dibenzenesulphohydroxylamine appears to decompose essentially as in equation (2), a small fraction of it decomposing in a different manner, so as to give rise to tribenzenesulphohydroxylamine. But as the quantity of this substance is very small, its production may, for the present, be left out of consideration.

All the facts combined make it, therefore, highly probable that the reduction of dibenzenesulphohydroxylamine takes place according to equations (1) and (2). Further, the relation between the quantities of the gaseous and other products of the reaction obtained in the experiment, described on p. 11, agrees sufficiently well with the theory that, out of a hundred molecules of dibenzenesulphohydroxylamine, eighty four molecules decompose according to equation (1), and sixteen molecules decompose according to equation (2).

In the following table the weights of the dibenzenesulphimides and of the sulphurs of the total sulphates, obtainable from 2.21 grammes of dibenzenesulphohydroxylamine (p. 9), are given, the numbers under I and II having been calculated on the supposition that 84 and 86 per cent, respectively, of the substance decomposed according to equation (1), the rest decomposing in accordance with equation (2).

	I	II	Found
Dibenzenesulphimide.	1.9294	1.9504	1.9276
Total sulphate sulphur.	0.1900	0.1945	0.1893
Gas calc. as nitrous oxide.	0.0124	0.0109	0.0083

It will be seen that the calculation on the assumption, that 86 per cent of the substance decomposed according to equation (1), gives larger figures for dibenzenesulphimide and total sulphate sulphur than those actually found. The difference is a little more than can be explained by errors of analysis. The quantity of nitrous oxide found is considerably below that calculated under I, but, as has already been stated, the quantity actually collected was probably below the true amount.

Reduction of Dibenzenesulphohydroxylamine by Sodium Amalgam.

While the reduction of dibenzenesulphohydroxylamine by sulphur dioxide produces a large quantity of dibenzenesulphimide, reduction by sodium amalgam produces a quantity of benzenesulphinic acid, with liberation of ammonia. Benzenesulphinic acid was identified by preparing the free acid from the sodium salt and determining its melting point, which was found to be 87°C., and its production was further confirmed by preparing the insoluble zinc salt. Dibenzenesulphimide can be obtained by using limited quantities of sodium amalgam, but only in a very small quantity. The poor yield of dibenzenesulphimide is not a matter of surprise, as the sulphimide itself, when treated with sodium amalgam, is converted into ammonia and benzenesulphinate. Again tribenzenesulphohydroxylamine, when treated with sodium amalgam, decomposes into benzenesulphinate and ammonia, while the hydroxylamine-trisulphonates, when similarly treated, produce imidosulphonates and sulphates. These facts show that aromatic sulphohydroxylamines are much more readily attacked by reducing agents than are inorganic hydroxylamine-sulphonic acids. A small quantity of dibenzenesulphimide can be obtained from tribenzenesulphohydroxylamine by the action of sodium, but only by the use of a limited quantity of this reagent. No benzenesulphamide could be detected. Sulphur dioxide acts neither on hydroxylaminetrisulphonates nor on tribenzenesulphohydroxylamine in an alcoholic solution.

Respecting the Reduction by Sulphur Dioxide of the Oximido-Nitrogen not united to Sulphur.

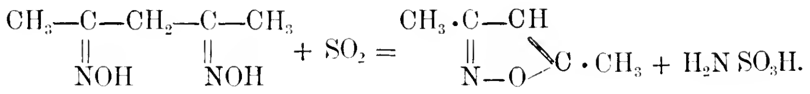
Nitrogen shows a greater tendency to unite with the sulphonic radical than with carbon. An oximido-nitrogen atom, united with carbon alone, becomes sulphonated when treated with sulphur dioxide and is, at the same time, detached from the carbon (Krafft and Bourgeois: Ber., 1892, **25**, 472). But this tendency of nitrogen to unite with the sulphonic radical becomes considerably weakened, when the nitrogen is already united with other atoms of sulphur. When hydroxylaminedisulphonates are treated with an alkali bisulphite and sulphur dioxide they are converted into the trisulphonates (this Journ., 1901, **17**, Art. 2, 2). But, on account of the presence of two sulphonic radicals already in union with the same nitrogen atom, the third sulphonic radical is very readily removable by hydrolysis. In the case of the reduction of dibenzenesulphohydroxylamine, the sulphonate $(C_6H_5SO_2)_2N.SO_3H$ is, probably, formed as the intermediate product. But, owing, doubtless, to the presence of two benzenesulphonic radicals already united with the nitrogen atom, the sulphonic group is so readily separated from the nitrogen by hydrolysis, that the existence of the intermediate compound can not be proved.

When a compound contains two oximido-radicals united with two separate carbon atoms in the molecule, reduction with sulphur dioxide produces a remarkable result. Only one of the nitrogen atoms is separated in the form of amidosulphonic acid: the other nitrogen atom, from some unknown cause, resists the action of sulphur dioxide and remains united with the carbon. Acetylacetonedioxime is a good example of this.

Twenty grammes of acetylacetonedioxime were dissolved in two hundred and fifty cubic centimetres of hot water and treated with an excess of sulphur dioxide. After leaving the mixture to stand over night in a well-stoppered bottle the excess of sulphur dioxide was neutralised with sodium hydroxide. On now distilling the mixture by means of a current of steam, an oily liquid passed over. On saturating the aqueous distillate with potassium carbonate, more of this oily substance was separated. The total quantity of it weighed 11.3 grammes. It boiled constantly at 143½°C., and had the peculiar smell and all other properties of 3:5-dimethylisoxazol. On analysis, the substance yielded the following result :—

	Found	Calculated for C_5H_7ON
Carbon	61.66	61.86
Hydrogen	7.49	7.22
Nitrogen	13.77	14.45

The reaction must have, therefore, occurred according to the equation :—



The quantity of the dimethylisoxazol actually obtained agrees nearly with that calculated according to the above equation, being 94.4 per cent of the theory.

After distilling off the isoxazol, the solution was treated with an excess of dilute nitric acid and the sulphurous acid thus liberated was completely removed by passing a current of air through the liquid. On adding a solution of mercuric nitrate to it, an abundant precipitate of mercuric amidosulphonate was thrown down from which the free acid was obtained in the crystalline state by decomposing it with hydrogen sulphide and evaporating the filtered solution in a vacuum desiccator at ordinary temperatures.

When the reaction between the dioxime and sulphur dioxide is carried out in presence of absolute alcohol, the greater part of amidosulphonic acid separates out in the form of crystals, having the melting point of 205°C. The quantity of this acid estimated from the amount of ammonia, formed on hydrolysis with hydrochloric acid at 150°C., after the removal of the isoxazol, showed that the reaction took place quantitatively.

Acetonylacetonedioxime and Sulphur Dioxide:—Acetonylacetonedioxime was dissolved in about five times its weight of water and treated with a current of sulphur dioxide. So much heat was evolved that it required external cooling with water. On leaving the mixture over night, and then expelling the excess of sulphur dioxide and evaporating the solution in a vacuum desiccator, an oily product was left mixed with crystals of amidosulphonic acid. On now treating the mixture with alcohol, the oily substance dissolved away, leaving behind the amidosulphonic acid. The quantity of this acid thus obtained was a little more than half of that calculated for one molecule of the acid from one molecule of the dioxime used.

The oily substance was soluble in water and in alcohol, but insoluble in ether. It could be neither brought into the crystalline state, nor obtained as compounds with other substances sufficiently pure for analysis. Attempts to reduce it to the corresponding amine by stannous chloride and hydrochloric acid gave no satisfactory result. An aqueous solution of the substance did not reduce Fehling's solution in the cold, but did so strongly, when heated. After boiling with hydrochloric acid, however, the solution reduced it strongly even in the cold. Acetonylacetonedioxime reduces Fehling's solution freely in the cold, without previous heating with hydrochloric acid. These facts show that, in the oily product one of the nitrogen atoms still remained in union with carbon in a form capable of yielding hydroxylamine on hydrolysis. The non-removal of one of the nitrogen atoms by the action of sulphur dioxide is therefore, not due to its tendency of forming a heterocyolic ring like isoxazol.

These experiments are very imperfect, but they sufficiently show the remarkable difference in the behaviour of two oximido-groups towards sulphur dioxide. The author intends to make a fuller investigation of this reaction on some future occasion.

Dibenzenesulphohydroxylamine $(C_6H_5SO_2)_2NOH$.

This substance was prepared by acidifying the mixture of two molecules of sodium benzenesulphinate and one molecule of sodium nitrite with dilute sulphuric acid, and purifying the crystals that separated out by repeated crystallisations from alcohol (W. Königs: Ber., 1878, **11**, 615). When crystallised from alcohol it forms thick tabular crystals, containing one molecule of alcohol of crystallisation. 100 c.c. of 78.2 per cent alcohol dissolved only about 7.1 grammes of these crystals at 18°C. The compound loses all its alcohol when powdered and left over sulphuric acid in a vacuum desiccator.

		Calc. for	
	Found	$(C_6H_5SO_2)_2NOH,C_2H_6O$	$(C_6H_5SO_2)_2NOH$
Loss in weight	12.7	12.81	—
Nitrogen.	3.89	3.90	4.47

The anhydrous substance, dried in a vacuum desiccator, melted at 132°C. and, on analysis, gave the following results:—

	Found	Calc.
Sulphur	20.72	20.47
Nitrogen	4.36	4.47

Königs gives the melting point of the substance as 109°C. (loc. cit.). His preparation was obtained by crystallisation from alcohol and, therefore, probably retained some alcohol of crystallisation, but he never seems to have recognised this possibility. More recently, Angeli, Angelico and Scurti gave the melting point as 126°C. (Chem. Central-Blatt, 1902, II, 692). The author can not find, at present, any adequate explanation of the discrepancy.

When an alcoholic solution of dibenzenesulphohydroxylamine is poured into an excess of water the substance is precipitated in the form of microscopic crystals, containing two molecules of water of crystallisation.

	Found	Calc. for $(C_6H_5SO_2)_2NOH,2H_2O$
Sulphur	18.27	18.36

Dibenzenesulphimide $(C_6H_5SO_2)_2NH$.

When crystallised from water this substance forms thick prismatic crystals, consisting largely of twins. It contains water of crystallisation and is slightly efflorescent. The quantity of water was ascertained from loss in weight on heating at 105–110°C., the crystals having been previously powdered and air-dried. Two preparations were analysed and they yielded somewhat discordant results. In the one case, the loss was found to amount to 8.97 per cent, while in the other it was found to be 7.85 per cent. The substance after dehydration melted, in both cases, at 157°C. The compound probably crystallises with one and a half molecules of water, corresponding to 8.33 per cent. Analysis of the substance dried at 130°C. gave the following results:—

	Found	Calculated
Carbon	49.22	48.44
Hydrogen	4.34	3.73
Sulphur	21.81	21.57
Nitrogen	4.73	4.72

Dibenzenesulphimide is conveniently purified in the form of its barium salt, and the free imide obtained by decomposing the latter with the calculated quantity of sulphuric acid. It dissolves approximately in fourteen times its weight of water. Hydrochloric or sulphuric acid precipitates it from its aqueous solution.

Determination of the Molecular Weight:—The following were obtained for the molecular weight of dibenzenesulphimide by the ebullioscopic method, taking acetone as the solvent and using the apparatus devised by Prof. K. IKEDA (Jour. Tokyo Chem. Soc., 1899, **20**, 600). 1.0382 grammes of the substance dried at 140°–150°C. were taken.

Volume of the solution, 22 c.c.; elevation of the boiling point, 0.31°C.; hence the molecular weight, 348.

Volume of the solution, 26 c.c.; elevation of the boiling point, 0.27°C.; hence the molecular weight, 338.

Volume of the solution, 31 c.c.; elevation of the boiling point, 0.25°C.; hence the molecular weight, 306.

	Found	Calculated
Molecular weight	330.7 (mean)	297.2

Barium dibenzenesulphimide, $\{(C_6H_5SO_2)_2N\}_2Ba+2H_2O$, crystallises from water in fine needles, freely soluble in water when hot, but less so when cold, one part of the salt dissolving in about twenty seven parts of water at 15.6°C. Two separate preparations were analysed with the following results:—

	Found		Calc. for $C_{24}H_{20}S_4O_8N_2Ba+2H_2O$
Barium	18.34	17.95	17.95
Sulphur	17.04	16.95	16.75
Nitrogen	—	3.70	3.67
Water (loss in weight at 140°C.)	—	2.19	2.96

This compound sometimes forms microscopic prisms, containing no water of crystallisation. Two such preparations gave the following results on analysis:—

	Found (1)	Found (2)	Calculated
Barium	18.85	18.29	18.83
Sulphur	17.21	17.75	17.57
Nitrogen	3.79	3.89	3.85

Preparation (1) was obtained by the spontaneous decomposition of dibenzenesulphohydroxylamine in an aqueous alcoholic solution. Preparation (2) was obtained in one of the experiments, in which dibenzenesulphohydroxylamine was reduced by sulphur dioxide in presence of aqueous alcohol and the resulting liquid was concentrated, after neutralisation with barium hydroxide. That these preparations differed from the previous ones only in containing no water of crystallisation was ascertained from the fact that the melting point of the free imide prepared from both was found to be identical, namely 157°C.

Mercury dibenzenesulphimide, $\{(C_6H_5SO_2)_2N\}_2Hg$, is obtained by mixing a solution of the imide or any of its soluble salts with one of mercuric nitrate. It forms almost insoluble microscopic scales, which dry up to a chalk-like mass, difficult to wet, and which, when once dried, can hardly be completely decomposed by hydrogen sulphide solution. Its solubility is so small that washings of it are scarcely coloured by hydrogen sulphide.

	Found	Calculated
Mercury	26.38	25.26
Sulphur	15.90	16.18

Mercurous dibenzenesulphimide, $(C_6H_5SO_2)_2NHg$, is obtained when mercurous nitrate solution is added to a solution of the imide or its salt. It forms fine microscopic needles nearly as insoluble as the mercuric compound.

Silver dibenzenesulphimide is obtained as fine silky needles by adding silver nitrate to a solution of sodium dibenzenesulphimide. It is sparingly soluble in water one part of it dissolving in about 170 parts of water at 23°C.

Potassium dibenzenesulphimide $(C_6H_5SO_2)_2NK$, crystallises in thin pearly scales, also sparingly soluble in water. One hundred parts of water at 28°C. dissolves only about 0.76 parts of this salt. Its solution does not give any precipitate with silver nitrate.

	Found	Calculated.
Potassium	11.71	11.67
Sulphur	19.09	19.12
Nitrogen	4.20	4.18

Sodium dibenzenesulphimide forms bundles of silky needles which are easily soluble in water, but non-deliquescent.

Ammonium dibenzenesulphimide forms prisms and sometimes thick tables, which are easily soluble in water and melt at about 240°C.

	Found	Calculated
Nitrogen	8.93	8.93

Diorthtoluenesulphohydroxylamine, $(CH_3C_6H_4SO_2)_2NOH$.

This substance has as yet received no mention in the literature although the corresponding para-compound has already been described (E. v. Meyer: J. prak. Chem., 1901, **63**, 173). With the object of obtaining it orthotoluenesulphinic acid was first prepared by diazotising orthotoluidine and, after a large excess of sulphur dioxide has been added, treating the mixture with finely divided copper (Gattermann: Ber., 1899, **32**, 1136). The sulphinic acid thus produced was then converted into the sodium salt, mixed with half its equivalent of sodium nitrite and acidified, when the diorthotoluenesulphohydroxylamine separated out in the crystalline state. 8 grammes of orthotoluidine yielded 9⅓ grammes of diorthotoluenesulphohydroxylamine. It was purified by dissolving it in sodium hydroxide, reprecipitating by hydrochloric acid, and then twice recrystallising it from alcohol. Finally, an alcoholic solution of the purified substance was mixed with an excess of water, when it separated out in the form of small prismatic crystals, free from alcohol but containing one molecule of water, and melting at 106—107°C.

	Found		Calc. for $C_{14}H_{15}O_5NS_2,H_2O$
Sulphur	17.87	17.84	17.85
Nitrogen	—	3.81	3.91
Water	—	—	5.01

Triorthotoluenesulphohydroxylamine, $(C_7H_7SO_2)_3NO$.

This substance was obtained by treating diorthotoluenesulphohydroxylamine, in alcoholic solution, with an excess of nitrous fumes, evolved from arseneous oxide and nitric acid of sp. gr. 1.32. Six grammes of diorthotoluenesulphohydroxylamine yielded about 2½ grammes of the compound. It forms small, almost microscopic needles, which melt at 129½°C., and is almost insoluble in cold alcohol, being only sparingly soluble even in boiling alcohol.

	Found	Calc. for $C_{21}H_{21}S_3O_7N$
Sulphur	19.98	19.41
Nitrogen	3.07	2.83

Diorthotoluenesulphimide, $(C_7H_7SO_2)_2NH$.

This substance was prepared in exactly the same way as the corresponding dibenzenesulphimide, by treating an alcoholic solution of diorthotoluenesulphohydroxylamine with sulphur dioxide. To avoid the complications observed in the preparation of dibenzenesulphimide when the sulphur dioxide was not in a sufficiently large excess, this was passed nearly to saturation, and the mixture left for two hours, before the excess of sulphur dioxide was removed by a current of air. On evaporating the solution on a water-bath, diorthotoluenesulphimide separated out as a crystalline crust. This was recrystallised from hot water, when it separated out in thick tables and short prisms. The preparation, when powdered and dried in a sulphuric acid desiccator, melted completely at 184°C. with previous sintering at about 178°C. The compound is only very sparingly soluble in water, and is practically completely thrown out of the solution by the addition of hydrochloric or sulphuric acid. Analysis of the air-dried crystals gave the following results:—

	Found	Calculated for	
		$C_{14}H_{15}O_4NS_2,H_2O$	$2C_{14}H_{15}O_4NS_2,3H_2O$
Sulphur	18.47	18.68	18.20
Nitrogen	4.27	4.08	3.98
Water (loss of weight at 120°)	6.50	5.25	7.67

Determination of the Molecular Weight:—The following numbers were obtained for the molecular weight of diorthotoluenesulphimide by the ebullioscopic method, using acetone as the solvent.

The weight of the anhydrous substance taken, 1.4988 grammes; volume of the solution, 24 c.c.; elevation of the boiling point, 0.39°C.; hence the molecular weight, 366.

Volume of the solution, 25.5 c.c.; elevation of the boiling point, 0.37°C.; hence the molecular weight, 356.

Volume of the solution, 29 c.c.; elevation of the boiling point, 0.35°C.; hence the molecular weight, 338.

	Found	Calculated
Molecular weight	353.3 (mean)	325.3

Barium diorthotoluenesulphimide forms minute needle-shaped crystals, easily soluble in water.

Analysis of the air dried salt gave the following results:—

	Found	Calc. for $C_{14}H_{14}O_4NS_2Ba\frac{1}{2},H_2O$
Barium	16.85	16.62
Sulphur	15.00	14.95
Water (loss of weight at 165°C.)	7.85	8.46

The salt continues to lose water very slowly even at 150°C. It is, therefore, necessary to heat it for a long time at 160–170°C., before the weight becomes constant.

The production of diorthotoluenesulphimide from the corresponding hydroxylamine was accompanied by the formation of free sulphuric acid, as was to be expected. But, just as in the case of dibenzenesulphimide, the quantity of this acid, which was formed, was found to be only about two-thirds of the quantity calculated on the supposition that one molecule of sulphuric acid is formed along with one molecule of the imide. This is, no doubt, likewise due to the formation of ethylsulphuric acid. The possible formation of toluenesulphonic acid by the hydrolysis of the diorthotoluenesulphohydroxylamine in presence of aqueous alcohol was prevented, as far as possible, by having an excess of sulphur dioxide.

Diparatoluenesulphimide, $(C_7H_7SO_2)_2NH$.

Paratoluenesulphinic acid was first prepared by GATTERMANN's method (loc. cit.). Ten grammes of paratoluidine gave eleven grammes of the sulphinic acid, equal to seventy six per cent of the theoretical yield. This was converted into the sodium salt, dissolved in water and mixed with the calculated quantity of sodium nitrite. On acidifying the mixture with dilute sulphuric acid, diparatoluenesulphohydroxylamine separated out in the crystalline state. Seven grammes of the sulphinic acid yielded seven grammes of diparatoluenesulphohydroxylamine, corresponding to 92 per cent of the theoretical yield.

Seven grammes of the crude diparatoluenesulphohydroxylamine were suspended in about a hundred cubic centimetres of alcohol and treated with a current of sulphur dioxide, keeping the mixture cool by means of water. The whole substance soon went into solution, but the current of sulphur dioxide was continued, until the solution was nearly saturated with it. The whole was then left in a well-stoppered bottle over night. On expelling the sulphur dioxide and evaporating the solution, about five grammes of diparatoluenesulphimide was obtained in the crystalline state and this was purified by repeated crystallisation from hot water. It melted at 168–170°C. Analysis of the substance yielded the following results:—

	Found		Calc. for $C_{14}H_{15}O_4NS_2$
Sulphur	19.47	19.40	19.71
Nitrogen	4.40	4.43	4.31

The molecular weight of this substance was determined by the ebullioscopic method, using ether as the solvent.

Substance taken, 0.3752 grammes; volume of the solution 25.5 c.c.; elevation of the boiling point, 0.15°C.; hence the molecular weight, 301.

Volume of the solution, 26.0 c.c.; elevation of the boiling point, 0.13 c.; hence the molecular weight, 334.

Volume of the solution, 26.5 c.c.; elevation of the boiling point 0.15 c.; hence the molecular weight, 284.

	Found	Calculated
Molecular weight	306.6 (mean)	325.3

The method of preparing sulphimides described in this paper is evidently applicable to all the aromatic sulphohydroxylamines and, probably, also to the aliphatic compounds. The results obtained with benzenedisulphonic acids by Mr. T. SUZUKI will be recorded in Article 14 of this volume. The work is being continued and extended to the aliphatic series by Mr. NAGAOKA.

In conclusion, I wish to thank Mr. NAGAOKA for the help he has given me in the preparation and examination of diparatoluenesulphimide.

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The Oximes and Imides of Benzenedisulphonic Acids.

By

Tsuneo Suzuki, *Rigakushi.*

I. m-Benzenedisulphoxime.

By the action of nitrous acid upon m-benzenedisulphinic acid AUTENRIETH and HENNINGS (Ber., 35, 1399; 1902) obtained the corresponding oxime, to which they gave a cyclic constitution. In order to see whether this view of its constitution could be confirmed and, at the same time, to obtain further knowledge of the oxime, the following experiments were performed.

The disulphinic acid was prepared, according to C. PAULY's method (Ber., 9, 1595; 1876), by reducing m-benzenedisulphochloride with an excess of zinc dust in the presence of water at a slightly elevated temperature. After the reaction had taken place, a solution of sodium carbonate was added to the resulting mixture of zinc m-benzenedisulphinate, zinc oxychloride, unchanged zinc, and water, so as to change the zinc salts into the more soluble sodium salts. The filtered solution was concentrated on a water-bath, mixed with strong hydrochloric acid, and after removing the precipitated sodium chloride, if any, the strongly acid liquor was shaken with ether. The free acid then separated as a viscous liquid between the aqueous and the etherial layers.

The following procedure was also adopted and found to answer the purpose equally well. To the resulting mixture of zinc salts and unchanged zinc a slight excess of potassium carbonate was added, and the solution of the potassium salts so obtained was slowly evaporated in vacuo over sulphuric acid. Prismatic crystals of potassium m-benzenedisulphinate separated along with the crystals of potassium chloride. The latter often formed clusters of octahedra and could be easily mechanically separated from the prismatic crystals of the m-benzenedisulphinate. The yield is very small, as is also the case with the method above described, owing to the great solubility in water of both the free acid and the potassium salt.

To a mixed solution of an alkaline nitrite and m-benzenedisulphinate, dilute sulphuric or hydrochloric acid was added drop by drop with constant stirring, care being taken not to let the mixture become warm. A white voluminous precipitate of m-benzenedisulphoxime, consisting of fine short needles, was thrown down. This was washed with water and recrystallised from acetone or alcohol.

This substance is tolerably soluble in acetone or alcohol, slightly so in ether or acetic ether, insoluble in benzene, chloroform, carbon bisulphide and water; but the last solvent takes up a small quantity of it at higher temperatures and separates it as long needles on cooling. Crystallised from acetone the oxime forms hard colourless prisms, whilst from alcohol it crystallises in plates; both crystals contain the solvents which are partly given off on exposure to the air and completely driven away on heating at 100°. When boiled with alcohol for many hours the oxime is changed into a non-crystalline viscous substance. An aqueous solution of caustic soda or potash dissolves the oxime, which can be reprecipitated by an acid. When the crystals of the oxime are heated in a capillary tube they begin to darken at 180°, become almost black at 210°, and decompose suddenly at 216° with evolution of a gas containing the oxides of nitrogen, and leaving a carbonaceous viscous residue of a strongly acid reaction. This temperature of decomposition is so sharply defined that it can be employed for the identification of the substance. The decomposition temperature is, however, very markedly lowered by the presence of even a small quantity of impurities.

The methods described above are not well suited for the preparation of the oxime on a large scale, as the yield of pure m-benzenedisulphinic acid is too small. The following procedure is found to give better results.

20 grammes of crystallised m-benzenedisulphochloride in powder are added in three or four portions to a flask containing 32 grammes of zinc dust, 20 c.c. of alcohol and 30 c.c. of water. Slight warming causes the reaction to begin. The addition of alcohol prevents the floating of the sulphochloride on the surface, this precaution being advantageous to the progress of the reaction. When the reaction is once started the temperature rises considerably, and care must be taken to maintain it at 50°–60°, the flask being shaken constantly during the process and any sulphochloride adhering to the neck of the flask being, from time to time, washed down into the flask with a fine jet of water. When all the sulphochloride has been added and a sensible heat evolution is no longer observed, the flask is warmed on a water-bath to complete the reaction and to boil off the greater part of the alcohol. While the flask is still kept warm on the water-bath a solution of sodium carbonate is added little by little until its contents acquire a faint alkaline reaction, so as to

ensure the complete precipitation of zinc carbonate. The solution is filtered, and the filtrate, together with the washings, is evaporated on a water-bath, in order to reduce the volume. After cooling it down to the ordinary temperature, or better to below 10°, 6 grammes of sodium nitrite are dissolved in it, and then dilute sulphuric acid is added in small quantities with constant stirring, the solution being kept continually cooled so as to avoid the rise of temperature. At first the solution acquires a red tint,[1] which, however, fades away on the continued addition of the acid, and then a white crystalline precipitate of m-benzenedisulphoxime begins to appear. After adding an excess of dilute sulphuric acid the precipitated oxime is set aside for some time, which is then collected upon a filter, washed with water, and dried in a desiccator over sulphuric acid. When the operation is well conducted the dried mass amounts to over 15 grammes, or about 90% of the theoretical yield. The crude oxime is recrystallised from hot acetone, which is the best solvent for it. The solubility of the oxime in boiling acetone is about 5 parts in 100; but the solution can attain a considerable degree of supersaturation and furnishes well formed crystals on evaporation or cooling. The decomposition point of the pure crystals is exactly 216°.

Analytical data.

a) 0.2237 gr. of the crystals from the alcoholic solution, on drying at 100°, lost 0.0286 gr.

	Found	Cal. for $\{C_6H_4(SO_2)_2NOH\}_2 \cdot 1\frac{1}{2}C_2H_6O$
Alcohol	12.78%	12.79%

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[1] The coloration seems to be due to some impurity, because on repeating the same reaction with a salt of pure m-benzenedisulphinic acid no coloration was observed.

b) 0.2616 gr. of the crystals from the solution in acetone, on drying at 100°, lost 0.0199 gr.

	Found	Cal. for $\{C_6H_4(SO_2)_2NOH\}_2 \cdot \frac{2}{3}C_3H_6O$
Acetone	7.61%	7.60%

Estimations of nitrogen and sulphur were made with the crystals containing acetone.

c) Nitrogen.

0.1374 gr. gave 6.8 c.c. of moist nitrogen at 25°, 751 m.m.
0.1604 ,, ,, 8.0 ,, ,, ,, ,, ,, 23°, 756 ,,

Nitrogen found	5.56% 5.51 ,,
,, calculated	5.52 ,,

d) Sulphur.

0.1199 gr. gave 0.2214 gr. of barium sulphate.

Sulphur found	25.36%
,, calculated	25.19 ,,

e) Molecular weight.

It seldom happens that a divalent radical closes itself upon the meta-positions. This led me to suspect that the group NOH must be connected with two SO_2 groups of different benzene rings and that, consequently, the oxime must have a double formula. In order to decide this point the molecular weight of the oxime was determined by observing the elevation of the boiling point of acetone solutions.

Molecular weight found	452, 477, 485
Calculated for $HON\left\{\begin{matrix} SO_2 \cdot C_6H_4 \cdot SO_2 \\ SO_2 \cdot C_6H_4 \cdot SO_2 \end{matrix}\right\}NOH$	470

The results are in good agreement with the foregoing supposition and make AUTENRIETH and HENNING's view of the cyclic constitution of this compound doubtful.

The oxime strongly resists the action of bromine, and sulphuric and hydrochloric acids, concentrated as well as dilute. No hydroxylamine is obtained on heating the substance with dilute hydrochloric acid to 140° in a sealed tube. Zinc dust and caustic soda reduce the oxime and give ammonia and m-benzenedisulphinic acid. Sulphur dioxide reduces it to the corresponding imide with a good yield. The action of fuming nitric acid is also a reducing one, the imide being formed ; but the greater portion of the substance seems to be decomposed by it, and a notable quantity of sulphuric acid can be detected among the products of decomposition. The last two reactions will be specially described in the sequel.

II. m-Benzenedisulphimide.

This compound may be prepared by reducing the corresponding oxime in an alcoholic solution in the same manner as in the case of the monosulphonic acid (see Art. 13 of this volume).

For this purpose 5 grammes of the crude oxime were placed in a flask, covered with 20 c.c. of alcohol, and a small quantity of water was added to it. A current of sulphur dioxide was passed into this mixture to saturation, the temperature being kept, at first, at about 50°, afterwards at 60° or a little higher, until all the oxime had gone into the solution. The completion of the reaction was ascertained by taking out a small portion of the solution and adding water to it, and seeing whether it gave any precipitate or not. When the reduction was complete, air was passed through the mixture to remove the excess of sulphur dioxide; and then some water was added. On neutralising the solution with potassium carbonate, voluminous crystals of the potassium salt of the imide filled the liquid, which, however, dissolved again on warming. The solution was concentrated on a water-bath, and set aside to crystallise. 3.25 grammes of the pure potassium salt, crystallised in needles, were thus obtained. In order to get the free imide, an excess of a solution of mercurous nitrate was added to the warm solution of the potassium salt, when the mercurous salt appeared as a white crystalline precipitate. This precipitate was washed, suspended in water, and decomposed by a current of hydrogen sulphide. The precipitated sulphide was filtered off, and the solution was evaporated on a water-bath until it became somewhat syrupy. On setting it aside for a while, the solution gave prismatic crystals of the imide, containing two molecules of water of crystallisation. The water of crystallisation can be removed at 100°.

When a considerable quantity of the imide is to be prepared, the conversion of the potassium salt into the mercurous salt, with the subsequent removal of mercury by means of hydrogen sulphide becomes a very tedious operation. It is better to evaporate the reduced alcoholic solution at once with the addition of a little water, until the crystals begin to appear. In this way a crop of tolerably pure imide can be obtained. The mother liquors from the recrystallisation can be worked up for various salts of the imide, or the free imide may be obtained through the mercurous salt as described above.

The free imide, which is very soluble in water, as well as in alcohol, has a strong acid reaction. It can be precipitated from the aqueous solution by adding strong sulphuric or hydrochloric acid. Even a very dilute solution of the imide gives a crystalline precipitate on the addition of an equal volume of strong hydrochloric acid. The imide has a bitterish sour taste. The ammonium salt is tolerably soluble in water and readily crystallises in short prisms. The potassium salt is also somewhat soluble in water and crystallises in long needles of a pearly lustre.

The most remarkable property of this imide is the slight solubility of the sodium salt, the solution saturated at 24° being about 0.04 normal. It can, therefore, be employed for the detection of sodium. The sodium salt is, however, tolerably soluble in hot water, from which it can be obtained in flat plates. The salts of barium and lead form prismatic crystals of less solubility. The silver salt is also slightly soluble and crystallises in white needles. It can be obtained by adding a solution of the free imide to a solution of silver nitrate. A double salt of silver and potassium was obtained as a white crystalline precipitate by adding silver nitrate to a warm solution of the potassium salt. The mercurous salt forms an insoluble white heavy crystalline precipitate.

Analytical data.

m-Benzenedisulphimide.

a) Water of crystallisation.

0.1217 gr., on drying at 100°–105°, lost 0.0093 gr.

Water found	7.64%
Calculated for $HN\left\{\begin{matrix} SO_2 \cdot C_6H_4 \cdot SO_2 \\ SO_2 \cdot C_6H_4 \cdot SO_2 \end{matrix}\right\}NH,\ 2\,H_2O$	7.60 ,,

b) Sulphur and nitrogen were estimated with the anhydrous substance.

0.1124 gr. gave 0.2420 gr. of barium sulphate.

Sulphur found	29.56%
,, calculated	29.25 ,,

0.1688 gr. gave 9.3 c.c. moist nitrogen at 11.5° and 750 m.m.

Nitrogen found	6.45%
,, calculated	6.40 ,,

The potassium salt.

a) Water of crystallisation.

0.1403 gr., on heating to 200°, lost 0.0071 gr.

Water found	5.06%
Calculated for $KN\left\{\begin{matrix} SO_2 \cdot C_6H_4 \cdot SO_2 \\ SO_2 \cdot C_6H_4 \cdot SO_2 \end{matrix}\right\}NK,\ 1\frac{1}{2}\,H_2O$	4.99 ,,

b) Potassium, determined as sulphate by heating the salt with sulphuric acid and igniting.

0.1403 gr. gave 0.0453 gr. potassium sulphate
0.2026 gr. ,, 0.0653 gr. ,, ,,

Potassium found	14.50% 14.47 ,,
,, calculated	14.45 ,,

c) Solubility.

1.6293 gr. of the aqueous solution saturated at 24° gave 0.0250 gr. of potassium sulphate on evaporation and ignition with sulphuric acid.

Hence 100 parts of the solution contain 4.76 parts of the anhydrous salt.

The sodium salt.

a) Water of crystallisation.

0.1358 gr., on drying at 100°–105°, lost 0.0240 gr.

Water found	18.11%
Calculated for $\mathrm{Na\,N}\left\{\begin{matrix}\mathrm{SO_2 \cdot C_6H_4 \cdot SO_2} \\ \mathrm{SO_2 \cdot C_6H_4 \cdot SO_2}\end{matrix}\right\}\mathrm{N\,Na},\ 6\,\mathrm{H_2O}$	18.31 ,,

b) Sodium.

0.1358 gr. gave, on ignition with sulphuric acid, 0.0322 gr. sodium sulphate.

0.1678 gr. gave 0.0404 gr. sodium sulphate.

Sodium found	$\begin{cases}7.69\% \\ 7.81\ ,,\end{cases}$
,, calculated	7.81 ,,

c) Solubility.

1.9852 gr. of the aqueous solution saturated at 24° gave 0.0057 gr. of sodium sulphate.

Hence 100 parts of the solution contain 0.97 parts of the anhydrous salt.

The silver salt.

This salt contains no water of crystallisation.

0.2787 gr. gave, on ignition, 0.0924 gr. metallic silver.

Silver found	33.16%
Calculated for $\mathrm{Ag\,N}\left\{\begin{matrix}\mathrm{SO_2 \cdot C_6H_4 \cdot SO_2} \\ \mathrm{SO_2 \cdot C_6H_4 \cdot SO_2}\end{matrix}\right\}\mathrm{N\,Ag}$	33.10 ,,

The double salt of silver and potassium.

0.1943 gr. gave, on boiling with dilute hydrochloric acid, 0.0463 gr. silver chloride.

0.2127 gr. gave 0.0496 gr. silver chloride.

Silver found	17.94% 17.56 ,,
Calculated for $Ag\,N\left\{\begin{matrix} SO_2 \cdot C_6H_4 \cdot SO_2 \\ SO_2 \cdot C_6H_4 \cdot SO_2 \end{matrix}\right\}NK$	18.52 ,,

III. p-Benzenedisulphoxime and the Imide.

These compounds can be prepared from p-benzenedisulphochloride in the same manner as that already described for the meta-isomer, pure p-benzenedisulphochloride being obtained as a by-product in the preparation of benzenetrisulphochloride according to the method of JACKSON and WING (Amer. Ch. Journ., 9, 332 ; 1889). The disulphochloride obtained in this way seems to be the purest ever prepared, there being no need of purifying it from the meta- and ortho-isomers. The disulphochloride was repeatedly crystallised from ether, until its melting point was found to be 140.5°.

p-Benzenedisulphoxime.

The reduction of p-benzenedisulphochloride by zinc dust took place as easily as in the case of the meta-compound, and gave the sparingly soluble zinc salt of the corresponding sulphinic acid. This was converted into an alkaline salt, and treated with sodium nitrite and dilute sulphuric acid. The oxime of p-benzenedisulphonic acid was obtained as a very fine white precipitate, difficut to filter and wash without loss. The yield was about 60% of the theoretical amount.

This oxime is slightly soluble in alcohol and acetone, and almost insoluble in other ordinary solvents. Acetone is the only solvent that can be employed for the purpose of recrystallisation. From this menstruum the oxime crystallises out on evaporation in thin plates, the crystals retaining a part of the solvent, which can be driven off on heating to 100°. There is practically no loss on recrystallisation. On heating this compound in a capillary tube it decomposes suddenly at 210° in the same manner as the meta-oxime, and the temperature can be used for the purpose of identification. Like the latter it changes into a viscous substance when boiled with alcohol, and, indeed, so quickly that crystals are hardly obtainable from an alcoholic solution. The oxime dissolves easily in caustic alkalies, and is reprecipitated on acidulation. The reactions with zinc and caustic soda, ammonia, and nitric acid are almost analogous to those of the meta-compound.

It is possible and even likely that this oxime has also a double molecular formula, but the molecular weight determination was not attempted on account of its slight solubitity in acetone.

Analytical data.

a) Acetone of crystallisation.

0.1398 gr., on drying at 100°, lost 0.0221 gr.

Acetone found 15.81%

Calculated for $HON\left\{\begin{matrix} SO_2 \cdot C_6H_4 \cdot SO_2 \\ SO_2 \cdot C_6H_4 \cdot SO_2 \end{matrix}\right\}NOH.\ 1\frac{1}{2}\ C_3H_6O$ 15.61 ,, *b*) Nitrogen.

0.1373 gr. of the crystals gave 6.0 c.c. moist nitrogen at 15° and 754 m.m.

Nitrogen found	5.04%
,, calculated	5.04 ,,

c) Sulphur.

0.1245 gr. of the crystals gave 0.2075 gr. of barium sulphate.

Sulphur found	22.90%
,, calculated	23.01 ,,

p-Benzenedisulphimide.

This imide was obtained by reducing the oxime by means of sulphur dioxide. The powdered oxime was suspended in aqueous alcohol contained in a flask, sulphur dioxide passed to saturation, and the whole kept at a temperature of about 50°. Complete dissolution did not take place even when the reduction was complete, owing to the slight solubility of the imide in alcohol and consequent precipitation of it as the oxime was dissolved and reduced. Three or four hours were necessary before complete reduction took place, which could be ascertained by adding a drop of the reacting mixture into water, when complete disappearance of the turbidity was observed. The small solubility of the imide in water and especially in alcohol made the purification of this substance very easy. The contents of the flask were transfered into a dish and evaporated over a water-bath to a small bulk. The mother liquor was pressed out of the crude crystals of the imide which separated out on cooling, and the latter washed with a small quantity of alcohol.[1] Recrystallisation from water yielded the pure product.

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[1] From 2.3 gr. of the oxime 1.6 gr. of the crude imide were obtained.

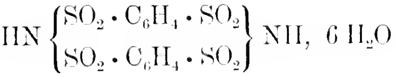
p-Benzenedisulphimide crystallises in colourless prisms, with two molecules of water, which can be driven off at 100°. This imide behaves much like the corresponding meta-compound and can be precipitated from its aqueous solution by strong acids. The alkaline salts of the imide are sparingly soluble in water, even hot water not taking up much of them. Under the microscope they present the appearance of rhombic plates. Silver and mercurous salts form white, heavy, crystalline precipitates. The free imide has a sour taste, not accompanied, however, by any bitterness like that of the meta-compound. The small quantity of pure p-benzenedisulphochloride at my disporal made any further examination of these salts impossible.

Analytical data.

p-Benzenedisulphimide.

a) Water of crystallisation.

0.1220 gr., on drying at 100°–105°, lost 0.0092 gr.

Water found		7.54%
Calculated for	 $HN\left\{\begin{matrix} SO_2 \cdot C_6H_4 \cdot SO_2 \\ SO_2 \cdot C_6H_4 \cdot SO_2 \end{matrix}\right\}NH,\ 6\,H_2O$	7.60 ,,

b) Sulphur.

0.1128 gr. of the anhydrous imide gave 0.2440 gr. of barium sulphate.

Sulphur found	29.72%
,, calculated	29.25 ,,

c) Nitrogen.

0.1861 gr. of the anhydrous imide gave 9.9 c.c. of moist nitrogen at 13° and 767 m.m.

Nitrogen found	6.30%
,, calculated	6.40 ,,

IV. Oximes and Imides of o-Benzenedisulphonic Acid.

The difficulty of procuring the materials was strongly felt in the investigation of the oxime and the imide of o-benzenedisulphonic acid. The starting point was p-bromaniline-o-sulphonic acid, and this was transformed into p-brom-o-benzenedisulphonic acid according to the method of Armstrong and Napper (Chem. News, **82**, 46; 1900). Only two grammes of p-brom-o-benzenedisulphochloride was at my disposal, from which I had to prepare the oxime and also the imide.

A small quantity of potassium p-brom-o-benzenedisulphonate was debrominated with zinc dust and caustic potash, and from the product o-benzenedisulphochloride was prepared. But the quantity under manipulation was less than one gramme.

From these sulphochlorides the corresponding oximes and imides were prepared according to the methods already described but owing to the small quantity of the materials it was difficult to make many analyses.

The *oxime of p-brom-o-benzenedisulphonic acid* is tolerably soluble in acetone and alcohol, and crystallises from the former solvent in well defined prisms. Sulphur was estimated in the sample dried at 100°–150°, with the following result:

0.1374 gr. gave 0.2076 gr. of barium sulphate.

Sulphur found	20.75%
Calculated for $HON:(SO_2)_2C_6H_3Br$	20.38 ,,

In order to see whether this ortho-compound has the cyclic monomolecular constitution or not, its molecular weight was determined by observing the elevation of the boiling point of acetone. The result agreed exactly with the monomolecular formula.

The oxime decomposes on heating with an evolution of gas bubbles, but without charring; the decomposition point is 82°. On reducing it with sulphur dioxide a crystallisable acidic imide was obtained, which gave sparingly soluble alkaline salts. But no analysis was attempted.

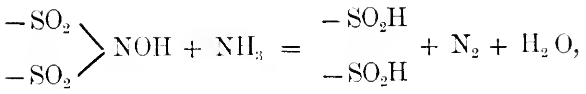
The *oxime of o-benzenedisulphonic acid* was obtained in colourless prismatic crystals from its solution in acetone. Its decomposition point was very low and found to be about 45°. It was, therefore, impossible to recrystallise this compound from boiling acetone. On reduction it gave an acidic imide, but the substance was not analysed.

Both oximes are insoluble in water. They are readily decomposed by ammonia, with a brisk evolution of gas bubbles.

It can not be doubted that o-benzenedisulphonic acid gives the corresponding oxime and imide, but as no analyses were made it will be necessary to renew the investigation with larger quantities of the materials.

V. Action of Ammonia and Fuming Nitric Acid upon the Oximes.

Aqueous ammonia acts violently upon the sulphoximes described above with evolution of nitrogen and formation of the corresponding sulphinic acids, while a good deal of heat is liberated during the reaction. Evolution of nitrogen by the action of ammonia upon benzenesulphohydroxylamine $C_6H_5 \cdot SO_2 \cdot HNOH$ was observed by PILOTY (Ber., 29, 1559; 1896), but without any special study of that reaction. The action of ammonia upon m-benzenedisulphoxime may be considered to be a typical reaction of an aromatic sulphoxime, and may be formulated as follows:



$$\begin{matrix}-SO_2\\-SO_2\end{matrix}\!\!>NOH + NH_3 = \begin{matrix}-SO_2H\\-SO_2H\end{matrix} + N_2 + H_2O,$$

the group SO_2 being directly attached to the benzene ring. In order to ascertain to what extent this reaction takes place, the nitrogen gas liberated by the action of ammonia upon m-benzenedisulphoxime was measured in the following manner.

0.1387 gr. of m-benzenedisulphoxime crystals containing acetone was put into a small thin glass bulb, which was evacuated by means of a water-pump and then sealed. This bulb was introduced into a wider tube of about 100 c.c. capacity, the lower end of which had been drawn out and sealed. The upper end of the tube was then drawn out to a capillary, through which moderately strong ammonia water was introduced, until about one third of the tube was filled, and the capillary connected with the water pump in order to evacuate the tube. The ammoniacal liquid effervesced, and the escaping ammonia gas completely drove away the air from the tube in a few minutes, when the latter was sealed up at the capillary. The tube was then shaken violently so as to break the small bulb in it. The shaking was continued for a few minutes in order to ensure the complete liberation of the nitrogen. After the completion of the reaction the tube was opened under water, which had been previously boiled to expel the dissolved air, and the nitrogen was transferred into a graduated tube and measured. The volume of nitrogen, reduced to 0° and 760 m.m., amounted to 11.3 c.c., while, according to the equation given above, it ought to have been 12.2 c.c.

We may, therefore, conclude that the equation actually represents the reaction which takes place between the sulphoxime and ammonia. The small deficiency of nitrogen can readily be accounted for by the solubility of this gas in the liquid and also by the incompleteness of the reaction under the conditions of the foregoing experiment.

When the ammoniacal liquid, in which the brisk reaction had taken place, was evaporated on a water-bath, small gas bubbles continued to appear until the liquid attained a syrupy consistency. On cooling, beautiful star-like clusters of pure ammonium m-benzenedisulphinate, consisting of elongated tetrahedra, separated out. This salt melts at 113°–115°, and the melting point was not altered by repeated crystallisation from water. There was nothing which indicated the presence of any other reaction products.

This method of changing a crude alkaline disulphonate into the oxime and then decomposing it by ammonia may be employed for the preparation of the pure disulphinate, in large quantities, which may, otherwise, be very difficult to obtain.

Ammonium p-benzenedisulphinate was obtained in the same way from the corresponding oxime. This substance crystallises in fine needles, and decomposes without melting at about 200°.

Benzene-monosulphoxime also yielded the ammonium salt of benzenemonosulphinic acid in good quantity.

Analytical data.

Ammonium m-benzenedisulphinate.

a) Nitrogen.

0.1421 gr. gave 13.1 c.c. of moist nitrogen at 14° and 763 m.m.

Nitrogen found	10.8%
Calculated for $C_6H_4(SO_2NH_4)_2$, H_2O	10.9 ,,

b) Sulphur.

0.1272 gr. gave 0.2305 gr. barium sulphate.

Sulphur found	24.88%
,, calculated	24.82 ,,

Ammonium p-benzenedisulphinate.

a) Nitrogen.

0.0939 gr. gave 8.75 c.c. of moist nitrogen at 17° and 758 m.m.

Nitrogen found	10.7%
Calculated for $C_6H_4(SO_2NH_4)_2$, H_2O	10.9 ,,

b) Sulphur.

0.0966 gr. gave 0.1729 gr. barium sulphate.

Sulphur found	24.6%
,, calculated	24.8 ,,

The silver salts of m- and p-benzenedisulphinic acids were also obtained. The former is crystalline, while the latter is amorphous and difficult to purify. Silver m-benzenedisulphinate was analysed with the following result:

0.0900 gr. gave on ignition 0.0466 gr. of metallic silver.

Silver found	51.8%
Calculated for $C_6H_4(SO_2Ag)_2$	51.4 ,,

The zinc salt of the meta-acid is soluble, but that of the para-acid is only slightly soluble in water.

The peculiarity of the reaction between the sulphoxime and ammonia reminds one of the decomposition of ammonium nitrite on heating. It may be that the oxime forms an unstable ammonium salt, which soon decomposes into the sulphinic acid, nitrogen and water. The similarity of the reaction makes it probable that the sulphoximes are the substitution products of nitrous acid and not of hydroxylamine. The difficulty of their hydrolysis into hydroxylamine and the corresponding sulphonic acid seems to support this view.

When m-benzenedisulphoxime was treated with fuming nitric acid, it dissolved to some extent. On diluting the solution with water the oxime was reprecipitated unchanged. But when the nitric solution was allowed to stand for four or five days the colour of the fuming nitric acid had faded a little, and small crystals made their appearance on the surface of the liquid and on the sides and bottom of the vessel. The crystals dissolved readily in water, and the solution behaved as that of an acid. On neutralisation with caustic soda, a crystalline precipitate of a difficultly soluble sodium salt was formed. This precipitate was collected, recrystallised from hot water, and analysed. The amount of water of crystallisation, sodium, nitrogen, and sulphur found, as well as the form of the crystals, left no doubt as to its identity with the sodium salt of m-benzenedisulphimide. The formation of the imide in this case was, indeed, a surprise, and it was thought possible that the crystals first formed in fuming nitric acid might have been a complex compound, which gave rise to the imide on hydrolysis. In order to settle this point the crystals were dried upon a porous tile, then in a desiccator containing strong sulphuric acid and caustic soda, and a weighed quantity of the substance was titrated with $\frac{1}{10}$ N soda solution. The titer agreed exactly with that calculated for the imide, showing that the crystals were nothing but the pure imide.

p-Benzenedisulphoxime also gave a similar result. This substance is almost insoluble in fuming nitric acid; yet, on allowing the mixture to stand from five to ten days a small quantity of the compound was changed into the corresponding imide. Although the quantity produced was so small that it was difficult to isolate it, its presence could be proved by the formation of the almost insoluble potassium salt on neutralising the diluted solution with caustic potash.

A notable quantity of sulphuric acid was found in the nitric solution in both cases. This is perhaps due to the complete decomposition of the oximes.

The unexpected reducing action of fuming nitric acid upon the disulphoximes here observed may be due to the lower oxides of nitrogen which exist in the acid. But further investigation is necessary to settle the question.

In concluding this communication, the author desires to express his great obligation to Prof. Haga, who has taken a great interest in the work and aided him with valuable advice.

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Preliminary Note on a New Element in Thorianite.

By

Masataka Ogawa, *Rigakushi.*

While working on thorianite in University College, London, under Sir WILLIAM RAMSAY's direction a few years ago, an element believed to be new was met with in the iron group in the usual course of analysis, but, owing to the small quantity, its nature could not be fully established. The subject has been resumed since my return to Japan, and it has fortunately been found that the same element also occurs in other minerals, such as reinite and molybdenite, both found in this country. This somewhat incomplete paper is now published as a preliminary notice of the work, which is still going on.

Treatment of Thorianite.

Preparation of the oxide. Finely powdered thorianite was treated with boiling concentrated nitric acid and the solution decanted off, this process being repeated until the fresh nitric acid was no longer coloured yellow. The residue, amounting to about 3 per cent and now nearly free from the chief constituents of thorianite, viz. thorium, uranium, iron and lead, was boiled with concentrated hydrochloric acid, by which treatment a considerable quantity of titanium and antimony passed into solution and was decanted off. The residue was then treated with hydrofluoric acid in the presence of concentrated sulphuric acid in order to remove the silica and, after ignition and fusion with hydrogen potassium sulphate, the whole mass was dissolved in cold water.

On boiling the diluted solution, however, a slight turbidity occurred, which was found to be due to the separation of a basic titanium compound. Hydrogen sulphide was then passed through the filtered solution, and some brown precipitate thereby formed was filtered off. To the filtrate, ammonia was added after oxidation with nitric acid, and the precipitate formed was dissolved in dilute hydrochloric acid. To this solution, oxalic acid was added, which produced a small quantity of a white precipitate, consisting of the oxalates of thorium, etc., and this was filtered off. Ammonia and ammonium sulphide were then added to the filtrate; the black precipitate thereby formed was dissolved in dilute hydrochloric acid and reprecipitated by ammonium sulphide in the presence of an excess of ammonium carbonate, thus keeping in solution any uranium, which might still be present. The ammonium sulphide precipitate was again dissolved in dilute hydrochloric acid and reprecipitated by ammonia in the presence of an excess of ammonium chloride. The precipitate, consisting chiefly of the hydroxides of iron, aluminium and zirconium, was dissolved in dilute hydrochloric acid, the solution nearly neutralised with sodium carbonate and boiled after the addition of sodium thiosulphate. The precipitate now formed was dissolved in hot concentrated hydrochloric acid, the separated sulphur filtered off, and the solution reprecipitated by sodium thiosulphate, the usual precautions being taken.

The precipitate was once more dissolved in concentrated hydrochloric acid and, after evaporating off the excess of the acid and heating with some sulphuric acid, a saturated solution of potassium sulphate was added to the solution. After standing for 24 hours, the double sulphate of zirconium and potassium, which was formed, was filtered off. The filtrate was evaporated to a small bulk, and the crystals formed of potassium sulphate and alum were removed. After mixing the greenish coloured mother liquor with 90% alcohol and filtering, ammonia was added to the solution, when a pale yellow precipitate, believed to consist of the hydroxide of the new element, was obtained.

Properties of the oxide. The hydroxide above obtained is insoluble in ammonium chloride. It dissolves in alkalies, but not so easily as aluminium hydroxide. On drying at 100°, it becomes nearly black and, on ignition, it changes to a dark brown powder. The ignited oxide is insoluble in acids, even in hot concentrated sulphuric acid to which some hydrofluoric acid has been added. On fusion with hydrogen potassium sulphate, however, and extracting the fused mass with water, the oxide may again be brought to solution. On fusion with sodium carbonate and potassium nitrate, the oxide gives a green mass, having much the same appearance as that of an alkaline manganate. This dissolves in water and forms a green coloured solution, from which a current of carbonic acid produces a brown precipitate, soluble in hydrochloric acid.

A solution of the hydroxide in hydrochloric acid has a yellowish green colour and gives a chocolate brown precipitate on boiling with sodium thiosulphate. The same solution gives a greenish black precipitate with ammonium sulphide, insoluble in an excess of the reagent, and a yellowish brown precipitate with potassium chromate, insoluble in acetic acid and quite different in appearance from that of lead chromate. Potassium iodide gives no precipitate.

The yield of the oxide was a few contigrams from one kilogram of the mineral. The portion of the mineral soluble in nitric acid also yielded a small quantity of the oxide.

I had also in store all the ammonia precipitate separated from the crude hydrogen sulphide precipitate given by Sir WILLIAM RAMSAY. The whole of this precipitate was ignited and treated as if it had been the original mineral, and a little over one decigram of the oxide was obtained from this source.

Salts. Several attempts have been made to get well crystallised salts, but thus far without success. After fusing the oxide with hydrogen potassium sulphate, dissolving the fused mass in water, precipitating the hydroxide by ammonia, dissolving the precipitate in different acids, and evaporating these solutions, very soluble imperfect crystals were, indeed, obtained; but these crystals change to basic insoluble compounds on treatment with water. Attempts to get well defined crystals of double salts, containing the element in question, also ended in failure.

Anhydrous chloride. The oxide was heated in a porcelain boat in a current of chlorine gas, saturated with the vapour of carbon tetrachloride. There was formed a very slight white sublimate, the main portion of the product remaining in the boat as a white powder having a slightly yellow tinge. On continued heating at low redness, a pale green sublimate was formed; but it was very slow in formation and insignificant in amount.

The residue in the boat, doubtless consisting of the anhydrous chloride, became deep green on being moistened with water and dissolved into a pale green solution on the addition of more water, acidified with nitric acid. A portion of the solution was tested for thorium with negative results.

Equivalent weight. (1) A known weight of the chloride, prepared as above and contained in a small tube, was dissolved in acidified water, precipitated by ammonia, and the precipitate was ignited and weighed as oxide. 0.1092 gr. of the chloride gave 0.0742 gr. of the oxide, from which the number 50.3 was calculated as the equivalant weight of the element. (2) The oxide was fused with hydrogen potassium sulphate, dissolved in water, and precipitated by ammonia. This precipitate was dissolved in dilute sulphuric acid, the solution evaporated to dryness and heated over a sulphur bath, until the weight became constant. The residue was ignited and weighed as oxide. 0.1253 gr. of the sulphate gave 0.0747 gr. of the oxide, again leading to the value 50.3. (3) The chloride, of which 0.0652 gr. was taken, was dissolved in water, acidified with nitric acid, and precipitated by silver nitrate, which gave 0.1120 gr. of silver chloride, whence follows the number 48 as the equivalent weight of the element.

Judging from the mode of working, the properties of the oxide and the chloride, as well as from the equivalent weight, the element in question must be considered as hitherto unknown, and this view has been further confirmed by

Spectroscopic examinations. The oxide was fused with sodium carbonate and potassium nitrate, the fused mass dissolved in water, and the brown precipitate obtained by passing a current of carbonic acid through the solution, was dissolved in dilute hydrochloric acid and subjected to spectroscopic examinations.

The lines were not remarkably strong, but three lines could be observed in the green-blue part of the spectrum. There were no manganese lines. Of the three lines, the strongest was the one having the wave-length 4882, believed to be correct within 10 units. The other two lines could also be measured, but owing to their feebleness, the statement of their wave-length is here reserved.

Examination of Reinite.

The finely powdered mineral was fused with a mixture of sodium carbonate and potassium nitrate, the fused mass treated with water, ferric oxide filtered off, and the filtrate was saturated with carbonic acid gas. A brown precipitate, containing a little iron and silica, but, otherwise, apparently the same as that obtained, under like conditions, from the oxide extracted from thorianite, was produced. This was dissolved in dilute hydrochloric acid and examined spectroscopically. The spectrum was exactly the same as before, though other lines were observed in addition.

Another portion of the powdered mineral was digested with hot nitro-hydrochloric acid, until its brown colour was completely changed into yellow, the solution evaporated to dryness, and the residue extracted with water acidified with hydrochloric acid. The solution, separated from insoluble tungstic acid, was saturated with hydrogen sulphide, the black precipitate thereby formed was filtered off, and the filtrate, after evaporation and oxidation, was treated with ammonia. The hydroxides of the iron group thus precipitated were redissolved in dilute hydrochloric acid, boiled with sodium thiosulphate in order to remove iron, and the reprecipitated hydroxides were filtered and ignited. The ignited oxides were then heated in a current of chlorine gas and carbon tetrachloride vapour. A difficultly volatile chloride, apparently identical with that obtained from thorianite, was thus produced. Its spectrum, also, was exactly the same as before. The yield of the oxide was, however, very much better, about one decigram having been obtained from 200 gr. of the mineral.

Examination of Molybdenite.

The powdered mineral was roasted in air, until sulphurous acid gas was no longer given off. The residue, which was yellow when hot and pale greenish yellow when cold, was digested with a dilute solution of ammonia. The portion insoluble in ammonia was then digested with dilute hydrochloric acid, and the solution filtered from some undecomposed portion of the mineral. The acid solution was nearly neutralised with ammonia and, after saturation with ammonium chloride and on standing, a pale yellow precipitate was formed. The precipitate, apparently ammonium vanadate, was removed by filtration. To the yellowish green filtrate, hydrogen sulphide was passed to saturation, and the black precipitate thereby formed was filtered off. The filtrate was freed from hydrogen sulphide by boiling, and then ammonia and hydrogen peroxide were added. The precipitated hydroxides were redissolved in dilute hydrochloric acid and boiled, as before, with sodium thiosulphate in order to remove iron.

The reprecipitated hydroxides were filtered, ignited and fused with a mixture of sodium carbonate and potassium nitrate, and the fused mass dissolved in water. After decomposing the solution with hydrochloric acid, ammonia gave only a slight turbidity, due apparently to the presence of a small quantity of aluminium. On reduction, however, with zinc and hydrochloric acid, the solution gave an abundant precipitate with ammonia in the presence of an excess of ammonium chloride. The spectrum of the hydroxide thus obtained and dissolved in hydrochloric acid showed the same lines as those observed in the case of thorianite and reinite. The zinc used for reduction was prepared by the electrolysis of a pure solution of zinc ammonium sulphate.

The ammoniacal solution obtained on treating the roasted mineral with ammonia was also found to contain a portion of the element in question originally existing in the mineral; for, this solution, after acidification with acetic acid and the removal of molybdic acid as barium molybdate, gave no precipitate with ammonia, but, on reduction with zinc and hydrochloric acid, ammonia in the presence of ammonium chloride produced some precipitate from it, which, on examination, was found to be the same hydroxide as that obtained, under like conditions, from the hydrochloric acid solution of the roasted mineral.

Thorianite, Reinite and Molybdenite.

It will be seen from what has been stated that the new element is contained in reinite and molybdenite, as well as in thorianite, and, although it can not yet be definitely stated, it is almost certain that molybdenite contains it in even a larger proportion than reinite.

It may be remembered that Dr. E. H. BUCHNER, in the course of his analysis of thorianite, observed the precipitation of a small quantity of a black sulphide in the arsenic group and occurence of two other unknown substances in the bismuth-cadmium group (*Chem. News*, 1906, **94**, 233). I have not only confirmed his observations with thorianite, but have also met with the same unknown substances in the course of my examination of reinite and molybdenite. It is a striking case of coincidence that the three different minerals should contain these same unknown substances, besides the new element which forms the subject of this paper.

Conclusions.

Thorianite, reinite and molybdenite contain, in common, a new element, which is characterised by the following properties:

1. The hydroxide, precipitated by ammonia in the presence of an excess of ammonium chloride, has an almost white colour with a pale yellow tinge. It is soluble in alkalies, but not so readily as aluminium hydroxide.

2. On drying at 100°, it becomes nearly black. The ignited oxide has a dark brown colour and is insoluble in acids, but becomes soluble in water after fusion with hydrogen potassium sulphate.

3. A solution of the hydroxide in hydrochloric acid has a yellowish green colour and gives a chocolate brown precipitate on boiling with sodium thiosulphate.

4. When ammonium sulphide is added to a solution of the chloride, a greenish black precipitate, insoluble in an excess of the reagent, is formed.

5. A solution of the chloride, acidified with acetic acid,

gives a yellowish brown precipitate with potassium chromate. Potassium iodide gives no precipitate.

6. On fusing the oxide with sodium carbonate and potassium nitrate, a green mass is obtained, soluble in water. This solution gives a brown precipitate on passing a current of carbonic acid gas, the precipitate readily dissolving in dilute hydrochloric acid.

7. After fusion in the above manner, neither ammonia nor ammonium sulphide gives any precipitate ; but on acidifying the solution, to which ammonium sulphide has been added, with hydrochloric acid a brown precipitate is formed.

8. After the reduction of the above solution with zinc and hydrochloric acid, ammonia in the presence of an excess of ammonium chloride again precipitates the hydroxide.

9. When the oxide is heated in a current of chlorine gas saturated with the vapour of carbon tetrachloride, a difficultly volatile anhydrous chloride is obtained, which dissolves in water to form a pale green solution.

10. The chloride gives a characteristic line, besides two other feebler lines, in the green-blue part of the spectrum, having a wave-length of 4882.

11. The equivalent weight of the element is about 50, this element probably filling the gap between molybdenum and ruthenium and having an atomic weight of about 100.

12. The element appears to exist in two degrees of oxidation. The lower oxide behaves as a basic oxide and comes along with alumina in the ordinary course of analysis. Its separation from the latter is, indeed, very difficult, the conversion into the difficultly volatile chloride by heating in a current of chlorine gas and carbon tetrachloride vapour being, at present, the only

means of separation. The higher oxide behaves as an acidic oxide, similar to molybdenum trioxide, and is reducible into the basic oxide by means of zinc and hydrochloric acid.

The name Nipponium, with the symbol Np, was once suggested by Sir WILLIAM RAMSAY, and this name will be provisionally employed to indicate the new element.

I can not conclude without expressing my heartiest thanks to Sir WILLIAM RAMSAY for his kind assistance and advice and for his generosity in supplying me with the valuable material for this research, while I was working in his laboratory.

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Preliminary Note on a New Element allied to Molybdenum.

By

Masataka Ogawa, *Rigakushi.*

Introduction.

In the course of an examination of molybdenite in connection with my work on nipponium, a substance, which was supposed to be ammonium vanadate, was obtained and set aside as such (This Volume, Art. 15, p. 7). A further examination of this substance has shown, however, that it is not ammonium vanadate, but that it is a compound of a new element, closely allied to molybdenum and, indeed, associated with it in this compound; and, although the results so far obtained are still very incomplete, they are now published in the hope that they may prove of sufficient interest.

It is possible and even likely that the "new tin-group element in thorianite", an account of which has been recently given by Miss EVANS (J. C. S., 1908, **93**, 666), is identical with this element, inasmuch as the latter has been found not only in molybdenite but also in thorianite and two, at least, of the very few characteristic reactions ascribed to her element by Miss EVANS, namely the formation of a brown sulphide, insoluble in hydrochloric acid but soluble in hot nitric acid, and its solubility in ammonium carbonate to form a deep brown solution, are likewise produced by the element now to be described. The formation of a golden-brown syrup on evaporation of a nitric acid solution of the sulphide, which she appears to regard as another characteristic of her element, could, however, in the case of the element forming the subject of this paper, be observed only with the impure sulphide, which, in some form or other, was found to contain a small quantity of iron, besides, perhaps, some other elements. Again, on reducing with hydrogen, the oxide prepared from such sulphide, produced a metal, which, in agreement with Miss EVANS' observation, was fusible at a bright red heat, but the metal obtained from the purified oxide was found to be non-fusible. It appears, therefore, that, if Miss EVANS' element is really identical with mine, I have got it in a much purer state. In any case, it is unfortunate that, in consequence of her account being much too short, no exact comparison can be instituted between the two. It is also unfortunate that, in spite of her positive statement as to the existence of molybdenum in thorianite, she does not tell us how this element has been completely removed, the sulphide of molybdenum also dissolving in ammonium carbonate to form a deep brown solution.

There is one other point, which should be noted before going further. Miss EVANS says that the sulphide of her element is soluble in water. The solubility of the sulphide, upon which I worked, may be inferred from the fact that one of its sources was the sulphide residue from thorianite, which had escaped precipitation by hydrogen sulphide (p. 10), and also from the fact that a solution of the purified oxide in ammonia was almost completely precipitated by hydrogen sulphide, *only* after acidification and *on boiling*. The presence of the element in the filtrate from the hydrogen sulphide group may, therefore, be most probably ascribed to the incomplete heating during precipitation by hydrogen sulphide.

Preparation from Molybdenite of a Compound containing the New Element and its Examination.

As the condition, under which the supposed ammonium vanadate was previously obtained, was such that it did not ensure its separation quantitatively and in the pure state, supposing it to be really ammonium vanadate, the following procedure has been adopted. After igniting in oxygen, the powdered mineral was extracted with ammonia. The residue, still containing some unaltered mineral, was repeatedly boiled with concentrated nitric acid, and the whole evaporated to dryness and again extracted with ammonia. The final residue, on digestion with ammonium sulphide, gave a deep reddish brown solution, which was filtered from the insoluble portion, containing the sulphides of lead, bismuth (?), iron, nipponium and zinc, and the hydroxide of aluminium. The dark brown precipitate, obtained on acidifying the solution with hydrochloric acid and heating, was decomposed with nitric acid, and the yellowish brown syrupy residue, left on evaporation of the nitric acid solution, ignited in the air. The dark brown residue thus obtained was fused with potassium nitrate, and the fused mass extracted with water, when a small quantity of a reddish brown substance, consisting chiefly of ferric oxide, was left undissolved. The aqueous alkaline extract was neutralised with nitric acid and, after concentration, mixed with an equal volume of a saturated solution of ammonium chloride, followed by the addition of one-third of the total volume of 90% alcohol. A crystalline precipitate, apparently the same as that, which had been previously obtained and set aside as ammonium vanadate, was produced on standing for some time, and this was washed, first, with a saturated solution of ammonium chloride and, then, with dilute alcohol.

Judging from the mode of procedure, no other known substance but ammonium vanadate could have come down as a crystalline precipitate under the conditions above detailed, but the reactions described below clearly show that it is not ammonium vanadate. Neither can it be ammonium molybdate, for this salt is not known to be precipitated by ammonium chloride. It is true that the compound gives some of the reactions of molybdenum, which it undoubtedly contains in one form or another, but the fact above alluded to that it has been obtained under conditions, which exclude the possibility of ammonium molybdate being precipitated pure and simple, makes it exceedingly probable either that the compound above obtained is a complex salt containing molybdenum and the new element or that it belongs to the class of mixed crystals.

The yield of the compound was about 7 grams from 400 grams of molybdenite. It is remarkable that the existence, in this mineral, of such a comparatively large amount of a new element should have hitherto escaped observation, but this may be explained by the fact that the element is very closely allied to molybdenum and that its equivalent weight does not differ much from that of the latter.

Properties of the compound. The compound, above obtained, which is evidently an ammonium salt, crystallises in minute prisms, easily soluble in water, and its aqueous solution gave the following reactions:

(1) Hydrogen sulphide, in presence of hydrochloric acid, only gave a brown colouration without producing any precipitate, but, on heating the solution to boiling, a dark brown precipitate was formed (difference from a vanadate, which is not precipitated by hydrogen sulphide either in the cold or when heated), the filtrate from it being quite colourless (difference from a molybdate, which gives a blue coloured filtrate).

(2) On reducing the solution with zinc and hydrochloric acid, no colour appeared for some time, but, on standing, a blue colour changing to brown was produced; at the same time, a substance having a metallic lustre adhered to the zinc. A solution of pure ammonium molybdate of the same concentration similarly treated at once turned blue, ultimately changing to brown, and the brown solution, on long standing, deposited a dirty brown amorphous substance.

(3) Barium chloride, lead acetate, silver nitrate and mercurous nitrate all gave precipitates, soluble in nitric acid and similar in appearance to the respective salts of molybdic acid, except the mercurous salt. The barium salt forms a white crystalline powder, slightly soluble in water; the lead salt is a white amorphous powder, insoluble in water; the silver salt forms a pale yellow precipitate, slightly soluble in water; and the mercurous salt consists of golden yellow crystals, insoluble in water. Mercurous molybdate is obtained, under like conditions, as a white or pale yellow amorphous substance.[1]

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[1] Struve has observed that the milky precipitate of mercurous molybdate changes into golden yellow needles through prolonged washing or on standing (Journ. prak. Chem., 467, quoted in Dammer's Handbuch der anorg. Chem., II,I 628).

(4) After strongly acidifying the solution with nitric acid, sodium phosphate gave a compound apparently similar to ammonium phospho-molybdate.

(5) In presence of potassium thiocyanate, zinc and hydrochloric acid gave a blood red colouration.

Besides the above described reactions, which were observed with an aqueous solution of the salt, the following must also be mentioned.

(6) The residue, obtained on heating the ammonium salt and consisting of the oxide, either alone or mixed with molybdenum trioxide, did not possess the characteristic yellowish red colour of vanadium pentoxide, but was similar in appearance to molybdenum trioxide and slowly volatilised at a red heat, becoming crystalline at the same time. It produced a deep blue colouration on heating with concentrated sulphuric acid.

(7) The oxide, when heated in a current of hydrogen gas, was reduced into the metal, which was non-fusible at a bright red heat, and the metal could be easily brought back into the oxide by heating it in the air. The equivalent weight of the metal was determined, both by reducing the oxide into the metal and by converting the metal back into the oxide; the values obtained were 16.4 and 16.6, not very far from the equivalent weight of molybdenum.

Thinking that the ammonium salt above obtained might be a mixture of two salts, one containing molybdenum and the other the unknown element, an attempt was made to separate them, if possible, by fractional crystallisation. For this purpose, the salt was again prepared according to the method already described, collecting, however, one crop of crystals shortly after the addition of ammonium chloride and without using alcohol, and another crop after adding alcohol to the mother liquor and allowing it to stand for two days. From these two fractions, which looked exactly alike, water of crystallisation, ammonium oxide and the residual oxide or oxides were determined with practically the same results.

The attempt, which was next made, to prepare the sodium salt resulted in showing the compound nature of the ammonium salt. The oxide, obtained from the ammonium salt, was fused with an equivalent quantity of sodium carbonate, calculated from the equivalent weight already determined on the supposition that the sodium salt would have the composition Na_2XO_4; the fused mass was dissolved in water and the solution evaporated, when hygroscopic crystals were obtained. Under a microscope, these were found to consist partly of thin plates and partly of small needles, but, owing to their hygroscopic nature, their mechanical separation was found to be impossible.

Isolation of the element was, at last, effected through the electrolysis of the ammonium salt. On electrolysing an aqueous solution of the ammonium salt at a temperature of 60°–70°, using a current density of 1 ampere per 100 sq. cm. and a potential difference of 4 volts, a black substance deposited on the cathode. It was found to contain molybdenum, doubtless, as a hydrated sesquioxide, and, on heating it with 2N-hydrochloric acid, the molybdenum compound gradually dissolved away to form a dark brown solution. Treatment with hydrochloric acid was repeated, until the fresh acid was no longer coloured brown. A portion of the residue (hydrated lower oxide of the new element?), which was graphitic in appearance, was boiled with nitric acid, the whole evaporated to dryness and extracted with ammonia. The ammoniacal solution was also evaporated to dryness and the residue dissolved in water. This aqueous solution gave all the reactions described on page 5–6, with the exception of the colour reactions mentioned in (2), (5) and (6), but these reactions are exactly those which are characteristic of molybdenum. It is true that a faint colouration was produced with zinc and hydrochloric acid, in presence of potassium thiocyanate, but so faint that, considering the delicacy of this colour reaction, we may reasonably believe that almost every trace of molybdenum has been removed and that the new element or, rather, its oxide or the hydrated oxide has been obtained in an almost pure state.

Properties of the element. The supposed new element, obtained by heating the above described graphitic substance in a current of hydrogen gas, has a metallic lustre and looks somewhat like magnesium powder. It burns brilliantly when heated in the air, producing the oxide, a part of which volatilises at the same time. The oxide, when heated in hydrogen gas, reproduces the metal in the form, however, of a gray powder, resembling molybdenum, produced under like conditions. It is non-fusible at a red heat. On prolonged boiling, it dissolves in concentrated hydrochloric acid, producing a faint greenish-yellow solution. In this latter respect, it is distinguished from molybdenum, which is insoluble in the acid. The hydrochloric acid solution, on evaporation to dryness at 100°, gives a white residue of the chloride, soluble in water. This residue, on ignition, becomes difficutly soluble, doubtless, due to its conversion into the oxide or the oxychloride.

The equivalent weight was again determined, using the purified metal. (1) 0.1464 gr. of the metal gave 0.2149 gr. of the oxide, from which the number 17.1 was calculated. (2) 0.2149 gr. of the oxide gave 0.1451 gr. of the metal, which led to the value 16.7. Of these two results, the lower value, 16.7, which was obtained from the reduction of the oxide, must be regarded as more exact, there being an unavoidable slight loss by volatilisation of the oxide produced, when the metal is heated in the air, however carefully the heating be conducted. The reduction of the oxide can, on the contrary, be carried on with perfect safety, a lower oxide which is non-volatile at full red heat being, apparently, formed during the first stage of the reduction, so that, if the heating is regulated at the beginning, there is no danger of any loss being incurred.

The atomic weight of the element becomes 100, if calculated from the equivalent weight on the supposition that it is hexavalent, like molybdenum. But the number 100 is that already given to nipponium as its atomic weight (This Volume, Art. 15, p. 19), and nipponium differs from the element now under consideration in its oxide not being reducible by hydrogen, and in other respects. It is possible that nipponium, instead of being divalent, as was supposed, may prove to be a trivalent element, with an atomic weight of 150, but discussion on this point, as well as on the atomic weight of the new element, will be reserved, until the specific heat determinations of the two elements, now being undertaken by Prof. IKEDA of the Science College, and my analyses of their different compounds shall have been completed.

It may be here stated, by way of parenthesis, that a new rich source of nipponium has been discovered. On carefully examining samples of thorianite, there have been found, here and there, small, translucent, prismatic crystals, varying in colour from yellow to red. They are very hard and can scratch glass quite easily. The specific gravity of the mineral is 4.5, being about one-half of that of thorianite. This mineral was once thought to be zircon, but, on further examination, it has been found that it is a double silicate of zirconium and nipponium, and about 50 grs. of it have been picked out from 5 kilograms of thorianite. It is hoped that several grams of nipponium may now be obtained from this source, about a gram of the metal having been already prepared by the electrolysis of the double fluoride of nipponium and potassium.

Examination of the Sulphide Residue from Thorianite.

While in University College, London, Sir WILLIAM RAMSAY gave me for investigation 1½ kilograms of crude hydrogen sulphide precipitate obtained from 5 cwt. of thorianite. This was ignited, in the air, fused with hydrogen potassium sulphate, extracted with water and reprecipitated by hydrogen sulphide. The filtrate from the precipitated sulphides was treated as in the ordinary course of analysis, and the solution, after the iron-group precipitate had been removed, had a deep reddish brown colour. It did not, however, produce any precipitate with ammonium sulphide, but the colour was suspected to be due to the presence of an unknown element. The sulphur, separated out from the solution on the addition of hydrochloric acid after ammonium sulphide had been added, was found to possess a deep brown colour and to leave a brown residue on ignition. About 100 grams of this sulphur have been brought with me to Japan, and recently examined with the following results.

On ignition, the sulphur gave about 8 per cent of the residue. This was repeatedly extracted with hot concentrated nitric acid, and it was found that the first portions of the extract had a bluish green, and the later portions a reddish brown colour. Treatment with nitric acid was continued, until no more colour was imparted to it, but a considerable fraction of the brown residue was still left undissolved.

The colour of the first portions of the extract was somewhat like that of a cupric salt, but that it was not due to the presence of this element was shown by the fact that the dark brown—almost black—precipitate produced by sodium sulphide, after nitric acid had been evaporated off, was completely dissolved by an excess of the reagent. The sulphide, reprecipitated from the solution on the addition of hydrochloric acid, was moistened with concentrated nitric acid and ignited, and then fused with potassium nitrate. The brown residue, left on extracting the fused mass with water, was found to consist of an unknown oxide, mixed with ferric oxide, it being this unknown oxide which dissolves in nitric acid with a bluish green colour. The aqueous extract did not contain any molybdenum, but it did contain the same new element as occurs in molybdenite, forming the subject of the present paper, as was shown by the formation of a brown sulphide, soluble in ammonium carbonate to form a deep brown solution, the precipitation of the salts of barium, lead and silver, and, more especially, of the characteristic mercurous salt, as well as by the volatility and the crystalline nature of the oxide obtained from it.

The later portions of the nitric acid extract, which had a reddish brown colour, were evaporated to dryness, when a deliquescent, gummy mass of a brown colour was left behind. On ignition and subsequent fusion with potassium nitrate, it was found to be resolved into the same three constituents as were obtained from the first portions of the nitric acid extract, namely ferric oxide and the unknown oxide in the residue, after extracting the fused mass with water, this unknown oxide dissolving in nitric acid to form a bluish green solution, and the oxide of the new element in the aqueous extract. It must be here remarked that, although the nitric acid extracts, both green and brown, undeniably contain iron, as is shown by their subsequent treatment, they give no reactions with potassium ferrocyanide.

With regard to the unknown oxide, which dissolves in nitric acid with a bluish green colour, above referred to, no further observation has been made than that it is radioactive, and it is likely that the radioactivity of the sulphide residue from thorianite is due to the presence of this substance. It can be definitely stated that it does not contain any uranium. Since the brown coloured nitric acid extracts also give the same unknown oxide, dissolving in nitric acid with a bluish green colour, after fusion with potassium nitrate, it is possible that the difference in colour may be due to the existence of two different oxides of one and the same unknown element.

Conclusions.

1. Both molybdenite and thorianite contain a new element, which is closely allied to molybdenum.

2. It forms a complex salt (?) with ammonium molybdate, precipitable, from its aqueous solution, in a crystalline form on saturation with ammonium chloride.

3. It appears to form two different oxides, the higher oxide being similar in its properties to molybdenum trioxide and acting as an acidic oxide. The salts of barium, lead and silver, formed

from the higher oxide, resemble the corresponding molybdates, but the mercurous salt consists of golden yellow crystals.

4. The hydrated lower oxide (?) has a graphitic appearance and is insoluble in hot, dilute hydrochloric acid.

5. On heating in a current of hydrogen gas, either of the oxides produces the metal, which is non-fusible at a red heat. It burns brilliantly in the air, producing the higher oxide.

6. The equivalent weight of the metal is somewhat above that of molybdenum, being about 16.7.

7. In producing a brown sulphide and in other respects, above referred to, the new element resembles molybdenum, but is distinguished from the latter in producing no colour reactions, when a soluble salt of its higher oxide is reduced with zinc and hydrochloric acid, either in the presence or absence of potassium thiocyanate, and also by the fact that the metal dissolves in hot, concentrated hydrochloric acid.

8. The "new tin-group element", recently described by Miss EVANS is probably identical with the element, forming the subject of this paper.

9. A new rich source of nipponium has been discovered and, incidentally, described.

10. Besides nipponium and the new element now under consideration, thorianite appears to contain still another new element, the oxide of which is radioactive and dissolves in nitric acid to form a bluish green solution.

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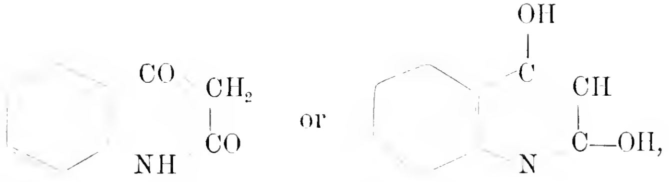
JOURNAL OF THE COLLEGE OF SCIENCE, IMPERIAL UNIVERSITY,
TŌKYŌ, JAPAN.
VOL. XXV., ARTICLE 17.

Formation of γ-Oxycarbostyril from *o*-Nitrobenzoylacetic Acid.

By

Kōichi Matsubara, *Rigakushi.*

γ-Oxycarbostyril or 2 : 4-dihydroxyquinoline,



the inner anhydride of *o*-aminobenzoylacetic acid, was first obtained by Baeyer and Bloem (Ber., 1882, **15**, 2151), by heating *o*-aminophenylpropiolic acid with concentrated sulphuric acid to 145°, in their attempt to prepare *o*-aminobenzoylacetic acid. Owing to the close relationship which exists between *o*-aminobenzoylacetic acid and several members of the indigo group, many other investigators have attempted to prepare this acid. All these attempts have, however, been unsuccessful, the product being always found to be γ-oxycarbostyril, which can also be obtained in other ways. Thus it was obtained by Friedlander and Weinberg (Ber., 1882, **15**, 2683) by the potash-fusion of γ-chloro- or γ-bromo-carbostyril; by Bischoff (Ber., 1889, **22**, 387 ; Ann., 1889, **251**, 377), by the reduction of ethyl *o*-nitrobenzoylacetate in alcoholic solution with tin and hydrochloric acid; by CAMPS (D. R. P., 1898, 102894; Ber., 1899, **32**, 3228; Arch. Pharm., 1899, **237**, 690; 1901, **239**, 601) by treating an absolutely dry solution of ethyl acetanthranilate in toluene with metallic sodium, and also by boiling *o*-acetophenyl urethane with an aqueous alcoholic solution of caustic soda for several hours. ERDMANN (Ber., 1899, **32**, 3570) obtained it by the action of metallic sodium on a mixture of ethyl anthranilate and ethyl acetate, ethyl acetanthranilate which is first formed giving off alcohol spontaneously or more easily on acidification. The BADISCHE ANILIN- UND SODA-FABRIK (D. R. P., 1900, 117167) patented a method of preparing it by heating an alkali or alkaline earth salt of acetanthranilic acid with dry alkali or alkaline earth to 150°.

During the course of some experiments with *o*-nitrobenzoylacetic acid, it was observed that this acid gave γ-oxycarbostyril on reduction with ferrous sulphate and ammonia. The use of ferrous sulphate and an alkali as a reducing agent is not new. WÖHLER in 1828 (Pogg. Ann., **13**, 448) had already used ferrous sulphate in presence of baryta to reduce picric acid and obtained picramic acid. BAEYER and BLOEM (Ber., 1882, **15**, 2147) reduced ethyl *o*-nitrophenylpropiolate by pouring its solution in ammonia into a saturated solution of ferrous sulphate, and obtained ethyl *o*-aminobenzoylacetate. Many other examples of the application of this salt with one or other alkali as a reducing agent can be found in the literature of the subject.

o-Nitrobenzoylacetic acid was prepared according to the method described by NEEDHAM and PERKIN (Jour. Chem. Soc., 1904, **85**, 148). After recrystallising from benzene, in which it dissolves slightly, its melting point was found to be 122°. NEEDHAM and PERKIN give 117°–120° as its melting point.

Ferrous sulphate (8 grams) was dissolved in water (20 c.c.) and an excess of ammonia was added to it. *o*-Nitrobenzoylacetic acid (1 gram) dissolved in ammonia was then added. The reaction took place at once in the cold, the greenish coloured ferrous hydroxide changing into the reddish coloured ferric hydroxide, which was filtered off. On neutralising the filtrate with hydrochloric acid, a colourless precipitate separated out, which was collected on a filter and drained on a porous porcelain plate. This precipitate does not dissolve in most of the ordinary organic solvents. It can be dissolved in a solution of sodium carbonate and is reprecipitated from this solution on acidification. It does not melt at 300°. All these properties correspond to those of γ-oxycarbostyril or 2 : 4-dihydroxyquinoline, which is the inner anhydride of *o*-aminobenzoylacetic acid, the reduction-product.

A sample recrystallised from glacial acetic acid gave the following percentage of nitrogen on analysis:

0.1663 gr. substance gave 12.2 c.c. nitrogen at
16° and 750.6 m.m. ... ... N = 8.44%,
$C_9H_7O_2N$ requires ... ... N = 8.70%.

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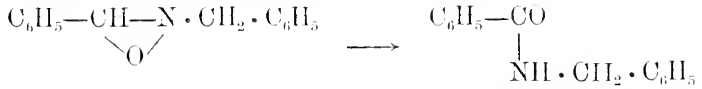
Molecular Rearrangement of N-Benzylbenzaldoxime.

By

Mitsuru Kuhara, *Rigakuhakushi, Ph. D.*

It has been shown by Beckmann[1] that, by the action of phosphorus pentachloride (or oxychloride) and water, as well as through the action of acetyl or benzoyl chloride, N-benzylbenzaldoxime undergoes a molecular rearrangement and yields benzylbenzamide:



N-Benzylbenzaldoxime. Benzylbenzamide.

The formation of the substituted acid amide in this manner evidently shows some similarity between the above change and the well known Beckmann rearrangement of ketoximes:

$$\begin{array}{c}R\text{—}C\text{—}R' \\ \| \\ NOH\end{array} \longrightarrow \begin{array}{l}R\text{—}CO \\ \quad | \\ NH\text{—}R'\end{array}$$

Ketoxime. Substituted acid amide.

With regard to the nature of the molecular rearrangement of N-benzylbenzaldoxime, Beckmann[2] states that a very small

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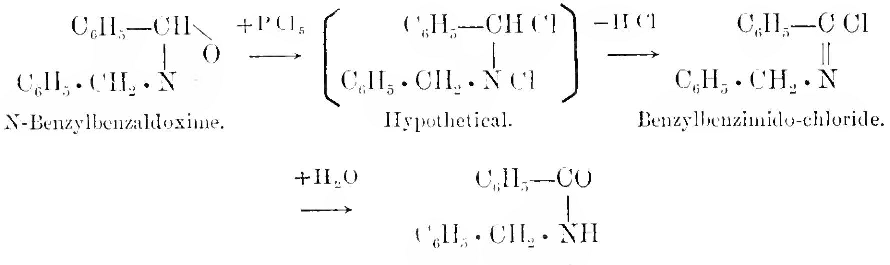
[1] Ber. deut. chem. Gesell., **26**, 2272.

[2] Ibid, **26**, 2280; **27**, 303.

quantity of the acid chloride suffices to transform smoothly a large quantity of the N-ether into the corresponding substituted acid amide by its catalytic action, and also that an attempt to isolate the intermediate product or products ended in a negative result.

Lately, however, the author has succeeded in isolating benzylbenzimido-chloride, $C_6H_5\cdot C\,Cl : N\cdot CH_2\cdot C_6H_5$, as an intermediate product of the rearrangement of N-benzylbenzaldoxime by the action of phosphorus pentachloride, and in converting the chloride into benzylbenzamide, $C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot C_6H_5$, by the action of water, and he is now able to put forward an explanation of the above molecular rearrangement, based upon the assumption that a hypothetical dichloro-substitution product is first formed, which, immediately parts with hydrochloric acid and yields benzylbenzimido-chloride as the intermediate product, this being followed by the formation of benzylbenzamide by the action of water. The change is evidently analogous, in part, to the molecular rearrangement of ketoximes, as may be seen from the following scheme:



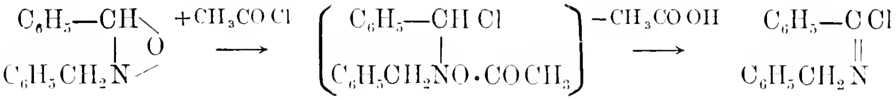
$$\begin{matrix} C_6H_5-CH\diagdown \\ |\quad O \\ C_6H_5\cdot CH_2\cdot N \end{matrix} \xrightarrow{+PCl_5} \left(\begin{matrix} C_6H_5-CH\,Cl \\ | \\ C_6H_5\cdot CH_2\cdot N\,Cl \end{matrix}\right) \xrightarrow{-H\,Cl} \begin{matrix} C_6H_5-C\,Cl \\ \| \\ C_6H_5\cdot CH_2\cdot N \end{matrix}$$

N-Benzylbenzaldoxime. Hypothetical. Benzylbenzimido-chloride.

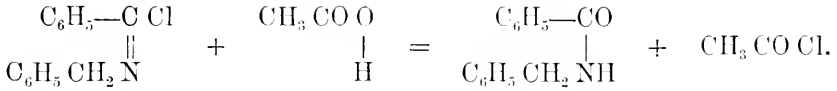
$$\xrightarrow{+H_2O} \begin{matrix} C_6H_5-CO \\ | \\ C_6H_5\cdot CH_2\cdot NH \end{matrix}$$

Benzylbenzamide.

It appears, therefore, highly probable that the molecular rearrangement of N-benzylbenzaldoxime by the action of an acid chloride, such as acetyl chloride, is due to the formation of the same intermediate product, benzylbenzimido-chloride, which is instantly changed into benzylbenzamide by the action of acetic acid generated in the reaction, the author and KAINOSHŌ[1] having already observed the actual production of phenylbenzamide, $C_6H_5\cdot CO\cdot NH\cdot C_6H_5$, from phenylbenzimido-chloride $C_6H_5\cdot CCl:N\cdot C_6H_5$, by the action of acetic acid. Thus, the rearrangement when acetyl chloride is used may be represented by the following scheme:



$$\begin{array}{l} C_6H_5\text{—}CH \\ \quad | \quad O \\ C_6H_5CH_2N \end{array} \xrightarrow{+CH_3COCl} \left[\begin{array}{l} C_6H_5\text{—}CHCl \\ \qquad | \\ C_6H_5CH_2NO\cdot COCH_3 \end{array}\right] \xrightarrow{-CH_3COOH} \begin{array}{r} C_6H_5\text{—}CCl \\ \| \\ C_6H_5CH_2N \end{array}$$



$$\begin{array}{r} C_6H_5\text{—}CCl \\ \| \\ C_6H_5\,CH_2N \end{array} + \begin{array}{c} CH_3COO \\ | \\ H \end{array} = \begin{array}{r} C_6H_5\text{—}CO \\ | \\ C_6H_5\,CH_2NH \end{array} + CH_3COCl.$$

The acetyl chloride thus formed in the last stage of the reaction will act upon the fresh portion of the N-ether, forming the addition product as before, immediately followed by the formation of benzylbenzimido-chloride with the separation of acetic acid, which will bring about the decomposition of the imido-chloride into benzylbenzamide, so that the same process continues until the N-ether is exhausted. A small quantity of the acid chloride must, therefore, be theoretically possible to convert an infinite quantity of N-benzylbenzaldoxime to benzylbenzamide, the acid chloride apparently remaining unchanged or acting as a catalyser.

The rearrangement of N-benzylbenzaldoxime in presence of an acid anhydride, such as acetic or benzoic anhydride, however, appears to proceed in a somewhat different way, because BECKMANN[2] claims to have obtained acetyl and benzoyl benzylbenzamides as the chief products of the rearrangement.

Experimental:—By gradually adding an equivalent quanti-

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[1] Memoirs, College of Science and Engineering, Kyoto, Vol. I, 259.

[2] Ber. deut. chem. Gesell., **26**, 2274.

ty of phosphorus pentachloride to a chloroform solution of benzylbenzaldoxime,[1] well cooled with cold water, a yellow coloured solution was produced. The residue, obtained by evaporating the solution, was treated with absolute ether in order to separate the product from phosphorus compounds. The ethereal solution thus formed left a yellow oil, on evaporation, which was again treated with absolute ether and the solution evaporated ; and by repeating the extraction several times, a yellow oil, free from phosphorus

YOSHIKAWA, one of our graduates, for his meritorious labour in carrying out these experiments.

Chemical Laboratory,
College of Science and Engineering, Kyoto.

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1. Ber. deut. chem. Gesell., **22**, 432.
2. Ibid, **30**, 1788.
3. Ibid, **30**, 1788.
4. Ibid, **23**, 3332; **26**, 2273.

JOURNAL OF THE COLLEGE OF SCIENCE, IMPERIAL UNIVERSITY,
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VOL. XXV., ARTICLE 19.

Flora Montana Formosæ

An
Enumeration of the Plants found on Mt. Morrison, the Central Chain, and Other Mountainous Regions of Formosa at Altitudes of 3,000–13,000 ft.

By

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With 41 plates and 16 woodcuts.

Introduction.

In the year 1905, Professor MATSUMURA and I jointly published an enumeration[1] of plants found in Formosa, comprising about two thousand species of flowering plants, ferns and their allies. At that time, our collections, with the exception of a few sets of plants found on Mt. Morrison, did not extend to elevations of any great altitude. It is, therefore, quite proper to regard it as an enumeration of the flora of the low districts.

On the botany of the montane zone, there exists no special

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[1] MATSUMURA, J., and HAYATA, B.—Enumeratio Plantarum Formosanarum, in Journ. Sci. Coll., Imp. Univ. Tōkyō, XXII., 702 pages, with 18 plates, 1906.

publication, except a few papers[1] that have appeared in the Tōkyō Botanical Magazine.

In the present work, it is my desire to give some complete information relating to the montane zone of the island. The majority of the collections upon which this work is based, were made by the officers of the Government of Formosa. Some materials were collected by Prof. S. HONDA in 1896, and by Mr. R. TORII in 1900, both from Mt. Morrison.

In November 1905, a botanical excursion was carried out for the first time on the above mountain by Messrs. T. KAWAKAMI, S. NAGASAWA and G. NAKAHARA, and numerous specimens were sent to me for determination by Mr. S. NAGASAWA. In October 1906, Messrs. T. KAWAKAMI and U. MORI made another excursion to the same mountain, and collected quite a number of plants. Another ascent of the same peak was made by Mr. G. NAKAHARA who had equal success. Other mountainous districts of Taitō and the central ranges were botanically explored by Mr. U. MORI in the same year. Some parts of the hill regions of Taihoku, Taichū, Tainan and Kōshūn have been little by little botanized for some years; but the greater part of the island remains as yet unexplored.

All the determinations of the species have been worked out by me; but a few families with which I am not yet thoroughly acquainted are almost entirely omitted in the present paper. The

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[1] MATSUMURA, J.—On Coniferæ of Loo-choo and Formosa, in Tōkyō Bot. Mag. XV. pp. 137-141.

HAYATA, B.—On the Distribution of the Formosan Conifers, in Tōkyō Bot. Mag. XIX. pp. 43-61.

HAYATA, B.—Contributions to the Alpine Flora of Formosa, in Tōkyō Bot. Mag. XX. pp. 14-22, Pl. I.

HAYATA, B.—Contributions to the Flora of Mt. Morrison, in Tōkyō Bot. Mag. XX. pp. 52-58, and pp. 73-75.

work on these families will be specially treated in the near future.

Although the materials here treated are rather limited and further exploration will reveal many new features, the present work will, I hope, throw some light upon the study of the montane flora of the island.

In conclusion, I wish to tender my sincere thanks to Prof. J. MATSUMURA under whose oversight this work has been carried out. Thanks are also due to Messrs. T. KAWAKAMI, S. NAGASAWA and G. NAKAHARA, who all have generously put their important collections at my disposal. Lastly, I desire to express my cordial gratitude to Mr. N. KONISHI whose valuable collections have enabled me to make most interesting discoveries on Coniferæ and Quercineæ. A new species of Coniferæ is named *Cunninghamia Konishii* in recognition of his kindness.

March 14th., 1908.

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I.) Elements of the Flora of the Montane Zone.

The montane zone treated in the present paper embraces a most extensive area from 3,000 ft. up to 13,000 ft. above sea level, including in its centre Mt. Morrison, the highest peak of the Japanese Empire. This mountain, lying a little within the tropic of Cancer, attains a height of 13,120 ft. It presents various climatal features from tropical through temperate up to those of cold regions, and in winter snow is frequently seen on the summit.

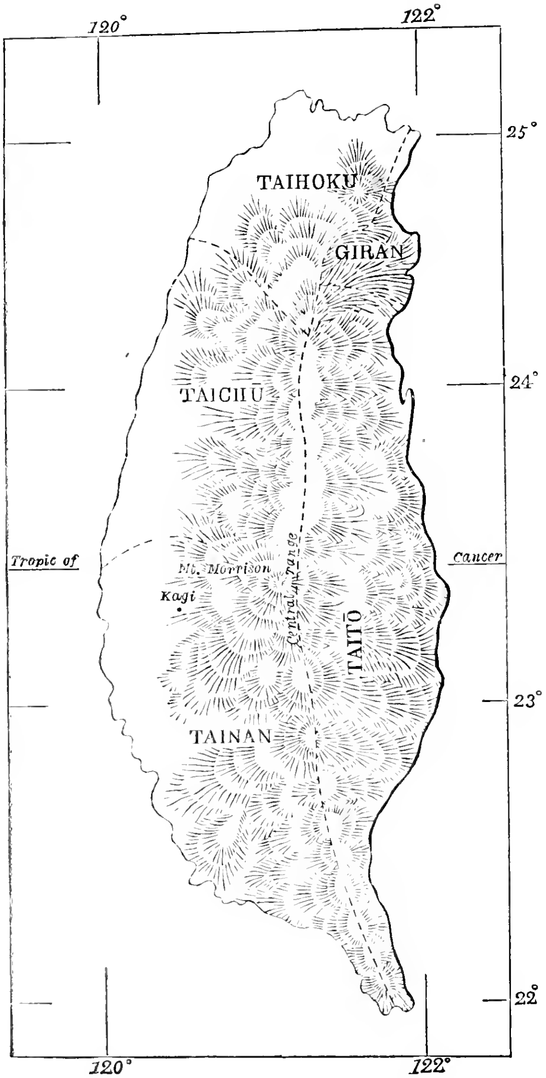

Fig. 1. Sketch-map of Formosa.
------ Prefectural boundaries.

The term flora used in this work includes flowering plants, ferns and their allies. The lower cryptogams are entirely omitted. I have enumerated 392 species belonging to 79 families and 266 genera. Most of the species are northern elements.

It is a very interesting matter to compare this flora with the floras of the neighbouring countries, and to consider their relations. So far as I am aware, no attempt of this kind has yet been made.

In the year 1905, I published a paper[1] "On the Distribution of the Formosan Conifers" in which I pointed out that the flora of the Conifers of Formosa has a far closer relation to that of Japan than to that of China, regardless of geographical proximity. In this paper, I have compared all families of flowering plants in the montane zone, and found that the conclusion I had made from the study of Conifers holds good for the general features of the flora. I shall refer to this matter later on.

Before we go further in the discussion of this interesting subject, it is necessary to consider the elements of the montane flora. A list of plants, therefore, should properly be given here, with indications as to their distribution.

Regarding the remarks as to distribution given in this list, I have referred to the following literature and herbarium.

1) The Malay peninsula and archipelago:

BLUME :—Flora Javæ, 4 vols.
MIQUEL :—Flora van Nederlandsch Indië, 3 vols.
VIDAL :—Revision de Plantas Vasculares Filipinas.
:—Phanerogamæ Cuningianæ Philippinarum.
MERRILL :—New or Noteworthy Philippine Plants, &c, ... in Publications from the Department of the Interior, Bureau of Government Laboratories.
The Philippine Journal of Science, I. Suppl. Botany.
HOOK. f. :—Flora of British India, 7 vols.

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[1] HAYATA, B.—On the Distribution of the Formosan Conifers, in Tōkyō Bot. Mag XIX. pp. 13-61.

TRIMEN :—A Hand Book of the Flora of Ceylon, 5 parts.

2) The Himalayas :—

HOOK. f. :—Flora of British India, 7 vols.

3) Central and southern China (including Tibet) :—

DIELS :—Die Flora von Central-China, in Engl. Bot. Jahrb. XXIX., pp. 169-657.

„ :—Beiträge zur Flora des Tsin ling shan und andere Zusätze zur Flora von Central-China, in Beiblatt zu den Bot. Jahrb. XXXVI. pp. 1-138.

FRANCHET :—Plantæ Davidianæ ex Sinarum Imperio.

FORBES and HEMSLEY :—Index Floræ Sinensis, 3 vols.

4) Northern China (including Korea, Manchuria, Amurland, and Saghalien :—

FORBES and HEMSLEY :—Index Floræ Sinensis, 3 vols.

MAXIMOWICZ :—Primitiæ Floræ Amurensis.

SCHMIDT :—Reisen im Amur-lande und auf der Insel Sachalin.

KOMAROV :—Flora Manshuriæ, 2 vols.

PALIBIN :—Conspectus Floræ Koreæ.

NAKAI :—Polygonaceæ Koreanæ, in Journ. Sci. Coll. XXIII. Art. 11.

5) Japan :—

FRANCHET et SAVATIER :—Enumeratio Plantarum Japonicarum, 2 vols.

Herbarium of the Botanical Institute, College of Science, Imperial University, Tōkyō.

ITO et MATSUMURA :—Tentamen Florae Lutchuensis, in Journ. Sci. Coll. XII. pp. 263-541.

MATSUMURA :—Index Plantarum Japonicarum, I. et II.-1.

„ :—Enumeration of selected scientific Names of both native and foreign Plants.

MAKINO :—Observations on the Flora of Japan, 6 Fascicles, (1901-'06).

LIST OF THE ELEMENTS OF THE MONTANE FLORA.

Formosa.	The Malay pen. & archipelago.	The Himalayas.	Central and southern China (including Tibet).	Northern China (including east Siberia & Amur).	Japan.	Arctic.	Antarctic.	North America.	Extra Asiatic Old World.
Anemone luzoniensis Rolfe	+	+1)							
Clematis lasiandra Maxim. var. Nagasawai Hayata.	......	......	......	......	type				
Clematis longisepala Hayata									
Clematis Morii Hayata									
Clematis tōzanensis Hayata	+2)								
Clematis Wightiana Wall.?	......	+							
Thalictrum Fauriei Hayata									
Trochodendron aralioides Sieb. et Zucc.	......	......	......	......	+				
Illicium sp.	......	+	+	......	+				
Kadsura japonica Linn	......	......	?	......	+				
Melodorum Oldhami Hemsl.									
Akebia sp.	......	......	+	+	+				
Berberis nepalensis Spreng.	+	+	+	+	+				
Berberis sp.									
Corydalis sp.	......	+	+	+	+				
Arabis alpina Linn	......	+	+	+	......	.....	......	......	Europe
Arabis taraxacifolia Anders.	......	+							
Arabis sp.									
Cardamine reniformis Hayata									
Cardamine sp.									
Viola japonica Langsd.	......	......	+	+	+				
Viola Kawakamii Hayata									
Viola Nagasawai Hayata									
Viola tōzanensis Hayata									
Viola sp.									
Idesia polycarpa Maxim.	......	......	+	......	+				
Polygala arcuata Hayata									

1) Anemone vitifolia Ham. 2) Clematis smilacifolia Wall.

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Polygala japonica Houtt.	......	+	+	+	+	......	......	......	Austr.
Dianthus superbus Linn.	......	......	+	+	+	......	.....	......	Europe
Dianthus sp.									
Silene Fortunei Vis.	......	......	+	+					
Cucubalus baccifer Linn.	.....	+	+	+	+	......	......	+	Europe
Cerastium morrisonense Hayata.									
Cerastium pilosum Ledeb.	......	......	......	+					
Stellaria stellato-pilosa Hayata									
Hypericum attenuatum Choisy.	......	......	+	+					
Ternstrœmia japonica Thunb.	+	....	+	......	+				
Eurya japonica Thunb.	+	?	+	......	+				
Eurya strigillosa Hayata									
Actinidia callosa Lindl.	......	+	+	......	+				
Stachyurus præcox Sieb. et Zucc.	......	......	+	......	+				
Schima Noronhæ Reinw.	+	......	......	......	Loo-choo.				
Thea brachycarpa Hayata									
Thea caudata (Wall.)	......	+	+						
Triumfetta pilosa Roth.	+	......	+	......	......	......	......	......	Africa
Elæocarpus decipiens Hemsl.	......	......	+	......	Loo-choo.				
Geranium Robertianum Linn.	......	......	+	+	+	......	......	......	+
Geranium uniflorum Hayata.									
Oxalis Griffithii Edgew. et Hk. f.	......	+	+						
Impatiens uniflora Hayata									
Bœnninghausenia albiflora Reichb.	+	+	+	......	+				
Evodia meliæfolia Benth.	......	+	+	......	South				
Skimmia japonica Thunb.	+	+	+	......	+				
Murraya exotica Linn.	+	......	+						

Formosa.	The Malay pen. & archipelago.	The Himalayas.	Central and southern China (including Tibet).	Northern China (including east Siberia & Amur).	Japan.	Arctic.	Antarctic.	North America.	Extra Asiatic Old World.
Euonymus echinatus Wall.	......	+	+	......	South				
Euonymus trichocarpus Hayata									
Celastrus articulatus Thunb.	......	......	+	+	+				
Rhamnus arguta Maxim. var. Nakaharai Hayata	......	.....	......	+					
Acer sp.									
Cardiospermum Halicacabum Linn.	+	......	+	......	Loo-choo	......	......	+	Africa
Rhus intermedia Hayata	......	......	......	.....	+1)				
Pistacia formosana Matsumura	......	......	+2)	+2)					
Crotalaria formosana Matsumura									
Desmodium parvifolium. DC.	+	.....	+	......	+				
Desmodium polycarpum DC.	+	......	+	......	+				
Desmodium pulchellum Benth.	+	......	+						
Desmodium sinuatum Blume.	+	+	+						
Dumasia bicolor Hayata									
Cajanus indicus Spreng.	+								
Flemingia strobilifera R. Br.	+	+							
Prunus campanulata Maxim.	......	......	+	......	Loo-choo.				
Prunus Kawakamii Hayata	......	......	+3)	+3)	+3)				
Spiræa prunifolia Sieb. et Zucc.	......	......	+	+	+				
Spiræa sp.									
Rubus elegans Hayata									
Rubus corchorifolius Linn. f. var. glaber Matsumura	......	......	type	......	type				
Rubus fraxinifolius Poir.	+								
Rubus pectinellus Maxim.	+	.....	......	......	+				
Rubus pentalobus Hayata									

1) Rhus Toxicodendron Linn. var. radicans Engl. 2) Pistacia chinensis Bunge.
3) Prunus japonica Thunb.

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Rubus Rolfei Vidal, var. lanatus Hayata	type								
Rubus rosaefolius Sm. var. hirsutus Hayata	......	type	type	......	type				
Fragaria sp.									
Potentilla gelida C. A. Mey.	....	......	+	+	+				
Potentilla leuconota Don. var. morrisonicola Hayata	......	type	type	type					
Sibbaldia procumbens Linn.	.....	+	+	+	+	......	......	+	+
Rosa sp.									
Astilbe chinensis Franch. et Sav.	......	......	+	+	+				
Astilbe chinensis Franch. et Sav. var. longicarpa Hayata									
Astilbe macroflora Hayata									
Chrysosplenium sp.	......	+	+	+	+	......	......	+	
Mitella japonica Miq	......	......	......	......	+				
Parnassia palustris Linn	......	Tibet.	......	+	+	......	......	+	+
Hydrangea chinensis Maxim	......	......	+	......	South.				
Hydrangea glabra Hayata									
Hydrangea integra Hayata									
Hydrangea Kawakamii Hayata									
Hydrangea longifolia Hayata									
Deutzia scabra Thunb	......	......	+	......	+				
Cardiandra formosana Hayata	......	......	+1)	......	+2)				
Ribes formosanum Hayata									
Sedum morrisonense Hayata									
Sedum sp.	......	+	+	+	+	......	......	+	

1) Cardiandra sinensis Hemsley   2) Cardiandra alternifolia Sieb. et Zucc.

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Kalanchoë sp.									
Haloragis micrantha R. Br. ..	+	+	+	......	+	......	......	......	Austr.
Myriophyllum spicatum Linn.	......	?	......	+	+	......	......	+	
Eugenia sinensis Hemsl.	......	......	+						
Osbeckia aspera Blume......	+								
Barthea formosana Hayata ..	......	......	+1)						
Sarcopyramis nepalensis Wall.	+	......	+						
Epilobium alpinum Linn. ...	......	+	......	......	......	......	......	......	Europe
Epilobium roseum Schreb. ..	......	+	+	+	+	......	......	+	+
Circæa alpina Linn.	......	+	+	+	+	+	......	+	+
Thladiantha formosana Hayata.	......	......	+2)						
Gynostemma pedatum Blume.	+	+	+	......	+				
Hydrocotyle javanica Thunb.	+	......	+	......	south +				
Hydrocotyle rotundifolia Roxb.	+	......	+	+	+	......	......	......	Africa
Hydrocotyle setulosa Hayata.									
Sanicula petagnioides Hayata.									
Acanthopanax aculeatum Seem.	......	+	+	......	+				
Fatsia multicarpa Hayata....	......	......	......	......	+3)				
Helwingia rusciflora Willd. ..	......	......	+	......	+				
Heptapleurum octophyllum Benth.	......	......	+	......	south				
Heptapleurum racemosum Bedd.	+								
Oreopanax formosana Hayata.	......	......	......	......	......	......	......	Tropical America	
Hedera Helix Linn.	......	+	......	+	+	......	......	......	Africa
Dendropanax sp.									
Marlea begoniæfolia Roxb. ..	......	+	+	......	+4)				
Aucuba japonica Thunb.	......	+	+	+	+				
Ophiorrhiza pumila Champ. ..	......	......	+						

1) Barthea chinensis Hook.

2) Thladiantha nudiflora Hemsl.

3) Fatsia japonica Decne. et Planch.

4) Marlea platanifolia S. et Z.

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Knoxia corymbosa Willd.	+	+	+	......	......	......	......	......	Austr.
Damnacanthus angustifolius Hayata.									
Damnacanthus indicus Gærtn. f.	......	+	+	......	+				
Lasianthus formosensis Matsumura.									
Pæderia tomentosa Blume.	+	+	+	......	+				
Nertera nigricarpa Hayata.	+1)	......	+2)	......	......	......	+1)		
Rubia cordifolia Linn.	+	+	+	......	+	......	......	......	+
Rubia lanceolata Hayata.									
Galium brachypodium Maxim.	......	......	......	......	+				
Patrinia scabiosæfolia Link.	......	......	+	+	+	....	......	+	
Patrinia villosa Juss.	......	.....	+	+	+				
Hoeckia Aschersoniana Engl. et Græbn.	......	......	+						
Scabiosa lacerifolia Hayata.									
Ethulia conyzoides Linn.	+								
Vernonia Andersoni Clarke.	......	+	+						
Vernonia cinerea Less.	+	?	+						
Adenostemma viscosum Forst	+	......	+	......	+	......	......	+	+
Ageratum conyzoides Linn.	+	......	+	+	+	......	......	+	+
Eupatorium formosanum Hayata.									
Eupatorium Lindleyanum DC.	....	+	+	+	+	......	....	+	
Eupatorium Tashiroi Hayata.									
Solidago Virga-aurea Linn.	......	+	+	+	+	+	+	+	+
Myriactis Wightii DC.	+	+	+3)						
Aster baccharoides Steetz.	......	......	+						
Aster scaber Thunb.	......	......	+	+	+	......	......	+	
Aster trinervius Roxb.	......	+	+	+	+	....	....	+	
Erigeron morrisonensis Hayata									

1) Nertera depressa Banks et Sol. 2) Nertera sinensis Hemsl.
3) Myriactis nepalensis Less.

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Laggera alata Sch. Bip.	+	+	+						
Leontopodium microphyllum Hayata.									
Anaphalis margaritacea B. et H. form. morrisonicola	......	type	type	type	type	......	......	type	
Anaphalis Nagasawai Hayata									
Blumea chinensis DC.	+	+	hieracifolia +						
Gnaphalium hypoleucum DC.	......	+	+	......	+				
Gnaphalium lineare Hayata									
Gnaphalium luteo-album Linn.	+	+							
Gnaphalium niitakayamense Hayata.									
Carpesium acutum Hayata									
Siegesbeckia orientalis Linn.	+	+	+	+	+	......	......	+	+
Spilanthes Acmella Linn.	+								
Chrysanthemum indicum Linn.	......	......	+	+	+				
Artemisia japonica Thunb.	......	+	+	+	+	......	......	+	
Artemisia niitakayamensis Hayata.									
Artemisia paucicarpa Hayata									
Artemisia scoparia Waldst. et Kit.	.....	......	+	+	+	......	......	+	Europe
Petasites tricholobus Franch.	......	......	+						
Gynura flava Hayata									
Senecio monanthus Diels.	......	......	+						
Senecio scandens Buch.-Ham.	+	+	+	......	south				
Echinops dahuricus Fisch.	......	......	+	+	+				
Cnicus Wallichii Hook. f.	+	+	+						
Saussurea japonica DC. var. longicephala Hayata.	......	......	type	type	type	......	......	+	
Saussurea sp.									

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Ainsliaea macroclinidioides HAYATA.									
Ainsliaea morrisonicola HAYATA.									
Ainsliaea reflexa MERRILL.	+								
Picris hieracioides LINN.	......	+	+	+	+				
Lactuca versicolor SCH. BIP.	......	......	+	+	+	......	......	+	
Pratia begonifolia LINDL.	+	+	+						
Lobelia affinis WALL.	+	......	+						
Lobelia pyramidalis WALL.	......	+	+						
Wahlenbergia gracilis A. DC.	+	......	+	......	south	......	......	......	Austr.
Codonopsis sp.	......	+	+	+	+	......	......	+	
Campanumoea axillaris OLIVER.	......	......	+	......	Loochoo				
Campanumoea javanica BLUME.	+	+	+	......	+				
Peracarpa carnosa HOOK. f. et THOMS.	......	+	+	......	+				
Adenophora verticillata FISCH.	......	......	+	......	+				
Adenophora verticillata FISCH. var. linearis HAYATA									
Adenophora polymorpha LEDEB. var. Lamarckii TRAUTV.	......	......	+	+	+	......	......	+	
Adenophora polymorpha LEDEB. var. coronopifolia TRAUTV.									
Vaccinium emarginatum HAYATA.									
Vaccinium Merrillianum HAYATA.									
Gaultheria Cumingiana VIDAL.	+								
Gaultheria Itōana HAYATA.									
Pieris formosa D. DON.	......	+	+						
Pieris ovalifolia D. DON.	......	+	+	......	+				
Rhododendron brachycarpum G. DON.	....	......	......	Manchuria	+				

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Rhododendron ellipticum MAXIM.	.....	......	south	......	Loo-Choo				
Rhododendron Nakaharai HAYATA.									
Rhododendron Oldhami MAXIM.									
Rhododendron Oldhami MAXIM. var. glandulosum HAYATA.									
Rhododendron pseudochrysanthum HAYATA									
Pyrola morrisonensis HAYATA									
Pyrola rotundifolia LINN. var. albiflora MAXIM.	......	+	+	+	+	......	......	+	+
Shortia rotundifolia MAKINO..	......	......	......	......	south				
Primula sp.									
Lysimachia sikokiana MIQ. ..	......	......	......	......	+				
Symplocos confusa BRAND. ...	+								
Symplocos modesta BRAND. ..									
Symplocos morrisonicola HAYATA									
Symplocos spicata ROXB......	+	......	+	......	+				
Osmanthus sp.									
Osmanthus sp.									
Dischidia formosana MAXIM.									
Logania dentata HAYATA	+	+1)							
Crawfurdia fasciculata WALL.	......	+	+	......	+				
Gentiana cæspitosa HAYATA									
Gentiana fasciculata HAYATA									
Gentiana flavescens HAYATA..									
Gentiana formosana HAYATA..									
Gentiana humilis STEV.	......	......	Tibet						
Gentiana tenuissima HAYATA									
Gentiana scabrida HAYATA ..									

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1) Hemiphragma heterophyllum WALLICH.

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Swertia alata Hayata........									
Swertia sp.									
Ellisiophyllum pinnatum Makino.	......	+2)	+3)	....	+				
Cynoglossum micranthum Desf.	+	......	+	....	......	......	......	.....	Africa
Trigonotis formosana Hayata									
Solanum sp.									
Scrophularia alata A. Gray, var. duplicato-serrata Miq.	......	......	+	....	+				
Mazus rugosus Lour	+	+	+	+	+				
Torenia peduncularis Benth..	+	......	+	....	?				
Bonnaya veronicæfolia Spreng.	+	......	+						
Rehmannia Oldhami Hemsl..									
Veronica morrisonicola Hayata									
Veronica spuria Linn........	......	......	+	+	+	......	......	......	Europe
Sopubia formosana Hayata ..	+4)	+4)	+4)						
Phtheirospermum chinense Bunge.	......	......	+	+	+	......	......	+	
Euphrasia borneensis Stapf..	+								
Euphrasia petiolaris Wettst.	......	+							
Orobanche cærulescens Steph.	.....	?	+	+	+	......	......	+	
Lysionotus pauciflora Maxim.	......	......	+	....	+				
Rhynchoglossum obliquum Blume.	+								
Chirita anochorata Hance....	......	......	+						
Conandron ramondioides S. et Z.	......	......	....	....	+				
Strobilanthes flaccidifolius Nees.	......	+	+	....	south				
Codonacanthus pauciflorus Nees.	......	+	+						
Justisia procumbens Linn....	+	......	+	....	+	......	......	......	Austr.
Rungia parviflora Nees.	+	......	+						

1) Ellisiophyllum pinnatum Makino. = Ellisiophyllum reptans Maxim.
= 2) Moseleya pinnata Hemsl. = 3) Hornemannia pinnata Benth. = Sibthorpia pinnata Benth.
4) Sopubia trifida Buch.-Ham.

Formosa.	The Malay pen. & archipelago.	The Himalayas.	Central and southern China (including Tibet).	Northern China (including east Siberia & Amur).	Japan.	Arctic.	Antarctic.	North America.	Extra Asiatic Old World.
Hypoëstes purpurea R. Br.	+	.....	+						
Mesona elegans Hayata									
Mesona procumbens Hemsl.									
Origanum vulgare Linn.	......	+	+	+	......	......	......	+	Europe, Africa
Salvia scapiformis Hance var. pinnata Hayata.	......	......	+						
Scutellaria luzonica Rolfe	+								
Anisomeles ovata R. Br.	+	......	+						
Leucas javanica Benth.	+	......	......	......	Loo-choo				
Polygonum biconvexum Hayata.									
Polygonum chinense Linn.	+	......	+	......	+				
Polygonum cuspidatum Sieb. et Zucc.	......	......	+	......	+				
Polygonum minutum Hayata.									
Polygonum morrisonense Hayata.									
Polygonum Posumbu Buch.-Ham.	+	+	+	+	+				
Asarum macranthum Hook. f.									
Piper Futokadsura Sieb.	......	......	......	......	+				
Peperomia dindygulensis Miq.	+	......	+						
Peperomia Nakaharai Hayata.									
Peperomia reflexa A. Dietr.	+	......	+	......	......	......	......	+	Austr. Africa
Chloranthus serratus Roem. et Schult.	......	......	+	......	+				
Cinnamomum Camphora Nees. et Eberm.	......	......	+	+	+				
Helicia formosana Hemsley									
Daphne Championi Benth.	......	......	+						
Stellera Chamæjasme Linn.	......	+	......	+					
Elæagnus umbellata Thunb.	......	+	+	+	+				
Loranthus Yadoriki Sieb.	......	......	+	......	+				
Loranthus Owatarii Hayata									

Formosa.	The Malay pen. & archipelago.	The Himalayas.	Central and southern China (including Tibet).	Northern China (including east Siberia & Amur).	Japan.	Arctic.	Antarctic.	North America.	Extra Asiatic Old World.
Viscum articulatum BURM.	+	+	+	......	south				
Viscum orientale WILLD. var. multinerve HAYATA.	+								
Balanophora parvior HAYATA.									
Balanophora spicata HAYATA.									
Buxus sempervirens LINN.	......	+	+	......	+	......	......	......	Europe Africa
Glochidion formosanum HAYATA.									
Glochidion zeylanicum A. JUSS.	+								
Aleurites cordata STEUD	......	......	+	......	+				
Mercurialis lasiocarpa SIEB. et ZUCC.	......	.....	+	+	+				
Mallotus cochinchinensis LOUR.	+	......	+						
Fatoua pilosa GAUD.	+	......	+	......	+				
Morus alba LINN.	......	......	+	+	+				
Urtica Thunbergiana SIEB et ZUCC.	......	......	+	......	+				
Girardinia heterophylla DECNE	+	+							
Pilea stipulosa MIQ.	+	+	+	......	Loo-choo				
Pilea Wattersii HANCE.									
Lecanthus Wightii WEDD.	+	+							
Elatostema minutum HAYATA.									
Elatostema sessile FORST. var. cuspidatum WEDD.	+	......	+	......	+				
Procris laevigata BLUME.	+	......	+						
Juglans sp.	......	+	+	+	+	......	......	+	
Engelhardtia spicata BLUME. var. formosana HAYATA.	+	+							
Alnus maritima NUTT. var. formosana BURKILL.	.....	......	......	+	+	......	......	+	

Formosa.	The Malay pen. & archipelago.	The Himalayas.	Central and southern China (including Tibet).	Northern China (including east Siberia & Amur).	Japan.	Arctic.	Antarctic.	North America.	Extra Asiatic Old World.
Carpinus sp.	......	+	+	+	+	......	......	+	
Quercus amygdalifolia Skan.									
Quercus dentata Thunb.	......	......	+	+	+				
Quercus formosana Skan.									
Quercus glauca Thunb.	......	+	+	......	+				
Quercus Kawakamii Hayata.									
Quercus Konishii Hayata.									
Quercus serrata Thunb.	......	+	+	+	+				
Quercus Junghuhnii Miq.	+								
Quercus variabilis Blume.									
Quercus sp.									
Castanopsis indica A. DC.	......	+							
Castanopsis taiwaniana Hayata.									
Fagus sp.	......	......	+	......	+	......	......	+	
Salix sp.									
Libocedrus macrolepis Benth.	......	......	+						
Chamaecyparis formosensis Matsumura.	......	......	......	......	+1)				
Chamaecyparis obtusa Sieb. et Zucc.	......	......	......	......	+	......	......	+2)	
Juniperus formosana Hayata.	......	+3)	+3)	+3)					
Juniperus morrisonicola Hayata.									
Cunninghamia Konishii Hayata.									
Taiwania cryptomerioides Hayata.									
Cephalotaxus sp.	......	......	+	+	+				
Taxus sp.	......	+	+	+	+				
Pinus Armandi Franch. var. Mastersiana Hayata.	......	......	+						

1) Chamaecyparis pisifera S. et Z. 2) Chamaecyparis Lawsoniana Parl.

3) Juniperus communis Linn.

Formosa.	The Malay pen. & archipelago.	The Himalayas.	Central and southern China (including Tibet).	Northern China (including east Siberia & Amur).	Japan.	Arctic.	Antarctic.	North America.	Extra Asiatic Old World.
Pinus formosana HAYATA	......	......	....	....	+1)				
Pinus sp.									
Pinus sp.									
Picea morrisonicola HAYATA.	......	......	....	*	*				
Keteleeria Davidiana BEISSN. var. formosana HAYATA.	......	.....	+						
Tsuga formosana HAYATA	.....	......	....	....	+2)				
Pseudotsuga japonica SHIRAS.	......	......	....	......	+				
Abies Mariesii MASTERS, var. Kawakamii HAYATA.	......	......	....	....	+				
Peliosanthes courtallensis WIGHT.	......	+	+3)						
Smilacina japonica A. GRAY.	......	.....	+	+	+				
Tricyrtis lasiocarpa MATSUMURA.									
Tricyrtis stolonifera MATSUMURA.									
Metanarthecium foliatum MAXIM.	......	......	....	....	+				
Disporum sp.	......	+	+	+	+	......	......	+	
Polygonatum officinale ALL. var. Maximowiczii MAXIM.	.....	......	+	+	+				
Paris lancifolia HAYATA									
Aneilema divergens CLARKE.	.....	+	+						
Cyanotis arachnoidea CLARKE.	+								
Luzula effusa BUCH.	.....	+	+						
Luzula spicata DC.	......	+	....	......	......	+	.....	+	
Juncus effusus LINN.	......	+	+	+	+	......	.....	+	Africa, Austr.
Juncus Maximowiczii BUCH.	......	......	....	....	+				
Arisaema sp.									

1) Pinus parviflora S. et Z.

2) Tsuga diversifolia MAXIM.

3) Peliosanthes Delavayi FRANCH.

* Picea Glehni FR. SCHM.

Formosa.	The Malay pen. & archipelago.	The Himalayas.	Central and southern China (including Tibet).	Northern China (including east Siberia & Amur).	Japan.	Arctic.	Antarctic.	North America.	Extra Asiatic Old World.
Alocasia sp.									
Bulbostylis capillaris Kunth, var. trifida Clarke.	......	+	+	......	+				
Scirpus morrisonensis Hayata									
Carex sp.									
Isachne Clarkei Hook. f.	......	+							
Panicum montanum Roxb. ..	+	......	+						
Oplismenus undulatifolius Beauv. var. imbecillis Hack.	+	+	+	+ ?	+				
Arundinella setosa Trin.	+	......	+						
Miscanthus sinensis Anderss. var. formosanus Hack.	type	......	type	type	type				
Saccharum Narenga Buch.-Ham.	......	+	+						
Spodiopogon Kawakamii Hayata									
Spodiopogon tainanensis Hayata									
Pollinia ciliata Trin. var. Wallichiana Hack.	+	......	+						
Cymbopogon Nardus Rendle subsp. marginatus var. Gœringii Rendle.	+	......	+	......	+				
Agrostis Clarkei Hook. f.	......	+							
Calamagrostis arundinacea Roth.	......	+	......	......	+	......	......	......	Europe
Calamagrostis arundinacea Roth. var. nipponica Hack.	+	......	......	......	+				
Deschampsia cæspitosa Beauv.	......	+	+	+	+	+	+		
Deschampsia flexuosa Trin...	......	......	......	......	+	......	......	......	Europe
Trisetum subspicatum Beauv.	......	+	+	+	+	+	+		
Arundo formosana Hack.									
Brachypodium Kawakamii Hayata									

Formosa.	The Malay pen. & archipelago.	The Himalayas,	Central and southern China (including Tibet).	Northern China (including east Siberia & Amur).	Japan.	Arctic.	Antarctic.	North America.	Extra Asiatic Old World.
Brachypodium sylvaticum BEAUV.	Philip. +	+	+	+	+	......	......	......	Europe
Festuca ovina LINN.	......	......	+	+	+	......	......	......	Europe
Arundinaria niitakayamensis HAYATA.									
Lycopodium clavatum LINN.	+	+	+	+	+	+			
Lycopodium complaratum LINN.									
var. Chamaecyparissus A. BR.	+	+	+	+	+				
Lycopodium obscurum LINN.	......	......	......	Manchuria	+	......	......	+	
Lycopodium serratum THUNB.	+	+	+	......	+				
Polystichum amabile SM.	+	......	+	......	south				
Polystichum niitakayamensis HAYATA.									
Asplenium laciniatum DON. ..	......	+	......	......	+				
Asplenium Trichomanes LINN.	......	+	+	+	+	+	+		
Coniogramme fraxinea FÉE.	+	+	+	Manchuria	+				
Plagiogyria glauca METT. var. philippinensis CHRIST.	+								
Plagiogyria Matsumureana MAKINO.	......	......	......	......	+				
Pteridium aquilinum KUHN. var. lanuginosum BORY.	+								
Polypodium lineare THUNB. ..	+	+	+	......	+				
Total number of the species = (including varieties) 392....	* 98 =25%	** 101 =26%	*** 192 =19%	**** 81 =21%	***** 163 =42%	7	5	37 =9.5%	

* Of these species, three are here represented by allied species, *Sopubia trifida*, *Nertera depressa* and *Clematis smilacifolia*.

** One of these species, is represented by an allied species, *Sopubia trifida*.

*** Of these species, ten are here represented by allied species, *Thladiantha nudiflora*, *Myriactis nepalensis*, *Blumea hieracifolia*, *Peliosanthes Delavayi*, *Cephalotaxus Fortunei*, *Barthea chinensis*, *Nertera sinensis*, *Cardiandra sinensis*, *Prunus japonica* and *Pistacia chinensis*.

**** Of these species, two are here represented by allied species, *Pistacia chinensis* and *Prunus japonica*.

***** Of these species, nine are here represented by allied species, *Rhus toxicodendron* var. *radicans*, *Cardiandra alternifolia*, *Fatsia japonica*, *Marlea platanifolia*, *Chamaecyparis pisifera*, *Cephalotaxus pedunculata*, *Taxus cuspidata*, *Pinus parviflora* and *Tsuga diversifolia*.

The following points of importance are taken from the above list.

a) *Arctic Elements.*

Arctic elements are represented by the following species :—

Asplenium Trichomanes Linn.
Circæa alpina Linn.
Solidago Virga-aurea Linn.
Leontopodium R. Br.
Luzula spicata DC.
Deschampsia cæspitosa Beauv.
Trisetum subspicatum Beauv.

b) *Antarctic Elements.*

Antarctic elements are represented by the following species :—

Asplenium Trichomanes Linn.
Nertera Banks.
Deschampsia cæspitosa Beauv.
Trisetum subspicatum Beauv.
Solidago Virga-aurea Linn.

c) *Alpine Elements.*

Alpine elements, by which I mean those plants that are found at elevations above 10,000 ft. in Asia or Europe, are represented by the following species :—

Arabis alpina Linn.
Arabis taraxacifolia Anders.
Potentilla gelida C. A. Mey.
Potentilla leuconota Don.
Sibbaldia procumbens Linn.
Epilobium alpinum Linn.
Circæa alpina Linn.
Leontopodium R. Br.
Peracarpa carnosa Hook. f. et Thoms.
Rhododendron brachycarpum G. Don.
Gentiana humilis Stev.
Origanum vulgare Linn.
Stellera Chamæjasme Linn.
Juniperus Linn.
Luzula effusa Buch.
Luzula spicata DC.
Agrostis Clarkei Hook. f.
Deschampsia cæspitosa Beauv.
Deschampsia flexuosa Trin.
Trisetum subspicatum Beauv.
Brachypodium sylvaticum Beauv.
Festuca ovina Linn.
Lycopodium obscurum Linn.
Asplenium Trichomanes Linn.

d) *Tropical American Elements.*

These elements are very few in number, but among them we have *Oreopanax*, a genus of Araliaceæ. The occurrence of this genus, which is all but peculiar to the flora of Tropical America, is exceptionally remarkable. It is perhaps the most anomalous case we meet with in the Formosan flora. This genus is here represented by a large tree, *Oreopanax formosana* HAYATA. As far as I am aware, we have had no representative of this American genus in any other region on the globe. The tree is found in the mountainous districts on the north-western side of the central ranges, and also on Mt. Morrison, both localities having elevations varying from 6,000—8,000 ft. As the plots are quite inaccessible, it does not seem probable that the tree was planted there by human agency.

e) *Malay Elements.*

These elements are rather less numerous. There are in all 98, or 25% of the whole number mentioned in the list. Among them, we have 45 tropical elements or 12% of the whole number. None of these species ascends to an altitude higher than 3,000 ft. An exceptional case is that of the tropical genus, *Heptapleurum*, which is found at an elevation of about 7,000 ft.

f) *North American Elements.*

These elements are comparatively well represented in this flora. As has been seen in the foregoing list, we have as many as 37 species, or 9.5% of the whole number. Of these American representatives, almost no species, except a very few cosmopolitans, extends any farther south than Formosa, not even to

Luzon. It is, therefore, certain that the flora under consideration has a far closer affinity to that of North America than the flora of the Philippines has to that of the new world.

It is very interesting to notice that the montane flora has some genera which are found in North America, North China, and Japan, but nowhere else. They are :—

Mitella (Formosa, Japan, North China, Siberia, and North America).
Chamæcyparis (Formosa, Japan, and North America).
Pseudotsuga (Formosa, Japan, and North America).

g) *Himalayan Elements.*

These elements are here represented by as many as 101 species, or 26% of the whole number. Most of them are found in Japan and also in China.

Those plants which are confined to Formosa, the Himalayas, and China are as follows :—

Arabis alpina Linn.
Thea caudata (Wall.)
Oxalis Griffithii Edgew.
Desmodium sinuatum Blume.
Vernonia Andersoni Clarke.
Pieris formosa D. Don.
Sopubia
Laggera alata Sch. Bip.
Codonacanthus pauciflorus Nees.
Origanum vulgare (also in Europe, America, and Africa)
Stellera Chamæjasme Linn.
Juniperus communis Linn. (represented by *J. formosana* Hayata.
Peliosanthes courtallensis Wight.
Aneilema divergens Clarke.
Luzula effusa Buch.

Those plants, which are found in the Himalayas and Formosa, but nowhere else, are :—

Arabis taraxacifolia Anders.
Epilobium alpinum Linn. (also in Europe).
Lecanthus Wightii Wedd (also in the Malay Archip.).
Castanopsis indica A. DC.
Luzula spicata DC.
Agrostis Clarkei Hook. f.
Isachne Clarkei Hook. f.

h) *Elements of central and southern China (including Tibet).*

This is the class best represented in the flora, comprising as many as 192 species, or 49% of the whole number. Most of them are also found in Japan.

The plants which are confined to this region and Formosa, are as follows:—

Hœckia Aschersoniana Engl. et Græbn.
Senecio monanthus Diels.
Petasites tricholobus Franch.
Gentiana humilis Stev.
Salvia scapiformis Hance.
Daphne Championi Benth
Libocedrus macrolepis Benth
Pinus Armandi Franch.
Keteleeria Davidiana Beissn.

They are in all 9 species, among which we have 2 genera, *Hœckia* and *Keteleeria*, which are found in this region and Formosa, but nowhere else.

Here we see that the strong affinity between the two regions is as clearly shown by the plants of peculiar character as by the number of the elements.

i) *Japanese Elements.*

The Japanese elements are, next to the Chinese, best represented in the flora. They comprise in all 163 species or 42% of the whole number.

The plants, which are known to exist only in Formosa and Japan, are as follows:—

Clematis lasiandra Maxim.
Mitella japonica Miq.
Trochodendron aralioides S. et Z.
Fatsia
Galium brachypodium Maxim.
Lysimachia sikokiana Miq.
Conandron ramondioides S. et Z.
Tsuga diversifolia Maxim.
Pseudotsuga japonica Shirasawa.
Abies Mariesii Masters.

Chamæcyparis pisifera S. et Z. represented by *C. formosensis* MATSUM.

Chamæcyparis obtusa S. et Z.

Pinus parviflora S. et Z. (represented by *P. formosana* HAYATA.)

Metanarthecium foliatum MAXIM.

Juncus Maximowiczii FR. et SAV.

Plagiogyria Matsumureana MAKINO.

They are in all 16 species, among which we have some genera which are all but peculiar to Japan and Formosa. They are as many as 4 genera :—

Trochodendron

Fatsia

Conandron

Metanarthecium.

The Japanese elements are, on the whole, a little less numerously represented in the Formosan flora than the elements of central and southern China, so far as the figures of the elements are concerned. We see, however, that the number of the plants peculiar to both islands far exceeds the number of those which are confined to the continent and Formosa.

Origanum vulgare LINN., which ranges over high mountains of the northern hemisphere, is wanting in Japan.

Luzula spicata DC., which spreads over the Himalayas, North America and the arctic regions, has not yet been found in Japan.

j) *Elements of northern China (including Manchuria, Saghalien, Amurland, and east Siberia).*

These are the least numerously represented in the flora. They number 81 species or 21% of the whole.

Those plants, which are only found in North China and the island, are as follows :—

Cerastium pilosum LEDEB.
Rhamnus arguta MAXIM. (represented by a variety.)

Here we see that the relation is far less close.

k) *Endemic Elements* (*excepting varieties.*)

Endemic plants are comparatively numerous as is to be expected in an island. There are as many as 99 species, or 25% of the total number of the plants found in the high elevations. This richness in endemic plants seems to indicate that the island has been entirely separate from neighbouring countries since geological epochs.

However opulent Formosa is in peculiar plants, the figure representing the number of the endemic species is not so large in the case of this island as it is in that of the Philippines.[1] This fact shows that the flora of Formosa is of continental character, while that of the archipelago is insular.

The numbers of the plants of endemic character under each genera are shown in the following list.

Clematis	2	*Eurya*	1	*Astilbe*	1
Thalictrum	1	*Thea*	1	*Hydrangea*	4
Melodorum	1	*Geranium*	1	*Ribes*	1
Cardamine	1	*Impatiens*	1	*Sedum*	1
Viola	3	*Euonymus*	1	*Hydrocotyle*	1
Polygala	1	*Crotalaria*	1	*Sanicula*	1
Cerastium	1	*Dumasia*	1	*Fatsia*	1
Stellaria	1	*Rubus*	2	*Oreopanax*	1

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[1] Mr. E. D. MERRILL states that 11% of the total number of the plants found in the Lamao Forest Reserve is endemic to the Philippines....(see Philipp. Journ. Sci. Vol. I. Suppl. p. 9.)

Damnacanthus	1	*Symplocos*	2	*Elatostema*	1
Lasianthus	1	*Dischidia*	1	*Quercus*	4
Rubia	1	*Gentiana*	6	*Castanopsis*	1
Scabiosa	1	*Swertia*	1	*Chamæcyparis*	1
Eupatorium	2	*Trigonotis*	1	*Juniperus*	1
Erigeron	1	*Rehmannia*	1	*Cunninghamia*	1
Anaphalis	1	*Veronica*	1	*Taiwania*	1
Gnaphalium	1	*Mesona*	2	*Pinus*	1
Carpesium	1	*Polygonum*	3	*Tsuga*	1
Artemisia	2	*Asarum*	1	*Paris*	1
Gynura	1	*Peperomia*	1	*Scirpus*	1
Ainsliæa	2	*Helicia*	1	*Spodiopogon*	2
Vaccinium	2	*Loranthus*	1	*Arundo*	1
Gaultheria	1	*Balanophora*	2	*Brachypodium*	1
Rhododendron	3	*Glochidion*	1	*Arundinaria*	1
Pyrola	1	*Pilea*	1	*Polystichum*	1

Among the above species, the most striking plants, with the endemic genus, *Taiwania*, are as follows :—

Fatsia multicarpa HAYATA.
Oreopanax formosana HAYATA.
Damnacanthus angustifolia HAYATA.
Leontopodium microphyllum HAYATA.
Pyrola morrisonicola HAYATA.
Helicia formosana HEMSLEY.
Chamæcyparis formosensis MATSUMURA.
Cunninghamia Konishii HAYATA.
Taiwania cryptomerioides HAYATA.
Pinus formosana HAYATA.
Brachypodium Kawakamii HAYATA.

l) General Character of the Elements.

The general features of the elements are shown in the following table.

Temperate elements	320 = 81 %	of the whole number
Tropical elements	45 = 12 %	,, ,,
Arctic, antarctic & alpine elements	27 = 7 %	,, ,,
Total	392 =100 %	

Thus, the flora is, in general, temperate, having as many as 320 species of temperate character, or 81 % of the whole number of the elements.

The total number of the species in the flora is 392, belonging to 79 families and 266 genera.

2) Floristic Relationship between Formosa and Neighbouring Countries.

The numbers of the elements in the regions under comparison are shown in the following table.

Regions	Number of elements	Ratio
The Malaypen. & archip.	98	25 %
The Himalayas	101	26 %
Central & southern China	192	49 %
Northern China	81	21 %
Japan	163	42 %
North America	37	9.5 %
Endemic	99	25 %

As shown in the above table, the island has the strongest affinity to central and southern China and Japan; next, to the

Himalayas; then, to the Malay peninsula and archipelago, and North China; and lastly, to North America.

As to central and southern China and Japan, the comparative strength of their floristic relationship to Formosa is not to be measured by the number of elements only; the character of the elements must also be taken into account.

So far as the number of the elements is concerned, it appears that the most striking affinity obtains between the island and central and southern China. It is not so, however, when we compare those elements which give the flora its peculiar features. The comparison of this class of elements, which plays so important a part in the study of phytogeography, is worthy of special attention.

As we have already seen, the species the distribution of which is limited to Formosa and Japan are far more numerous than those confined to Formosa and China. We have also observed that the number of the genera, which are found in the islands and nowhere else, is double that of such kinds in Formosa and China.

When we consider these species of peculiar character, we are forced to think that the flora of Formosa has a striking affinity to that of Japan. And it is even more so, when the genera, *Trochodendron*, *Fatsia*, *Conandron*, and *Metanarthesium* are taken into account.

Thus, I am much inclined to conclude that the montane flora of Formosa is nearest to that of Japan, regardless of geographical proximity to China.

A few lines should be here devoted to the cause of this similarity between the islands.[1] It is a very remarkable fact that so many plants of peculiar character are found in both regions.

---

1) Japan and Formosa.

This fact has led me to think that these plants once ranged over all the continent but became extinct there, while they have still survived in the islands, owing to their insular conditions[1].

This opinion will, however, not satisfactorily explain why the plants, which are found still living in the islands, do not also survive in so sheltered a place as Tein-ling-shan[2], where the flora is quite as rich as it is in Japan and Formosa. It is very reasonable to think that in the so called coast provinces of China, the disturbances were so severe as to destroy these inhabitants of peculiar character. But, why in the protected centre of China ?

It seems to me that insular conditions are not the only cause of the floristic affinity of the two regions, (Japan and Formosa) and I have wondered if this affinity were not due to a land-mass or mountain chains, which are by some geologists conjectured to have existed between the islands in former ages[3]."

In my paper "On the Distribution of the Formosan Conifers[3], I referred to the probable derivation of the coniferous flora of Formosa, and came to the conclusion that the floras of Japan and Formosa have been developed in the border regions of the former continent, the extention of which reached from Japan southwards to the Loo-choo islands as far as Formosa ; while the flora of central China has been formed in the centre of the continent.

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1) I am much impressed by the opinion of Mr. WALLACE who made the following conclusion in his "Island Life" ed-3, p. 101 :—" It is clear, therefore, that before Formosa was separated from the mainland the above named animals or their ancestral types must have ranged over the intervening country as far as the Himalayas on the west, Japan on the north, and Borneo or the Philippines on the south ; and that after that event occurred the conditions were so materially changed as to lead to the extinction of these species in what are now the coast provinces of China, while they or their modified descendants continued to exist in the dense forests of the Himalayas and the Malay Islands, and in such detached islands as Formosa and Japan. "

2) DIELS, L.—Flora von Central-China, in Engl. Bot. Jahrb. XXIX. pp. 169–659.

3) HAYATA, B.—On the Distribution of the Formosan Conifers, in Tōkyō Bot. Mag. XIX. pp. 43–61.

Thus, I divided the Chino-Japanese flora into two florulæ, one is the central florula, the other, the border florula.

Regarding the present subject of the montane flora of the island, I see that my former conclusion will hold equally good of the formation of this flora.

Taking all these cases into account, I have come to the conclusion that the similarity of the floras of Formosa and Japan may have been caused, on the one hand, by the existence formerly of a land-mass between the islands, and, on the other, by the same insular conditions caused by the depression forming the inner seas in more recent geological ages.

3) General Aspect of the Vegetation.

The vegetation of the montane zone of Formosa varies considerably according to the height. As Mt. Morrison presents various climatal features from subtropical through temperate up to cold regions, the vegetation of this mountain will give us a fair idea of the general aspect of the growth in the hill regions of the island.

As I have already mentioned, a botanical excursion was carried out on the mountain by Messrs. T. KAWAKAMI, S. NAGASAWA and G. NAKAHARA, and a report[1] of the journey was published by Mr. T. KAWAKAMI in the Tōkyō Botanical Magazine. As his report is the only publication relating to that mountain, I take the liberty of drawing some descriptions from it.

It was on the 28th of October, 1905, that the party left Kagi, a small town on the north-western foot of the mountain.

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[1] KAWAKAMI, T.:—Botanical Excursion to Mt. Morrison, in Tōkyō Bot. Mag. XX. pp. 30–36, (Japanese).

Passing over many hilly passes, they found themselves on an elevation of about 2,400 ft., where they saw a beautiful forest of *Dendrocalamus*[1] and *Bambusa*[2].

From a height of 3,000 ft. upwards, beautiful arbors of camphor[3] and *Quercus*[4] made a dense forest with a liana formation, and many epiphytes of ferns, orchids and mosses. In this forest, the undergrowth is also beautiful; large tree ferns[5], graceful stellate ferns[6], wild *Musa*[7], *Calamus*[8], *Alocasia*[9], all combining to form a glorious example of tropical vegetation.

At the height of 3,700 ft., a pretty herb[10] of the Urtica family occurred plentifully, and on it two species[11] of Balanophoraceæ were found attached to the host.

Further, at the height of 4,200 *ft., the trees of various Querci*[12] densely covered the plot, while many climbing plants hanging from the top of trees made the forest still more beautiful.

Ascending a little higher, they came to the boundary of the savage districts. In a grassy plot near by, they found an *Adenophora*[13], wild pinks[14], and violets[15], in full bloom. *Aleurites*[16] and *Idesia*[17] were found in bloom in the village.

Crossing this savage belt, they entered the virgin forest of the western slope. Here at an elevation of 4,500 ft., the camphor

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1) *Dendrocalamus latiflorus* MUNRO.

2) *Bambusa Oldhami* MUNRO.

3) *Cinnamomum Camphora* N. et E.

4) *Quercus* & *Castanopsis*.

5) *Alsophila*, *Cibotium*, & *Dicksonia*.

6) *Asplenium Nidus* LINN.

7) *Musa paradisiana* LINN. subsp. *seminifera* BAKER, var. *formosana* WARB.

8) *Calamus formosanus* BECC. & *Calamus Margaritæ* HANCE.

9) *Alocasia macrorrhiza* SCHOTT.

10) *Pilea Wattersii* HANCE?

11) *Balanophora spicata* HAYATA & *B. parvior* HAYATA.

12) *Quercus Junghuhnii* MIQ., *Q. Kawakamii* HAYATA, and other species of the genus.

13) *Adenophora verticillata* FISCH.

14) *Dianthus superbus* LINN.

15) *Viola japonica* LANGSD.

16) *Aleurites cordata* STEUD.

17) *Idesia polycarpa* MAXIM.

trees[1] and various kinds[2] of *Quercus* were so enormously great that the trunks attained a circumference of even 8 ft.

At the height of 6,800 ft., a dark forest of *Chamæcyparis*[3] was first met with. The Conifer was here wonderfully large attaining a diameter of even 10 ft. Intermixed with the tall trunks of the five leaved pine[4], with the gregarious undergrowth of a pretty variety of bamboo, this *Chamæcyparis*[5] occupies the greatest part of the Conifer regions and constitutes the most peculiar feature of the flora of Formosa. The vegetation of this kind is seen only in the mountainous districts of Japan, though the growth is there far less luxurious. This spot is, it is said, frequently haunted by deer[6] of the peculiar species of the Formosan fauna.

The climatal features here were temperate. The thermometer indicated 59° F. The familiar *Polygonum*[7] (near *P. Thunbergii*), *Smilacina*[8], and *Rhus* were all welcomed as old friends. The red tinted leaves of the *Rhus* twining about the trunk of the pine reminding them of the autumnal scenery of Japan. The season of flowers was past; still there remained a few flowers and some fruits.

From the elevation of about 8,000 ft., a full sight of the peak was clearly obtained. On the north, the immense forest of Mt. Arizan was seen far below the foot. *Tsuga*[10] was here first met with, intermixed with shrubberies of *Pieris*[11] and various kinds[12]

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1) *Cinnamomum Camphora* N. et E.

2) *Quercus* & *Castanopsis*.

3) *Chamæcyparis obtusa* S. et Z. form. *formosana*.

4) *Pinus Armandi* FRANCH. var. *Mastersiana* HAYATA.

5) *Chamæcyparis obtusa* S. et Z. form. *formosana*.

6) *Cervus taevanus* = Formosan spotted Deer. Allied to *C. Sika* of Japan.

7) *Polygonum biconvexum* HAYATA.

8) *Smilacina japonica* A GRAY.

9) *Rhus intermedia* HAYATA.

10) *Tsuga formosana* HAYATA.

11) *Pieris formosa* D. DON.

12) *Rhododendron Oldhami* MAXIM. var. *glandulosum* HAYATA.

of *Rhododendron.* Here, *Trochodendron*[1] of a enormous size was found most abundantly.

Further on, there was a grassy hillside with pines scattered here and there. Various plants including Thymelæaceæ[2], Rutaceæ[3], Rosaceæ[4], Onagrarieæ[5], Rubiaceæ[6], Juncaceæ[7] and Gramineæ[8] were also found. A large tree of Juglandaceæ[9] was met with, and the first example of a deciduous arbor[10] on this elevation of 8,250 ft.

Then, the slope became more and more gentle. At the height of 9,000 ft., a red berried *Vaccinium*[11] was found, and a kind of *Sphagnum*, Campanulaceæ[12] and Orobanchaceæ[13]; also a forest of *Picea*[14], with an undergrowth of Compositæ[15], Rubiaceæ[16], Saxifragaceæ[17], and Geraniaceæ[18]. A curious species of *Impatiens*[19], *Mitella*[20] and a long-leaved *Rubia*[21] were just coming into flower. The white *Parnassia*[22] was in full bloom. Nothing could be

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[1] *Trochodendron aralioides* Sieb. et Zucc.

[2] *Daphne Championi* Benth. & *Stellera Chamæjasme* Linn.

[3] *Bœnninghausenia albiflora* Reich., & *Skimmia japonica* Thunb.

[4] *Rubus pectinellus* Maxim.

[5] *Epilobium* sp.

[6] *Ophiorrhiza pumila* Champ., *Damnacanthus angustifolia* Hayata, & *D. indicus* Gærtn. f.

[7] *Juncus effusus* Linn.

[8] *Panicum montanum* Roxb., *Cymbopogon Nardus* Rendle., *Arundinella setosa* Trin., *Calamagrostis arundinacea* Roth. & *Miscanthus sinensis* Anderss. var. *formosanus* Hack.

[9] *Juglans* sp.

[10] *Carpinus* sp.

[11] *Vaccinium Merrilliana* Hayata & *V. emarginatum* Hayata.

[12] *Peracarpa carnosa* H. f. et T. & *Adenophora* polymorpha Ledeb.

[13] *Orobanche cærulescens* Stephn.

[14] *Picea morrisonicola* Hayata.

[15] *Eupatorium formosanum* Hayata, *Solidago Virga-aurea* Linn., *Myriactis Wightii* DC. *Aster baccharoides* Steetz, *Aster scaber* Thunb., & *A. trinervius* Roxb. *Laggera alata* Schultz-Bip., *Gnaphalium lineare* Hayata, *G. luteo-album* Linn., *Carpesium acutum* Hayata, *Artemisia scoparia* Waldst. et Kit. *Petasites tricholobus* Franch., *Senecio monanthus* Diels., *Senecio scandens* Ham., *Cnicus Wallichii* DC., *Ainsliaea macroclinidioides* Hayata, & *Picris hieracioides* Linn.

[16] *Damnacanthus.*

[17] *Astilbe chinensis* Fr. et Sav., *Astilbe chinensis* var. *longicarpa* Hayata, *Chrysosplenium*, *Mitella japonica*, Miq, *Hydrangea*, *Deutzia Scabra* Thunb. & *Ribes formosana* Hayata.

[18] *Impatiens*, *Geranium*, & *Oxalis.*

[19] *Impatiens uniflorus* Hayata.

[20] *Mitella japonica* Miq.

[21] *Rubia lanceolata* Hayata.

[22] *Parnassia palustris* Linn.

more interesting than to see these flowers of cold regions on this mountain lying within the tropics. A kind of *Fragaria*[1] with a yellow fruit and a beautiful flower[2] of Caryophylleæ were seen among the rocks.

At the height of 10,500 ft., the climate was rather cold. The temperature fell at night to 43 F. The frost was very heavy at that season of the year. There a dark forest of *Abies*[3], *Tsuga*[4], and *Chamæcyparis*[5] was very beautiful.

Passing through this forest, they came to a brook on the banks of which they found two species[6] of Umbelliferæ and a kind of *Primula*[7]. It was here that the beautiful flowers of *Thalictrum*[8] were found. *Epilobium*[9] of a very small size was also growing along the brook.

Further on, the coniferous forest gradually gave way to a shrubby formation of *Juniperus*[10], intermixed with dwarf trees of the *Berberis*[11] family. The ground was all covered with debris of clay slate fallen from the peak above.

From the height of 12,000 ft. and upwards, the mountain sides were grassy, where *Potentilla*[12], *Astilbe*[13], *Lycopodium*[14] and *Adenophora*[15] were growing abundantly. A small swampy plot was found, there were beautiful groups of various flowers of the blue *Scabiosa*[16], yellow *Hypericum*[17] and *Sedum*[18], *Oxalis*[19] of

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[1] *Fragaria* sp.

[2] *Cucubalus baccifer* Linn.

[3] *Abies Mariesii* Mast. var. *Kawakamii* Hayata.

[4] *Tsuga formosana* Hayata.

[5] *Chamæcyparis formosensis* Matsumura.

[6] *Sanicula petagnioides* Hayata & *Cnidium* sp.

[7] *Primula* sp.

[8] *Thalictrum Fauriei* Hayata.

[9] *Epilobium alpinum* Linn. & *E. roseum* Schreb.

[10] *Juniperus formosana* Hayata & *J. morrisonicola* Hayata.

[11] *Berberis* sp.

[12] *Potentilla gelida* C. A. Mey., *P. leuconota* Don. var. *morrisonicola* Hayata & *Sibbaldia procumbens* Linn.

[13] *Astilbe chinensis* Fr. et Sav.

[14] *Lycopodium obscurum* Linn., *L. clavatum* Linn. & *L. serratum* Thunb.

[15] *Adenophora polymorpha* Ledeb.

[16] *Scabiosa lacerifolia* Hayata.

[17] *Hypericum attenuatum* Choisy.

[18] *Sedum morrisonense* Hayata.

[19] *Oxalis Griffithii* Edgew. et Hook. f.

violet color, red *Epilobium*[1] and snow white *Spiræa*[2]. The flowering season was over, but still a few flowers remained.

On the top (13,120 ft.) of the peak, the ground is covered with blocks of rocks. The flora is here extremely scanty, and the flowers were all gone. The scene was very desolate. No sound save the humming of an insect broke the profound silence.

Thus ended the trying excursion carried out by Messrs. T. KAWAKAMI, S. NAGASAWA and G. NAKAHARA. It was a journey of more than a week. From this trip, they all brought back very good collections. The report of the botanical tour written by Mr. T. KAWAKAMI must, I infer, have thrown some light upon the study of the vegetation of the island.

Summarizing the description above referred to, the montane zone of the island may be divided into four regions.

1) Broad leaved tree region (*Trochodendron*, *Cinnamomum*, and *Quercus*) from 2,000 ft.—6,000 ft.

2) Coniferous region (*Abies*, *Picea*, *Pinus*, *Taiwania*, *Cunninghamia*, and *Chamæcyparis*) from 6,000 ft. up to 10,000 ft.

3) Shrubbery region (*Juniperus* and *Berberis*) from 10,000 ft. up to 12,000 ft.

4) Grass region (*Leontopodium*, *Potentilla*, *Origanum*, *Sibbaldia* *Luzula*, *Trisetum*, *Festuca*, *Brachypodium*, and *Lycopodium*) from 12,000 ft. up to 13,100 ft.

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[1] *Epilobium alpinum* LINN.

[2] *Spiræa* sp.

4) Enumeration of the Plants.

Dicotyledones.

Polypetalæ.

Ranunculaceæ.

Anemone LINN.

Anemone luzoniensis ROLFE[1]; HAYATA, in Tōkyō Bot. Mag. XX. p. 73.
HAB. Shintiku: Goshōrin, leg. T. KAWAKAMI, Mai. 1906.
DISTRIB. The Philippine islands.

Anemone sp. Herbacea perennis, basi apiceque longe sericeo-pubescens, undique pilis brevioribus adpressis tenuiter obtecta. Folia radicalia magna cum petiolis circ. 30 cm. longa trifoliolata palmatinervia, superne læte viridia subtus glauca; foliola petiolulata, circumscriptione cordato-rotundata, tri- vel multi-loba vel profunde incisa, margine inæqualiter inciso-serrata vel duplicato-serrulata, serraturis mucronatis, apice acuta 7–10 cm. longa totidemque lata; foliola terminalia majuscula valde obliqua, profunde cordata. Caulis 50–60 cm. longus erectus teres. Folia caulina opposita breviter petiolata, petiolis villosis basi vaginatis, patentia trifoliolata, foliolis petiolulatis basi cuneatis

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1) After completing this manuscript, I am informed by Mr. E. D. MERRILL of the Bureau of Science, Manila, that when he was in the Kew Herbarium he and Mr. ROLFE compared the Philippine material with the Himalayan specimen, and came to the conclusion that the Luzon plant is not distinctive from *Anemone vitifolia* HAM. The description of *Anemone luzoniensis* ROLFE has never been published. I think that the Formosan plant above mentioned is exactly the same as the Luzon plant, and Mr. MERRILL has the same opinion too. After considering all the above cases, I am much inclined to think that my plant should be referred to *Anemone vitifolia* HAM.

oblongo-lanceolatis, sursum attenuatis sub-3-lobatis, inæqualiter duplicato-serratis. Pedunculi plerumque 2 valde elongati tenues erecti.

HAB. in monte Morrison, leg. T. KAWAKAMI et U. MORI, ad 8000 ped. alt., Nov. 1906, (No. 1869).

Very near the preceding species, but possibly different from it. The specimens, however, being in too imperfect a state, are not determinable.

Clematis LINN.

Clematis lasiandra MAXIM. var. **Nagasawai** HAYATA, n. v. Caulis lignoso-scandens glaber sulcatus. Folia pinnata 3–5-foliolata, cum petiolis 10–15 cm. longa 5–9 cm. lata, foliolis longe petiolulatis simplicibus vel interdum trilobatis ovatis v. ovato-lanceolatis acuminatis inæqualiter argute serratis. Paniculæ axillares paucifloratæ, vel quasiterminales, folio breviores vel longiores, basin pedicelli bracteatæ, bracteis trilobatis vel elobatis linearibus minoribus, pedicellis gracilibus flore 2–3-plo longioribus. Flores nutantes, 2 cm. in diametro æquantes et totidem longi. Sepala 4, conniventia apice revoluta, oblonga v. ovato-oblonga obtusa v. emarginata, 23 mm. longa 8 mm. lata, utraque pagine subglabra leviter purpurea, margine velutinoso-tomentosa. Stamina 4-seriata, extima longissima, filamentis planis linearibus 17 mm. longis dorso longe denseque sericeo-pilosis, antheris 2 mm. longis apice non appendiculatis, stamina intima breviora, filamentis 9 mm. longis, antheris 3 mm. longis. Pistilla 8 mm. longa sericeo-plumoso-caudata. Receptaculum fructiferum erectum globosum 4 mm. in diametro æquans pilosum: carpellis sub maturitate numerosis ovato-lanceolatis acuminatis compressis 3 mm. longis marginatis rubescentibus pilosis, longe plumoso-caudatis, caudis 3½ cm. longis.

Hab. in valle Shūkoran, ad 11117 ped. alt., in monte Morrison, leg. S. Nagasawa, Nov. 1905, (No. 611).

Distrib. Type : Kiūshiū, southern part of Japan.

The present variety differs from the type in having many-flowered peduncles; this never has uni-flowered peduncles as the type.

Clematis longisepala Hayata, sp. nov. Caulis lignoso-scandens glaber striatus. Folia pinnatim 5-foliolata longe petiolata glaberrima, cum petiolis 15–20 cm. longa, petiolis volubilibus striatis, foliolis petiolulatis, petiolulis 1.5–2 cm. longis, oppositis ovato-oblongis apice acutis basi rotundatis integris 3–5-nerviis submembranaceis subtus pallidioribus 5 cm. longis 2½ cm. latis, stipulis connatis ad nodos caulis peltam formantibus. Paniculæ axillares, folio subæquilongæ 5–8-floratæ. Flores majusculi patentes 6–7 cm. in diametro æquantes, ad basin pedicelli 1-bracteati, bracteis pinnatim 3-sectis 3–4 cm. longis longe stipitatis, segmentis oblongo-lanceolatis, pedicellis 7–10 cm. longis. Sepala 4, lineari-lanceolata 3 cm. longa vel longiora apice obtusa carinato-mucronata, intus subglabra atro-purpurea, extus eburnea velutinosa paralleli-multi-nervia. Petala 0. Stamina multi-seriata (circ. 5-seriata), extima longiora 2 cm. longa, filamentis linearibus sursum leviter crassiusculis ad basin antherarum constrictis deorsum tenuibus dilatis glabris, antheris linearibus 2 mm longis apiculatis, stamina intima sensim breviora 7 mm. longa. Carpella longe sericeo-plumoso-caudata, circ. 1 cm. longa.

Hab. in monte Morrison, ad 6000 ped. alt., leg. T. Kawakami et U. Mori, Oct. 1906, (No. 2018).

Comes very closely to *Clematis crassifolia* Benth. Fl. Hongk. p. 7 ; but differs from that in having leaves of the round base.

Clematis Morii HAYATA, sp. nov. Caulis lignoso-scandens glaber striatus. Folia opposita vel quaternata trifoliolata, cum petiolis circ. 15 cm. longa, petiolis volubilibus, subcoriacea subtus glaucescentia exstipulata, foliolis terminalibus petiolulatis longe caudato-acuminatis deorsum obscure lobatis basi rotundatis margine subintegris vel remote mucronato-serrulatis subtus venis prominentibus supra venis impressis venulis prominentibus 5-nerviis 11 cm. longis 3½ cm. latis, petiolulis 1 cm. longis, foliolis lateralibus multo brevioribus sæpe elobatis caudato-ovatis remote mucronato-serrulatis petiolulatis, petiolulis 3 mm. longis, vel subsessilibus. Flores majusculi cernui semi-clausi, 1½ cm. in diametro æquantes totidem longi, axillares solitarii pedicellati, ad basin pedicelli 2-bracteati, bracteis minutissimis pubescentibus, pedicellis 3 cm. longis pubescentibus. Sepala 4, latiora 1.8 cm. longa 9 mm. lata, ovata mucronato-acuta, intus atro-purpurea, extus velutinoso-pilosa basi leviter cordata venulis parallelis, semi-clausa numquam patentia. Stamina 3–4-seriata, extima longissima, filamentis linearibus planis longe barbatis 13 mm. longis, antheris circ. 2 mm. longis apice emarginatis, stamina intima brevissima, filamentis 7 mm. longis, antheris 3 mm. longis. Carpella circ. 1 cm. longa longe plumoso-caudata.

HAB. in montibus centralibus, ad 10000 ped. alt., leg. U. Mori, Nov. 1906, (No. 1854).

Comes near to *Clematis barbellata* EDGEW., and still more to *Clematis lasiandra* MAXIM.; but differs from them in having silky pubescent sepals and subentire leaflets.

Clematis tozanensis HAYATA, sp. nov. Caulis lignoso-scandens glaber striatus. Folia majuscula pinnatim 5–3-foliolata longe petiolata glaberrima, cum petiolis circ. 20 cm. longa totidem lata, petiolis striatis volubilibus, foliolis oblongo-ovatis vel cordato-ovatis, basi cordatis vel truncatis 8 cm. longis 6 cm. latis palmatim 9–7–nerviis apice obtusis integerrimis leviter repandis submembranaceis vel crassiusculis, petiolulis 2–3 cm. longis valde volubilibus, stipulis latis connatis ad nodos caulis peltam formantibus. Paniculæ axillares pauci-floratæ folio subæquilongæ. Flores majusculi patentes 6 cm. in diametro æquantes, ad basin pedicelli 1-bracteati, bracteis majusculis foliaceis simplicibus stipitatis ellipticis apice acutis. Sepala 4, angusta 3½ cm. longa 8 mm. lata acuta vel obtusa intus glabra atro-purpurea, extus eburnea velutinoso-pubescentia multi-striata patentes. Stamina multi-seriata, extima longissima filamentis 2 cm. longis dilatis linearibus tenuibus antheris linearibus 2 mm. longis apiculatis, stamina intima brevissima filamentis 2 mm. longis antheris 3 mm. longis longiuscule apiculatis. Carpella longe sericeo-plumoso-caudata, circ. 9 mm. longa.

HAB. in Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906.

Comes closely to *Clematis smilacifolia* WALL., and still more to the preceding species. The present species differs from them in the shape of the bracts and stipules. In this new *Clematis*, the filaments of the stamens of the outer-most series are the longest, while the anthers of the same series are the shortest.

Clematis Wightiana WALL. ? ; HOOK. f. et THOMS. in HOOK. f. Fl. Brit. Ind. I. p. 5 ; WIGHT, Ic. Pl. Ind. or. t. 935.

HAB. Taitō : Iryokukakusha, leg. T. KAWAKAMI et U. MORI, Dec. 1906.

This *Clematis* is very like *C. Wightiana* WALL. ; but, owing to the imperfectness of the specimen, the determination is rather conjectural.

Clematis sp.

We have one more species belonging to this genus from Rakurakusha; but the specimen is very imperfect.

Thalictrum LINN.

Thalictrum Fauriei HAYATA[1], in MATSUMURA et HAYATA, Enumeratio Plantarum Formosanarum, in Journ. Sci. Coll. Imp. Univ. Tōkyō, XXII. p. 7.

HAB. in monte Morrison, leg. T. KAWAKAMI, 1906.

As the specimen is imperfect, the determination is rather conjectural.

Magnoliaceæ.

Trochodendron SIEB. et ZUCC.

Trochodendron aralioides SIEB. et ZUCC. Fl. Jap. I. p. 83, tt. 39 et 40; MIQ. Prol. Fl. Jap. p. 146; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 19; HENRY, List Pl. Formos. p. 16; MATSUM. in Tōkyō Bot. Mag. XII. p. 54; MATSUM. et HAYATA, Enum. Pl. Formos. in Journ. Sci. Coll. XXII. p. 11.

HAB. Suizan, ad 7702 ped. alt., in montibus Morrison, leg. S. NAGASAWA, Oct. 1905, (No. 648); Arizan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906; in monte Morrison, ad 6000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1710).

DISTRIB. Japan and the Loo-choo islands.

The plant spreads over from the main-island of Japan through Kiūshiū to the Loo-choo islands as south as Formosa. It grows the most luxuriously in this region of the island, forming

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1) In the year 1905, the present *Thalictrum* of Formosa was described by myself as a new species. The publication, however, in which my new plant is appeared had not been issued until August, 1906. In the same year, another new species from Japan was described by M. LÉVEILLÉ under the same name. As it is not desirable to maintain one and the same name for two different plants, Prof. J. MATSUMURA advisably proposes to change the name of the Formosan species to *Thalictrum Urbaini* MATSUMURA.

a pure forest on the boundary between the Conifer and broad leaved tree regions. The trunk is here so large as to attain a diameter of even 15 ft.

Illicium LINN.

In this genus, *I. anisatum* LINN.[1] has been the only species recorded from Formosa. We have another plant from the high elevations of the island. The specimens, however, are all wanting of flowers, so that accurate identification is impossible.

Illicium sp. Folia versus apicem ramorum plerumque approximata opposita vel sub-verticillata petiolata, petiolis 1½ cm. longis, superne sulcatis subtus convexis crassis, laminis oblongis oblongo-ellipticis vel obovatis utrinque attenuatis vel apice cuspidato-acuminatis integris coriaceis, superne nitidis et læte viridibus subtus pallidioribus, 10–12 cm. longis 3–4 cm. latis, nervo medio crasso leviter prominulo, venis lateralibus evanidis. Pedunculi circ. 4 cm. longi. Carpella plerumque 13, libera, stylo breviore extrorsum recurvato. Semina oblonga compressa 9 mm. longa 6 mm. lata.

HAB. in montibus centralibus, ad 8000 ped., alt., leg. U. MORI, Nov. 1906, (No. 1918); in monte Morrison, ad 6500 ped. alt., leg. T. KAWAKAMI et U. MORI, (No. 2028); Tōzan et Arisan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906.

The carpels are, in most cases, thirteen, in which respect, it resembles very much *I. Tashiroi* MAXIM.[2]

Kadsura JUSS.

Kadsura japonica LINN.; DC. Prodr. I. p. 83; MIQ. Prol. Fl. Jap.

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[1] MATSUM. et HAYATA, Enum. Pl. Formos. p. 9.

[2] S. MATSUDA, in Tōkyō Bot. Mag. XXI. p. 243.

p. 255; FRANCH. et SAV. Enum. Pl. Jap. I. p. 18; HENRY, List Pl. Formos. p. 16; ITŌ et MATSUM. Tent. Fl. Lutch. in Journ. Sci. Coll. XII. p. 285; MATSUM. in Tōkyō Bot. Mag. XV. p. 85; MATSUM. et HAYATA, Enum. Pl. Formos. p. 12.

Kadsura chinensis HANCE, in BENTH. Fl. Hongk. p. 8; FORBES et HEMSL. Ind. Fl. Sin. I. p. 25.

Uvaria japonica LINN. Sp. Pl. ed-2, p. 756; THUNB. Fl. Jap. p. 237.

HAB. Kagi: Kishirēi, leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. Japan and China.

The plant is found commonly in the low districts. But sometimes it ascends to the hilly regions in the prefecture of Kagi.

Anonaceæ.

Melodorum DUN.

Melodorum Oldhami HEMSL. in FORBES et HEMSL. Ind. Fl. Sin. I. p. 27; HENRY, List Pl. Formos. p. 16; MATSUM. in Tōkyō Bot. Mag. XV. p. 86; MATSUM. et HAYATA, Enum. Pl. Formos. p. 13.

HAB. Nanto: Kashinokiyama, leg. G. NAKAHARA, Feb. 1907.

DISTRIB. An endemic plant.

Berberideæ.

Akebia DECNE.

In this genus, *Akebia longeracemosa* MATSUM. has been the only species recorded from Formosa. On the high elevations, we have another, probably new, species. The specimen is, however, in too imperfect a state for exact determination.

Akebia sp. Folia trifoliolata subcoriacea, petiolis circ. 2 cm. longis, foliolis petiolulatis, terminalibus longioribus lanceolatis obtusis basi truncatis 4 cm. longis 1.3 cm. latis, petiolulis ½ cm.

longis, lateralibus pauce minoribus breviter petiolulatis, venis et venulis utraque pagine valde prominentibus.

HAB. in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2288).

DISTRIB. A genus confined to Japan and China.

Near A. *longeracemosa* MATSUM., but differs from it in having trifoliolate leaves.

Berberis LINN.

Berberis nepalensis SPRENG. has been the only species recorded from the island. Two more species are found in the hilly districts.

Berberis nepalensis SPRENG.; HANCE, "in Journ. Bot. (1882) p. 2"; HOOK. f. Fl. Brit. Ind. I. p. 109; FORBES et HEMSL. Ind. Fl. Sin. I. p. 31; MATSUM. in Tōkyō Bot. Mag. XII. p. 54; MATSUM. et HAYATA, Enum. Pl. Formos. p. 18.

Mahonia nepalensis DC. Prodr. I. p. 109; DIELS, Fl. Centr. China, in ENGL. Bot. Jahrb. XXIX. p. 338.

Berberis Bealei FORTUNE, Bot. Mag. t. 4852.

Ilex japonica THUNB. Fl. Jap. p. 79, et Ic. Pl. Jap. t. 12.

HAB. Ganzan, in montibus Morrison, ad 8012 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 567); Arizan, in isdem montibus, leg. G. NAKAHARA, Nov. 1906; in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 177 et 1870).

DISTRIB. Khasia, central China, Japan and the Philippine islands. Mr. E. D. MERRILL remarks that this Formosan form is just the same as the Luzon one.

Berberis sp. Frutex erectus ramosissimus, ramulis spinis ternatis. Folia fasciculata coriacea ovata spathulatave apice rotundata aristato-mucronata vel obtusa margine remote spinuloso-dentata basi cuneata sessilia vel breve petiolata, 1.5 cm. longa 7 mm. lata. Baccæ 3–fasciculatæ globoso-ellipsoidales, utrinque obtusæ rubræ, 9 mm. longæ 3-spermæ, stigmatibus parvis sessilibus, seminibus lunaribus 4 mm. longis, pedunculis 1½ cm. longis.

HAB. ad verticem montis Morrison, ad 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 595); in monte Morrison, ad 12500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 2289 et 2297).

The leaves and fruits of this plant are beautifully tinted by the autumnal coloration.

Berberis sp. Frutex erectus ramosissimus, ramulis angulatis sulcatis, spinis ternatis 2–3 cm. longis. Folia fasciculata coriacea obovata oblanceolata vel lanceolata acuta basi cuneata subsessilia remote spinuloso-dentata 5–3 cm. longa 2–1 c.m. lata, venis supra impressis subtus prominulis, venulis utraque pagine prominentibus, subtus pallidiora. Baccæ 5–10–fasciculatæ nigricantes oblongo-ovulares 7 mm. longæ, utrinque obtusæ, 2–3–spermæ seminibus lunaribus curvis 5 mm. longis pedunculis 1 cm. longis.

HAB. Seizan, in montibus Morrison, ad 11579 ped. alt., leg. S. NAGASAWA, Nov. 1906, (No. 712); in monte Morrison ad 12000 ped. alt., (No. 2133); ad 9000 ped. alt., in eodem monte, (No. 1941), leg. T. KAWAKAMI, Oct. 1906; Arizan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906.

The plant is very near *B. barandana* VIDAL.

Papaveraceæ.

Corydalis DC.

In this genus, two species have hitherto been known from the island. We have another species from the hilly regions, which is quite different from the others. The specimens are, however, in too imperfect a state either for determination or description.

Corydalis sp.

HAB. Taitō: Daironkōsha, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (Nos. 2170 et 2183).

Cruciferæ.

Arabis LINN.

In the lowland flora we have had nothing of *Arabis*. On the high elevations, there are found three species belonging to the genus.

Arabis alpina LINN. Sp. Pl. ed-2. p. 928; DC. Prodr. I. p. 142; HOOK. f. et THOMS. in Journ. Linn. Soc. V. p. 141; HOOK. f. et ANDERS. in HOOK. f. Fl. Brit. Ind. I. p. 135; DIELS, Fl. Centr. Chin. in ENGL. Bot. Jahrb. XXIX. p. 359; LEDEB. Fl. Ross. I. p. 117; HOOK. et ARN. Bot. Beech. Voy. p 112; WAGNER, Deut. Fl. ed-3, p. 290; THOMÉ, Fl. Deut. Ost. u. Schw. II. p. 175.

Arabis albida STEV.; DC. Prodr. I. p. 142.

Arabis pterosperma EDGEW. in Tran. Linn. Soc. XX. p. 33.

HAB. in monte Morrison, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 223).

DISTRIB. Asia, from Altai westward to Europe: east Himalaya, central China northward to east Siberia.

My specimen does not quite agree with the description of *A. alpina* LINN. It seems to me that the plant differs a little from the type in its individual character only. The leaves of the present form are subentire, while those of the type are more or less dentate.

Arabis taraxacifolia ANDERS.; HOOK. f. et ANDERS. in HOOK. f. Fl. Brit. Ind. I. p. 136.

HAB. ad verticem montis Morrison, ad 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 680); eodem loco, leg. T. KAWAKAMI et G. NAKAHARA, Nov. 1905; in monte Morrison, ad 11000 ped. alt., leg. T. KAWAKAMI et U. MORI, (No. 1864).

DISTRIB. Punjab, the Himalayas.

My specimen is quite agreeable with the description of the species above referred, written in HOOK. f. Fl. Brit. Ind. I. p. 136, and also very like the European *A. arenosa* SCOP. Although I have not yet seen an Indian specimen, I think that the plant should be referred to this species. The specimen bearing No. 680 is of a rather elongated form and of prostrate habit. This form has much more runners and more remote leaves than the type.

Arabis sp. Caulis stellato-tomentosus, 14–15 cm. longus, basi 2–3 foliolatus ramosus. Folia radicalia longe petiolata, petiolis 2 cm. longis, laminis obovatis apice rotundatis integris basi cuneatis et remote serratis, utrinque stellato-tomentosis, 9 mm. longis 4 mm. latis. Siliquæ lineares 2 cm. longæ.

HAB. in monte Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2234).

As the specimens are wanting of flowers, they are not specifically determinable.

Cardamine LINN.

Of this genus, two species have been recorded from the island. We have two more species from the high elevations of Mt. Morrison.

Cardamine reniformis HAYATA, sp. nov. Caulis humilis tenuis 8–9 cm. longus erectus glaber. Folia radicalia longe petiolata, petiolis circ. 5 cm. longis basi leviter dilatis, laminis rotundatoreniformibus apice obtusis basi reniformibus repandis palmatim-6–7-nerviis, 4 cm. longis totidem latis utraque pagine subglabris pauce ciliolatis. Folia caulina breve petiolata radicali similia. Scapi pauci-florati. Flores parvi, 3 mm. longi pedicellati. Sepala 4, oblongo-elliptica, utrinque obtusa, $2\frac{1}{2}$ mm. longa. Petala spathulata 2 mm. longa. Stamina 6, $2\frac{1}{2}$ mm. longa. Ovarium cylindraceum 2 mm. longum, stylo brevi, stigmate globoso. Siliquæ lineares 2 cm. longæ $\frac{1}{2}$ mm. latæ, seminibus oblongis compressis $\frac{1}{2}$ mm. longis.

HAB. in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1982).

The present species differs from the other species of this genus in having reniform leaves. The leaves are somewhat like *C. asarifolia* LINN., in which species they are never cordate or reniform.

Cardamine sp. Caulis glaber 10–15 cm. longus. Folia radicalia 15 cm. longa 2 cm. lata bi-pinnata longe petiolata, pinnis lateralibus breve petiolulatis, pinnulis partis superioris sessilibus majoribus lobatis, lobis rotundatis. Folia caulina multo minora.

HAB. in monte Morrison, ad 11000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2252).

As the specimens are sterile, the accurate identification is impossible.

Violaceæ.

Viola LINN.

Six species belonging to this genus are known from the low districts. In the mountainous regions, we have five species, among which two are new.

Viola japonica Langsd.; DC. Prodr. I. p. 295; Miq. Prol. Fl. Jap. p. 86; Maxim. in Mél. Biol. IX. (1877) p. 724; Franch. et Savat. Enum. Pl. Jap. I. p. 42, et II. p. 287; Forbes et Hemsl. Ind. Fl. Sin. I. p. 53; Henry, List Pl. Formos. p. 18; Itō et Matsum. Tent. Fl. Lutch. p. 207; Palibin, Conspect. Fl. Koreæ, I. p. 32; Matsum. et Hayata, Enum. Pl. Formos. p. 29.

Viola japonica var. *pekinensis* Maxim. "Bull. Soc. Nat. Mosc. (1879) p. 4."

Viola kamtschatica var. *pekinensis* Regel, Pl. Rad. I. p. 230.

Hab. Tappansha, ad 3138 ped. alt., leg. S. Nagasawa, Oct. 1905, (No. 774); eodem loco, leg. T. Kawakami et U. Mori, Oct. 1906, (No. 1759); in monte Morrison, ad 7000 ped. alt., leg. T. Kawakami et U. Mori, Oct. 1906, (No. 2011).

Distrib. Northern and central China, and Japan.

The same as the Japanese form.

Viola Kawakamii Hayata, sp. nov. Herba acaulis. Folia longe petiolata stipulata, petiolis gracilibus 10–15 cm. longis, laminis hastato-cordatis acuminatis vel obtusis crenulatis ad sinus crenæ pilosis ceterum glabris, subtus glauco-violascentibus circ. 3 cm. longis 2 cm. latis, stipulis laciniatis ad petiolum parce adnatis. Flores patentes 1.5 cm. in diametro æquantes, longe pedunculati, pedunculis petiolo æquilongis, bracteis 2 subulatis remote sitis, 5 mm. longis. Sepala subæqualia obtuso-acuminata 4 mm. longa 1 mm. lata, basi ultra insertionem ½ mm. producta glabra. Petala superiora et lateralia subæqualia ovato-cuneata apice emarginata, 12 mm. longa 5 mm. lata, inferius majus 15 mm. longum 9 mm. latum apice valde emarginatum vel leviter 2-lobatum basi longe calcaratum, calcare 6 mm. longo leviter curvo. Antheræ subsessiles, connectivo complanato apice in membranam 1 mm. longam producto; stamina 2 inferiora dorso basi calcarata, calcare 3 mm.

longo. Stylus fere rectus, stigmate terminali. Capsula ignota.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, (No. 649); in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, (No. 2010).

Very near *V. formosana* HAYATA, but differs from it in having more elongate leaves.

Viola Nagasawai MAKINO et HAYATA, in MATSUM. et HAYATA, Enum. Pl. Formos. p. 30.

HAB. in monte Morrison, leg. G. NAKAHARA, Oct. 1906.

Viola tozanensis HAYATA, sp. nov. Herba acaulis. Folia longe petiolata stipulata, petiolis 4 cm. longis, laminis late cordatis rotundatis crenulatis setoso-pubescentibus subtus glaucis violascentibus, circ. 2 cm. longis totidem latis, stipulis laciniatis ad petiolum parce adnatis. Flores patentes reflexi 1½ cm. in diametro æquantes longe pedunculati, pedunculis petiolo æquilongis, bracteis 2 subulatis oppositis 5 mm longis. Sepala sub-æquilonga obtuso-acuminata 4 mm. longa 1 mm. lata basi ultra insertionem 1 mm. producta glabra. Petala superiora et lateralia subæqualia ovato-cuneata apice truncata 10 mm. longa 5 mm. lata, inferius majus 18 mm. longum 8 mm. latum apice valde emarginatum basi longe calcaratum, calcare 4 mm. longo leviter curvo. Antheræ subsessiles, connectivo complanato apice in membranam 1 mm. longam producto; stamina 2 inferiora dorso basi calcarata, calcare 3 mm. longo. Stylus fere rectus, stigmate sub-terminali. Capsula ignota.

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906.

This *Viola* is found attaching on the large trunk of a tree. The flower is patent and of a whitish purple colour.

Viola sp.

HAB. Tōzan et Arizan, in montibus Morrison, leg. G. NAKAHARA. No flower, indeterminable.

Bixineæ

Idesia MAXIM.

Idesia polycarpa MAXIM. in Mél. Biol. VI. p. 9; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 45; Bot. Mag. t. 6794; HENRY, List Pl. Formos. p. 18; MATSUM. in Tōkyō Bot. Mag. XII. p. 67; DIELS, Fl. Centr. Chin. in ENGL. Bot. Jahrb. XXIX. p. 478; MATSUM. et HAYATA, Enum. Pl. Formos. p. 32.

HAB. Taitō: Iryokukakusha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2165); Kagi: Burakukansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1756).

DISTRIB. Central China and Japan.

Polygaleæ.

Polygala LINN.

Polygala arcuata HAYATA, sp. nov. (Pl. I.). Tota, præter ramulos novellos tenuiter pubescentes, glaberrima, caule lignescente plerumque simplici. Folia petiolata, laminis membranaceis crassiusculis elliptico-lanceolatis acuminatis integris 10 cm. longis 3 cm. latis basi in petiolum 1 cm. longum cuneatum attenuatis supra opacis subtus glaucescentibus, venis transversis primariis utrinque circ. 4–5 arcuatis prope marginem anastomosantibus. Racemi caulis apicem versus axillares vel terminales 5–6 cm. longi densiuscule multiflorati folium haud superantes. Flores lutei pedicellis brevibus 2 mm. longis. Sepala 5, exteriora 3, interiora 2, decidua, supremum exteriorum sepalorum globosum majusculum rotundatum saccatum 3 mm. longum, 2 inferiora exteriorum sepalorum late rotundata basi obliqua 1½ mm. longa; 2 interiora petaloidea oblique oblonga 5½ mm. longa. Petala alte coalita, lateralia arte imbricata 7 mm. longa apice rotundata, carina breviter cucullata dorso longe cristata incrassata bisaccata. Ovarium glabrum breviter stipitatum, disco late annulari. Stylus apice dilatus, infra stigma appendiculatus. Capsula 5 mm. lata 4 mm. longa, membranacea compressa obreniformis v. late orbiculata emarginata ad margines loculicide dehiscens. Semina ovoidea 2 mm. longa, pendula pilosa strophiolata, strophiolis in utroque latere 1.2 mm. longis.

HAB. Taichū: Kashigatani, leg. G. NAKAHARA, Feb. 1907.

Somewhat resembles *P. Wattersii* HANCE, in Journ. Bot. (1881) p. 209; but differs from it in having obreniform fruits, much smaller flowers, divided crests, and in many other points.

Polygala japonica HOUTT.; DC. Prodr. I. p. 324; BAKER et S. MOORE, in Journ. Linn. Soc. XVII. p. 379; FRANCHET, Pl. David. p. 45; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 45; HENRY, List Pl. Formos. p. 18; ITŌ et MATSUM. Tent. Fl. Lutch. p. 311; PALIBIN, Conspect. Fl. Koreæ, I. p. 37; MATSUM. et HAYATA, Enum. Pl. Formos. p. 34.

Polygala sibirica LINN. Sp. Pl. ed-2, p. 987; DC. Prodr. I. p. 324; A. W. BENN. in Journ. Bot. (1878) p. 277; HANCE, in "Journ. Bot. (1882) p. 257"; FORBES et HEMSL. Ind. Fl. Sin. I. p. 61.

HAB. in monte Morrison, leg. G. NAKAHARA, Oct. 1906.

DISTRIB. From Siberia to Japan and India, and occurs also in Australia.

Caryophylleæ.

Dianthus LINN.

Dianthus superbus LINN. Sp. Pl. ed-2, p. 589; DC. Prodr. I. p. 365; HANCE, in Journ. Bot. (1883) p. 296; FRANCHET, Pl. David. p. 46; LEDEB.

Fl. Ross. I. p. 533; MAXIM. Prim. Fl. Amur. p. 52; REGEL, Pl. Radd. I. p. 288; MIQ. Prol. Fl. Jap. p. 9; SCHMIDT, Reis. in Amur. p. 116; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 46; ENGL. in ENGL. Bot. Jahrb. VI. p. 57; FORBES et HEMSL. Ind. Fl. Sin. I. p. 64; DIELS, Fl. Centr. Chin. in ENGL. Bot. Jahrb. XXIX. p. 316; PALIBIN, Conspect. Fl. Koreæ, I. p. 39; MATSUM. et HAYATA, Enum. Pl. Formos. p. 35.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., (No. 700); Suizan, in isdem montibus, ad 7702 ped. alt., (No. 664); in monte Morrison, ad 9000 ped. alt., (Nos. 2040 et 1895); in montibus centralibus, ad 7000 ped. alt., (No. 1861); Taitō: Taironkōsha, (Nos. 1883 et 1950): Toroku: Gunkei; leg. T. KAWAKAMI et U. MORI, Nov. 1906; Nanto: Hinokiyama, leg. G. NAKAHARA, Feb. 1907.

DISTRIB. Europe to Mongolia; China throughout, Saghalien and Japan.

Dianthus sp.

HAB. in monte Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2259).

This differs from *D. superbus* LINN. in having elongate bracts, and especially two inferior ones.

Silene LINN.

Silene Fortunei VIS. in Linnæa, XXIV. p. 181, et XXXVI. p. 688; FRANCHET, Pl. David. p. 47; FORBES et HEMSL. Ind. Fl. Sin. I. p. 65; HENRY, List Pl. Formos. p. 19; DIELS, Fl. Centr. Chin. in ENGL. Bot. Jahrb. XXIX. p. 318; Bot. Mag. t. 7649; MATSUM. et HAYATA, Enum. Pl. Formos. p. 35.

HAB. in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, (No. 1917).

DISTRIB. Central and southern China.

The present plant found in the high regions is very like the specimen (No. 20, A. TASHIRO) collected on the sea shore. Excepting that the flowers of the former is almost as half as those of the latter, I can find no distinction whatever between the two. My specimen should, therefore, be regarded as a form of the shore plant.

Cucubalus LINN.

Cucubalus baccifer LINN. Sp. Pl. ed-2, p. 591; DC. Prodr. I. p. 367; LEDEB. Fl. Ross. I. p. 332; MAXIM. Prim. Fl. Amur. p. 56; REGEL, Fl. Radd. p. 333; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 48; KOMAROV, Fl. Manshuriæ, II. p. 205; WAGNER, Deut. Fl. ed-3, p. 244; DIELS, Fl. Centr. Chin. in ENGL. Bot. Jahrb. XXIX. p. 319; THOMÉ, Fl. Deut. Öst. u. Schw. II. p. 98.

HAB. in monte Morrison, ad 13000 ped. alt., et ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI. Oct. 1906, (Nos. 2253 et 1984); Rakurakusha, leg. G. NAKAHARA, Aug. 1905, (No. 454).

DISTRIB. The Himalayas, China throughout, eastward to Japan as far as North America; westward to Europe.

Cerastium LINN.

We have hitherto had no species belonging to this genus from Formosa. The following *Cerastium* is the first recorded from the island.

Cerastium morrisonense HAYATA, sp. nov. Herbæ diffusæ v. cæspitosæ, glanduloso-pubescentes demum glabræ. Folia plerumque remota interdum approximata lineari-lanceolata vel spathulato-acuminata basi interdum attenuata dilata semi-amplexicaulia apice calloso-acuta vel aristato-acuta 1–2 cm. longa 2–2½ mm. lata. Cymæ terminales, nunc uni-floræ, nunc tri-floræ, bracteatæ, bracteis scariosis, pedicellis 2–1½ cm. longis glanduloso-pubescentibus. Sepala 5, lanceolata 7½ mm. longa margine scariosa extus glanduloso-pubescentia intus glabra. Petala 5, oblanceolata 13 mm. longa apice 2–lobata, lobis oblongis obtusis 6 mm. longis, basi angusta. Stamina 10, filamentis petalo 2-plo brevioribus ad basin filamentorum sepalis oppositorum 2-glanduliferis. Ovarium ovoideum 2 mm. longum 1-loculare ∞ ovulatum. Styli 5, sepalis oppositi ovario longiores 3 mm. longi. Capsula cylindracea 7 mm. longa 2 $\frac{1}{2}$ mm. lata erecta apice in dentes 10 dehiscens, dentibus obtusis truncatis. Semina subreniformi-globosa, 1 mm. longa a latere plus minus compressa dorso granulata.

HAB. ad verticem montis Morrison, ad 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905, (Nos. 681 et 619); in montis Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 2127 et 2261).

The plant comes nearest to *C. grandiflorum* WALD. et KIT., but differs from it in having lanceolate leaves and smaller flowers.

Cerastium pilosum LEDEB. in "Mém. Acad. Pétersb. V. p. 539," "Fl. Alt. II. p. 173"; Fl. Ross. I. p. 398, et "Ic. Pl. Fl. Ross. t. 351"; FORBES et HEMSL. Ind. Fl. Sin. I. p. 67.

HAB. in monte Morrison, ad 13000 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 626).

DISTRIB. Ural eastward to North China, Manchuria and Korea.

In the imperfectness of the specimen, the determination is rather conjectural.

Stellaria LINN.

Two species belonging to this genus have been known from Formosa. We have here a more plant from the hilly regions.

Stellaria stellato-pilosa HAYATA, sp. nov. (Pl. II). Herbæ diffusæ ramosæ laxe adscendentes in totum præter caulem densissime stellato-pilosæ. Folia sessilia ovato-lanceolata basi cordata apice aristato-acuminata 12 mm. longa 3 mm. lata rarius ovato-cordata, supra pilis stellatis subtus pilis longioribus dense tectis, costis prominentibus. Flores 3–4, in cymas terminales v. rarius axillares dispositi pedicellati, pedicellis circ. 1 cm. longis, basi pedicelli bracteati, bracteis 2 oppositis ovato-lanceolatis. Sepala 5, lanceolata extus dense stellato-pilosa demum glabra 3½ mm. longa 1 mm. lata. Petala profunde 2-fida, lobis lanceolatis obtusis sepalo longioribus. Stamina 10; discus inter stamina in glandulas prominentes plus minus expansus. Ovarium 1-loculare, pauci-ovulatum. Styli 3. Capsula oblongo-ovoidea, 4 mm. longa in 3 valvas dehiscens, valvis 2-fidis. Semina globoso-reniformia a latere compressa, 1 mm. in diametro æquantia granulata v. muricata.

HAB. ad verticem montis Morrison, ad 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 622); in monte Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2258).

Near *Stellaria saxatilis* BUCH.-HAM.; but differs from it in having lanceolate leaves and entirely separate sepals.

Hypericineæ.

Hypericum LINN.

Among this genus, eight species were previously recorded from the island. A more species is found in the high regions.

Hypericum attenuatum CHOISY, in DC. Prodr. I. p. 548; HANCE, in Journ. Bot. (1874) p. 259, (1878) p. 104, et (1885) p. 321; MAXIM. in Mél. Biol. XI. p. 166; FRANCHET, Pl. David. p. 56; FORBES et HEMSL. Ind. Fl. Sin. I. p. 72.

HAB. ad verticem montis Morrison, ad 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 754); in monte Morrison, ad 12000 ped. alt., (No. 2260) ; et ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1800).

DISTRIB. Baical eastward to central and northern China.

Ternstrœmiaceæ.

Ternstrœmia LINN.

Ternstrœmia japonica THUNB. in Trans. Linn. Soc. II. p. 335 ; SIEB. et ZUCC. Fl. Jap. p. 148, t. 80 ; BENTH. Fl. Hongk. p. 27 ; DYER, in HOOK. f. Fl. Brit. Ind. I. p. 280 ; MIQ. Prol. Fl. Jap. p. 202 ; ENGL. in ENGL. Bot. Jahrb. VI. p. 60 ; FORBES et HEMSL. Ind. Fl. Sin. I. p. 75 ; HENRY, List Pl. Formos. p. 19 ; ITŌ et MATSUM. Tent. Fl. Lutch. p. 324 ; MATSUM. et HAYATA, Enum. Pl. Formos. p. 45.

Cleyera japonica THUNB. Fl. Jap. p. 224.

Cleyera fragrans et *Cleyera dubia* CHAMP. in Trans. Linn. Soc. XXI. p. 115.

Taonabo japonica SZYSZ. in ENGL. et PRANTL. Nat. Pf.-fam. III. 6. p. 188.

HAB. Nantō : Mushazan, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1141).

DISTRIB. South China and Japan. Western peninsula of India to Ceylon, and Khasia mountains to Sumatra and the Philippine islands.

Eurya THUNB.

Eurya japonica THUNB. Fl. Jap. p. 191, t. 25 ; DC. Prodr. I. p. 525 ; BENTH. Fl. Hongk. p. 28 ; DYER, in HOOK. f. Fl. Brit. Ind. I. p. 284 ; HOOK. et ARN. Bot. Beech. Voy. p. 260 ; BLUME, Mus. Bot. Lugd.-Bat. II. p. 105 ; MIQ. Prol. Fl. Jap. p. 202 ; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 57 ; FORBES et HEMSL. Ind. Fl. Sin. I. p. 77 ; HENRY, List Pl. Formos. p. 19 ; DIELS, Fl. Centr. Chin. p. 474 ; PALIBIN, Conspect. Fl. Koreæ, I. p. 46 ; MATSUM. et HAYATA, Enum. Pl. Formos. p. 46.

HAB. in monte centrali, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, (No. 1866); inter Arizan et Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 8000 ped. alt., (No. 1788), et ad 10000 ped. alt., (No. 2121), leg. T. KAWAKAMI et U. MORI, Oct. 1906; eodem loco, ad 11000 ped. alt., (No. 623), Ganzan, in montibus Morrison, ad 9041 ped. alt., (No. 623), leg. S. NAGASAWA, Nov. 1905; Rinkiho, ad 4500 ped. alt., leg. N. KONISHI, Feb. 1904; Taitō: Inikufuku, et Iryokukakusha, (No. 1840), leg. T. KAWAKAMI et U. MORI, Dec. 1906.

DISTRIB. The Malay archipelago, southern and central China, and Japan.

The same as the Luzon form.

Eurya strigillosa HAYATA, sp. nov. Ramuli graciles strigillosi primum sericeo-villosi. Folia disticha approximata sessilia coriacea oblongo-acuminata vel lanceolata 10 cm. longa 2½ cm. lata basi rotundata sæpiusque leviter inæqualia apice acuminata margine præter basin serrulata, serrulis acutis, supra glabra nitida subtus strigillosa, costis prominentibus, venis utraque inconspicuis. Flores ♂ breve pedicellati, pedicellis 1 mm. longis vel longioribus, ad axillas foliorum 2–3 congesti, patentes 8 mm. in diametro æquantes. Sepala 5–6, valde inæqualia late rotundata 1½ mm. longa totidem lata extus pilosula. Petala plerumque 5, obovato-oblonga 4 mm. longa 2½ mm. lata glabra basi leviter connata. Stamina circ. 15, glabra petalo breviora, filamentis planis 2½ mm. longis, antheris undulatis filamento duplo vel triplo brevioribus. Ovarii rudimentum brevissimum conicum apice barbatum. Flores ♀ ignoti.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2023).

The plant is very like *E. distichophylla* HEMSL.; but differs from it in having serrulate leaves and larger flowers which attain a diameter of even 8 mm.

Actinidia LINDL.

Actinidia callosa LINDL.; WALP. Ann. I. p. 15; DYER, in HOOK. f. Fl. Brit. Ind. I. p. 286; FORBES et HEMSL. Ind. Fl. Sin. I. p. 78; HENRY, List Pl. Formos. p. 20; DIELS, Fl. Centr. Chin. p. 470; MATSUM. et HAYATA, Enum. Pl. Formos. p. 47.

HAB. Kagi: in monte Kishirei, leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. Himalaya, central China to Japan.

Stachyurus SIEB. et ZUCC.

Stachyurus præcox SIEB. et ZUCC. Fl. Jap. I. p. 43, t. 18; MIQ. Prol. Fl. Jap. p. 204; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 59; FORBES et HEMSL. Ind. Fl. Sin. I. p. 79; MATSUM. et HAYATA, Enum. Pl. Formos. p. 48.

Stachyurus himalaicus HOOK. f. et THOMS. in HOOK. f. Fl. Brit. Ind. I. p. 288; DIELS, Fl. Centr. Chin. p. 475.

HAB. in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (Nos. 1873 et 1810); Kōshūn: Naibun, leg. G. NAKAHARA, Feb. 1907.

DISTRIB. The Himalayas through central China to Japan.

This is somewhat different from what we have in Japan. The plant should, I think, be regarded as a form of the Japanese species.

Schima REINW.

Schima Noronhæ REINW.; MIQ. Fl. Ind. Bat. I.-2, p. 492; BENTH. Fl. Hongk. p. 29; MAXIM. Mél. Biol. XII. p. 426; FORBES et HEMSL. Ind.

Fl. Sin. I. p. 80; HENRY, List Pl. Formos. p. 20; MATSUM. in Tōkyō Bot. Mag. XII. p. 63; ITŌ et MATSUM. Tent. Fl. Lutch. p. 328; MATSUM. et HAYATA, Enum. Pl. Formos. p. 49:

Gordonia javanica HOOK. f. Bot. Mag. t. 4539.

HAB. in monte Morrison, ad 6500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1711).

DISTRIB. The eastern frontier of India; from Cochinchina through the Malay archipelago, and South China to the Loo-choo islands.

Thea LINN.

Thea brevistyla HAYATA, sp. nov. (Pl. III.). Ramuli graciles primum pubescentes demum glabri. Folia breve petiolata, petiolis 5 mm. longis semi-teretibus supra sulcatis pubescentibus, laminis elliptico-oblongis 4–5 cm. longis 2 cm. latis basi apiceque acutis vel obtusis margine crenulatis leviter repandis basin versus sæpissime integris utraque pagine glabris, costis prominulis venis impressis coriaceis. Flores ad axillas foliorum semper solitarii sessiles patentes 3 cm. in diametro æquantes. Sepala decidua 4–5 valde inæqualia 2-seriata late ovata obtusa vel mucronata 6–8 mm. longa totidem lata extus medio pilosiuscula. Petala 5 alba obovato-cuneata apice sinuato-emarginata vel 2-lobata circ. 1½ cm. longa 1 cm. lata. Stamina circ. 30, 2-seriata, exteriora longiora, filamentis plerumque petalis duplo brevioribus basi connatis. Ovarium globosum sericeo-pilosum 1½ mm. longum. Styli 4, brevissimi basi connati apice recurvi 1 mm. longi. Fructus ignotus.

HAB. Arizan et Tōzan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906.

Thea caudata (WALL.).

Camellia caudata WALL. "Pl. As. Rar. III. p. 36"; DYER, in HOOK. f. Fl. Brit. Ind. I. p. 293.

HAB. Taitō: Iryokukakusha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2157).

DISTRIB. Himalaya, Khasia mountains, and South China.

Although I have seen no specimen of the Indian plant, my plant is, I think, quite referable to this species.

Tiliaceæ.

Triumfetta LINN.

Triumfetta pilosa ROTH; DC. Prodr. I. p. 506; BENTH. Fl. Hongk. p. 41; FORBES et HEMSL. Ind. Fl. Sin. I. p. 93; HENRY, List Pl. Formos. p. 23; MATSUM. et HAYATA, Enum. Pl. Formos. p. 63.

HAB. Sanchōki, leg. S. NAGASAWA, Nov. 1905, (No. 726).

DISTRIB. Tropical Asia and Africa; South China.

Elæocarpus LINN.

Elæocarpus decipiens HEMSL. Ind. Fl. Sin. I. p. 94; HENRY, List Pl. Formos. p. 24; ITŌ et MATSUM. Tent Fl. Lutch. p. 349; MATSUM. et HAYATA, Enum. Pl. Formos. p. 65.

HAB. Biōritsu: Sensuikō, leg. T. KAWAKAMI et U. MORI, Juli. 1906, (No. 1101).

DISTRIB. South China and the Loo-choo islands.

Geraniaceæ.

Geranium LINN.

Geranium Robertianum LINN.; DC. Prodr. I. p. 644; MAXIM. Mél. Biol. X. p. 613; FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 307. (var. *glabrum*);

Hook. f. Fl. Brit. Ind. I. p. 432; Diels, Fl. Centr. Chin. p. 419; Ledeb. "Fl. Alt. III. p. 233"; Thomé, Fl. Deut. Öst. u. Schw. III. p. 201; Wagner, Deut. Fl. ed-3, p. 431.

Hab. Taitō: Bunshisekisha, leg. T. Kawakami et U. Mori, Dec. 1906, (No. 2152).

Distrib. Southern part of Japan, China throughout, and westward to Europe.

This exactly agrees with the Japanese form.

Geranium uniflorum Hayata, sp. nov. Caulis 1–2 ped. altus erecto-patens glaber superne pilosus, ramis articulato-nodosis. Folia longe petiolata piloso-pubescentia, petiolis 2–4 cm. longis, laminis ambitu late orbicularibus vel pentagonis 5–7 cm. in diametro æquantibus profunde 5-partitis, segmentis acuminatis, pinnatifidis inciso-serratis, stipulis oblongis abrupte acuminatis 1 cm. longis extus pilosiusculis. Flores axillares vel subterminales longe pedunculati uniflori 2-bracteati, pedunculis 5–6 cm. longis pubescentibus, bracteis subulatis oppositis circ. 1 cm. longis. Sepala 5, elliptica 12 mm. longa 5 mm. lata extus distincte 5-nervia ad nervos pilosula apice aristato-acuta intus glabra. Petala 5, obovata cuneata integra 2 cm. longa vel longiora apice rotundata emarginata basi supra unguem ciliata. Glandulæ 5. Stamina 10, 2-seriata, filamentis basi dilatis brevissime ciliatis antheris oblongis deciduis. Ovarium pilosum. Capsulæ lobi oblongi pilosi 5 mm. longi 2½ mm. lati, caudis 14 mm. longis.

Hab. ad verticem montis Morrison, ad 13094 ped. alt., leg. S. Nagasawa, Nov. 1905, (No. 684); in eodem monte, ad 13000 ped. alt., leg. T. Kawakami et U. Mori, Oct. 1906, (No. 2254).

This new plant is somewhat like *G. pratense* Linn. in its foliage and flowers; but greatly differs from it in having uni-flowered peduncles. The flowers of the present species are always solitary as is the case with *G. sanguineum* LINN. and *G. sibiricum* LINN.

Oxalis LINN.

In this genus, *Oxalis corniculata* LINN. has been the only species recorded from the island. We have here another species found in the montane zone.

Oxalis Griffithii EDGEW. et HOOK. f. in HOOK. f. Fl. Brit. Ind. I. p. 436; S. MOORE, in Journ. Bot. (1875) p. 230; FORBES et HEMSL. Ind. Fl. Sin. I. p. 99; DIELS, Fl. Centr. Chin. p. 420.

HAB. Suizan, in montibus Morrison, ad 7700 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 654); in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1792); Arizan, in isdem montibus, leg. G. NAKAHARA, Nov. 1906.

DISTRIB. Eastern Himalaya and the Khasia mountains; also in central China.

Impatiens LINN.

Impatiens uniflora HAYATA, sp. nov. Herbæ erectæ circ. 30 cm. altæ pauce ramosæ sursum flexuosæ, caulibus (exsiccatis) stramineis præter apicem glabris. Folia versus apicem caulis approximata breviter petiolata, laminis oblongis ellipticis vel lanceolato-ellipticis circ. 8 cm. longis 2½ cm. latis apice caudato-acuminatis basi cuneatis in petiolum attenuatis margine serratis, serraturis setosis incurvis. Flores majusculi rosei terminales vel ex axillis superioribus, pedunculis gracilibus circ. 4 cm. longis 1-floris (rarius 2–) nudis medio bracteola minuta incurva instructis. Sepala 3: 2 lateralia oblique ovata acuminata integra 6 mm. longa 2½ mm. lata, posticum longe saccatum apice ad orem acutum, ore 1½ cm. in diametro, basi subito calcar breve incurvum apice incrassatum ac bilobum abeuns, a basi usque ad apicem calcaris 3½ cm. longum. Petala: vexillum alis duplo brevius late subreniforme medio dorso cristatum in cornu recurvum maculosum attenuatum; alæ ambitu ellipticæ 2⅓ cm. longæ latere superiore 2-lobatæ, lobo basilari exteriore lato, lobo apicali longiore oblongo. Stamina 5, filamentis inæqualibus brevioribus circ. 4 mm. longis complanatis medio appendiculatis, antheris ovatis apiculatis circa pistillum coherentibus, loculis introrsum dehiscentibus. Ovarium oblongum 4 mm. longum, stigma sessile 5-dentatum. Capsula elongata 2 cm. longa 5-valvata, valvis elastice dissilientibus, columna persistente. Semina longe elliptica vix longiora quam 2 mm., testa glabra sub microscopium minute papillosa.

HAB. Tozan et Arizan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, (No. 1724).

Rutaceæ.

Bœnninghausenia REICHB.

Bœnninghausenia albiflora REICHB. "Conspect. Reg. Veg. p. 197"; HOOK. f. Fl. Brit. Ind. I. p. 486; HANCE, in Journ. Bot. (1874) p. 259; FRANCHET, Pl. David. p. 66; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 71; MIQ. Prol. Fl. Jap. p. 209; ENGL. in ENGL. et PRANT. Nat. Pfl.-fam. III.-4, p. 130; FORBES et HEMSL. Ind. Fl. Sin. I. p. 102; DIELS, Fl. Centr. Chin. p. 423; HAYATA, in Tōkyō Bot. Mag. XX. p. 52.

HAB. Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 1738 et 1772).

DISTRIB. Himalaya to Japan and China; recently found in Luzon.

Evodia FORST.

Evodia meliæfolia BENTH. Fl. Hongk. p. 58; HOOK. f. Fl. Brit. Ind. I. p. 490; FORBES et HEMSL. Ind. Fl. Sin. I p. 104; HENRY, List Pl. Formos. p. 24; DIELS, Fl. Centr. Chin. p. 423; MATSUM. et HAYATA, Enum. Pl. Formos. p. 70.

Megabotrya meliæfolia HANCE, in WALP. Ann. II. p. 259.

Evodia glauca MIQ. in Ann. Mus. Bot. Lugd.-Bat. III. p. 23.

HAB. Taitō: Dakunsha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2177).

DISTRIB. South China and southern part of Japan.

Skimmia THUNB.

Skimmia japonica THUNB. Fl. Jap. pp. 4 et 62; FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 311; DC. Prodr. II. p. 18; ITŌ et MATSUM. Tent. Fl. Lutch. p. 357; DIELS, Fl. Centr. Chin. p. 424; HAYATA, in Tōkyō Bot. Mag. XX. p. 56; MERRILL, in Philipp. Journ. Sci. I. Supp. Bot. p. 201.

HAB. in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 2060 et 2059); Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906.

DISTRIB. Himalaya, central China and Japan throughout; recently found in the Philippine islands.

Murraya LINN.

Murraya exotica LINN.; DC. Prodr. I. p. 537; BENTH. Fl. Hongk. p. 56; FORBES et HEMSL. Ind. Fl. Sin. I. p. 159; HOOK. et ARN. Bot. Beech. Voy. p. 260; WIGHT, Ic. Pl. Ind. or. t. 96; BENTH. Fl. Austral. I. p. 369; OLIV. in Journ. Linn. Soc. V. Supp.-2, p. 28; HOOK. f. Fl. Brit. Ind. I. p. 502; MAXIM. in Mél. Biol. XII. p. 429; MATSUM. et HAYATA, Enum. Pl. Formos. p. 74.

HAB. Taitō: Kōshūsha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 1837).

DISTRIB. Widely spread in tropical Asia and Polynesia.

Ilicineæ.

There are three species belonging to this family; the specimens are all very imperfect and therefore they are not determinable.

Celastrineæ.

Euonymus LINN.

In this genus, we had previously four species from the lowland. Two more species are found in the montane zone.

Euonymus echinatus WALL.; LAWSON, in HOOK. f. Fl. Brit. Ind. I. p. 610; FORBES et HEMSL. Ind. Fl. Sin. I. p. 119; ITŌ et MATSUM. Tent. Fl. Lutch. p. 371.

HAB. in monte Morrison, ad 7000 ped. alt., (No. 1721); in eodem monte, ad 9000 ped. alt., (No. 2004), leg. T. KAWAKAMI et U. MORI, Nov. 1906; Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; Nantō: Mushazan, leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1122).

DISTRIB. The Himalayas, central China and the Loo-choo islands.

Euonymus trichocarpus HAYATA, sp. nov. Ramuli trichotomæ divaricati sub-tetragoni glabri. Folia opposita petiolata, petiolis circ. 1 cm. longis semi-teretibus, laminis oblongo-ellipticis 6–7 cm. longis 4 cm. latis apice obtusis vel acutis basi rotundatis vel obtusis rarius leviter angustis margine serrulatis, serrulis obtusis, venis utraque prominulis. Cymæ (ad ramulos terminales) laterales oppositæ paucifloræ. Flores ignoti. Capsula depresso-globosa 6–7 mm. in diametro æquans breve echinulata, echinulis 1 mm. longis.

HAB. in monte Morrison, 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1791).

This new plant resembles *E. echinatus* WALL.; but differs from it in having very short and densely covering spines on the fruit.

Celastrus LINN.

Celastrus articulatus THUNB. Fl. Jap. p. 97; DC. Prodr. II. p. 7; MAXIM. in Mél. Biol. XI. p. 200; FRANCHET, Pl. David. p. 70; MIQ. Prol. Fl. Jap. p. 17; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 80; SIEB. et ZUCC. Fl. Jap. Fam. Nat. I. p. 149; A. GRAY, Bot. Jap. p. 384; FORBES et HEMSL. Ind. Fl. Sin. I. p. 122; HENRY, List Pl. Eormos. p. 27; DIELS, Fl. Centr. Chin. p. 446; PALIBIN, Conspect. Fl. Koreæ, I. p. 54; MATSUM. et HAYATA, Enum. Pl. Formos. p. 84.

HAB. Taitō: Iryokukakusha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2178).

DISTRIB. Central and northern China, and Japan northward to Saghalien.

Rhamneæ.

Rhamnus LINN.

Rhamnus arguta MAXIM. var. **Nakaharai** HAYATA, n. v. Rami glaberrimi, subalterne divaricati. Folia rotundato-ovata basi rotundata vel acuta apice acuminata vel cuspidata 7 cm. longa $3\frac{1}{2}$ cm. lata margine præter basin apicemque crenulato-serrata, serraturis setaceo-acuminatis recurvatis, venis utrinque 5–6 omnibus angulo acuto emergentibus leviter arcuatis, membranacea, petiolis circ. 1 cm. longis. Flores ♂ ignoti. Flores ♀ in axillis foliorum inferiorum circ. 5–6 fasciculati, fasciculis paulo supra-axillaribus cum ramulo connatis interdum 5–6 mm. supra axillam quasi insertis, pedicellis tenuibus petiolum paulo superantibus 1 cm. longis apice incrassatis in tubum calycis turbinatum gradatim abeuntibus. Calycis lobi tubum triplo superantes circ. 3 mm. longi lanceolati apice callosi trinervii. Rudimenta petalorum staminaque filiformia minutissima ½ mm. longa. Ovarium globosum 1 mm. longum e tubo exsertum in stylum cylindraceum 2 mm. longum attenuatum, stylo apice 3–4 fido, ramis 1½ mm. longis stigmatosis recurvato-patentibus. Fructus ignotus.

HAB. Taichū: Binōshō, leg. G. NAKAHARA, Feb. 1907.

DISTRIB. Type: North China.

The present variety differs from the type in having slender flowers and longer styles, and especially in the supra-axillary inflorescence.

Sapindaceæ.

Acer LINN.

Three species belonging to this genus have been known hitherto from the low districts. We have here more four species, all confined to the high regions. The specimens are all in too imperfect a state for exact determination.

Acer sp. (aff. *A. micrantho* S. et Z.). Ramuli glabri. Folia ambitu orbicularia 7 cm. in diametro æquantia palmatim 7-loba, lobis lanceolatis acuminatis, duplicato-dentatis, lobo terminali 5 cm. longo 1½ cm. lato, lobis infimis brevioribus 2½ cm. longis, petiolis 2 cm. longis.

HAB. Taitō: Bataiankei, in monte Lagalan, ad 5000 ped. alt., leg. N. KONISHI, Juni. 1902.

Acer sp. (aff. *A. cratægifolio* S. et Z.). Ramuli glabri, atropurpurei Folia ovato-cordata 5-nervia, 8 cm. longa 5 cm. lata leviter 3-loba, lobis inconspicuis obtusissimis, margine præter apicem duplicato-serrata, apice acuminata vel cuspidata, cuspidibus serrulatis, petiolis circ. 3 cm. longis.

HAB. in monte Morrison.

Acer sp. (aff. *A. rufinervi* S. et Z.). Ramuli palliduli exsiccato nigricantes. Folia ambitu cordata octagona leviter 5-loba, lobis brevissimis cuspidatis, cuspidibus terminalibus angustis linearibus, lateralibus latioribus serrulatis, infimis brevissimis, basi cordata, margine præter cuspidem duplicato-serrata, 9–10 cm. longa 7 cm. lata coriacea longe petiolata, petiolis 6–7 cm. longis.

NOM. INDIG.: *Lankas-lain*=*Acer foliis magnis*.

HAB. Taitō: Bataiankei, ad 7600 ped. alt., leg. N. KONISHI, Juni. 1902, (No. A. 11); in monte Morrison, ad 7500 ped. alt., (No. 1874); ad 6000 ped. alt., (No 1798), leg. T. KAWAKAMI et U. MORI, Nov. 1906; Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906.

Acer sp. (aff. *A. picto* THUNB.). Ramuli palliduli glabri. Folia ambitu late orbicularia 7 cm. longa 10 cm. lata palmatim 5-loba basi cordata, lobis triangularibus cuspidatis 3–3½ cm. longis 2 cm. latis vel latioribus, margine serrulatis, serraturis acutis, venis subtus pilosiusculis demum glabris. Cymæ terminales. Flores ignoti. Carpella elliptico-oblonga lenticularia 4 mm. longa, alis dimidiato-obovatis divaricantibus cum carpello 2–2½ cm. longis.

HAB. Chōsōkei, leg. G. NAKAHARA, Juli. 1905, (No. 161); Shintiku, in rivulos Taitō, leg. T. KAWAKAMI et U. MORI, Juli. 1906, (No. 1426); Taitō: Taironkōsha, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1842).

Cardiospermum LINN.

Cardiospermum Halicacabum LINN. Sp. Pl. ed-2, p. 525; DC. Prodr. I. p. 601; BENTH. Fl. Hongk. p. 46, et Fl. Austral. I. p. 453; HANCE, in Journ. Bot. (1878) p. 226; Bot. Mag. t. 1049; HIERN, in HOOK. f. Fl. Brit. Ind. I. p. 670; FORBES et HEMSL. Ind. Fl. Sin. I. p. 138; HENRY, List. Pl. Formos. p. 28; DIELS, Fl. Cent. Chin. p. 450; MATSUM. et HAYATA, Enum. Pl. Formos. p. 94.

Cardiospermum microcarpum H. B. K.; HANCE, in Journ. Linn. Soc. XIII. p. 101, et in Journ. Bot. (1878) p. 226; DC. Prodr. I. p. 601.

HAB. Toroku, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 176).

DISTRIB. Common in the warm regions of Asia, Africa, and America, and also in Australia.

Anacardiaceæ.

Rhus LINN.

Rhus intermedia HAYATA, sp. nov. radicans vel volubilis. Folia trifoliolata cum petiolis circ. 30 cm. longa longe petiolata, petiolis 9–10 cm. longis puberulis foliolo terminali æquilongis, foliolis lateralibus oblongis acutis basi rotundatis obliquis 13 cm. longis breviter petiolulatis, petiolulis 3 mm. longis, foliolis terminalibus longe petiolulatis, petiolulis 3 cm. longis, laminis oblongo-ovatis apice acutis vel breviter acuminatis 15 cm. longis 7½ cm. latis, integris, subtus imprimis costis et nervis pilosis demum glabris Drupæ late globosæ compressæ breve apiculatæ 5 cm. latæ, totidem longæ viridi-flavescentes pilis setaceis brevioribus dense obtectæ.

HAB. in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2024).

The present plant is in every respect very like *Rhus Toxicodendron* LINN., but differs from it in having densely bristled fruits. At first sight, this new species appears to be referable to *Trichocarpæ*, on account of its bristled exocarpium. Studying the plant carefully, I have found that it should be referred to *Venenatæ* by reason of the mesocarpium and general characters of the fruit. The plant may better be placed between the two sections.

Pistacia LINN.

Pistacia formosana MATSUMURA, in Tōkyō Bot. Mag. XV. p. 40; MATSUM. et HAYATA, Enum. Pl. Formos. p. 99, t. 9.

HAB. in montibus Akō, leg. N. KONISHI, Oct. 1903, (No. A. 5.).

DISTRIB. An allied species *P. chinensis* BUNGE is found in central and northern China.

Leguminosæ.

Crotalaria LINN.

Crotalaria formosana MATSUMURA, in ITŌ et MATSUM. in Tent. Fl. Lutch. p. 395; MATSUM. et HAYATA, Enum. Pl. Formos. p. 103.

HAB. Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1760).

Closely resembles *C. linifolia* LINN.; probably a form of it.

Desmodium DESV.

Desmodium parvifolium DC.; ITŌ et MATSUM. l. c. p. 418; MATSUM. et HAYATA, Enum. Pl. Formos. p. 107.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 669); in monte Morrison, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1916).

DISTRIB. Widely distributed in India, Malay, and through central and southern China eastward to Japan.

Desmodium polycarpum DC.; ITŌ et MATSUM. l. c. p. 416; MATSUM. et HAYATA, l. c. p. 107.

HAB. Sanchōki, ad 3000 ped. alt., Oct. 1905, (No. 728), et Tōhosha, Nov. 1905, (No. 709), leg. S. NAGASAWA.

DISTRIB. Tropical Asia, Polynesia, through southern China to Japan.

Desmodium pulchellum BENTH.; ITŌ et MATSUM. l. c. p. 412; MATSUM. et HAYATA, l. c. p. 107.

HAB. Kagi: Shukukōshō, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1976).

DISTRIB. Tropical Asia and the Philippine islands.

Desmodium sinuatum BLUME; ITŌ et MATSUM. l. c. p. 416; MATSUM. et HAYATA, l. c. p. 108.

HAB. Kagi: Shukukōshō, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1746).

DISTRIB. Tropical Asia and southern China.

Dumasia DC.

Dumasia bicolor HAYATA, sp. nov. Herbæ volubiles in totum pubescentes. Folia bicoloria pubescentia pinnatim 3-foliolata 12 cm. lata 18 cm. longa longe petiolata, petiolis basi crassiusculis 9 cm. longis foliolo terminali subæquilongis, foliolis lateralibus brevissime petiolulatis, petiolulis 3 mm. longis, laminis rotundato-ovatis basi truncatis vel acutis apice rotundatis minutissime aristato-mucronatis 3-nerviis, foliolis terminalibus iis lateralibus conformibus longe petiolulatis, petiolulis 2½ cm. longis, laminis ovatis basi acutis majoribus 6½ cm. longis 4½ cm. latis, stipulis setaceis, stipellis filiformibus minutis, interdum folia superiora simplicia. Flores in racemos circ. 10 cm. longos axillares dispositi, bracteis parvis angustis, bracteolis minutis. Calycis tubus cylindraceus, 9 mm. longus basi postice gibberosus, ore valde oblique truncato antice acuto. Vexillum obovatum apice emarginatum 14 mm. longum 7 mm. latum late unguiculatum, lamina unguem subæquanti supra medium postice inflexa basin angusta ad unguem abeunti et auriculata. Alæ longe unguiculatæ 14 mm. longæ, laminis oblongis, unguibus linearibus laminam duplo superantibus, carina adhærentes. Carina alis brevior obtusa. Stamen vexillare liberum, cætera connata. Antheræ uniformes. Ovarium villosum substipitatum, stipite 1 mm. longo; stylus supra ovarium filiformis erectus supra medium dilatus, superne inflexus subulatus imberbis, stigmate terminali. Legumen subsessile villosum semper monospermum.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 667); Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906.

The present plant is, in all respects, like *D. villosa* DC. But, in this new species, the seed is always one in each pod and the standard has distinct spurs on both sides of the lamina. In these respects, I think the plant is specifically separable from *D. villosa* DC. The leaves of the specimen, upon which the above description is based, are of a thinly hairy form. Here is another form with villose leaves which are much smaller than the leaves of the other form. The villose form seems to be a young stage of the other.

Cajanus DC.

Cajanus indicus SPRENG.; ITŌ et MATSUM. l. c. p. 431; MATSUM. et HAYATA, l. c. p. 113.

HAB. Tōhosha, ad 2930 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 708).

DISTRIB. All over the tropics.

Flemingia ROXB.

Flemingia strobilifera R. BR.; ITŌ et MATSUM. l.c. p. 432; MATSUM. et HAYATA, l. c. p. 113.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 782).

DISTRIB. The Himalayas, Ceylon, east Bengal, Burma, Malacca, Malay, and the Philippine islands.

There is a little doubt about identifying my plant with the above species. In the present plant, the flowers in each bract are too few. In *F. strobilifera* R. BR., the flowers are arranged in a raceme or a short spike within a large bract, while in my plant the flowers are not so numerous as to form either raceme or spike.

Rosaceæ.

Prunus LINN.

Prunus campanulata MAXIM. in Mél. Biol. XI. p. 698; FORBES et HEMSL. Ind. Fl. Sin. I. p. 218; ITŌ et MATSUM. Tent. Fl. Lutch. p. 446; MATSUM. et HAYATA, Enum. Pl. Formos. p. 117.

HAB. Taichū: Kashigatani, leg. G. NAKAHARA, Feb. 1907.

DISTRIB. South China: Fokien; the Loo-choo islands.

Prunus Kawakamii HAYATA, sp. nov. Frutex, ramis novellis virgatis cortice cinereo-fusco glabro vestitis. Folia hysterantha annua alterna (novella) brevissime petiolata, petiolis 4 mm. longis semi-teretibus glabris, laminis basi acutis ovato-oblongis apice acutis margine glanduloso-serrulatis utraque pagine glabris, stipulis lanceolatis glanduloso-ciliolatis. Flores 5–6 fasciculati pedunculati, pedunculis 7 mm. longis teretibus glabris. Calyx hypogynus persistens; tubus breviter campanulatus glaber, intus disco adnato suffultus; lobis 5 ovatis 3 mm. longis obtusis glanduloso-ciliatis horizontaliter patentibus. Petala calycis fauci affixa, ex ungue breve cuneato-obovata, apice rotundata integerrima radiatim venosa tenera glabra horizontaliter patentia $6\frac{1}{2}$ mm. longa 4 mm. lata. Stamina calycis fauci affixa longe exserta petalo vix longiora. Ovarium superum, ovoideum cum stylo 6 mm. longum, stigmate capitato-peltato.

HAB. Toroku: Kanōsha, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1904).

DISTRIB. An allied species *P. japonica* THUNB. occurs in Japan and China.

Closely resembles *P. japonica* THUNB.; but differs from it in having peltately capitate stigmas, longer stamens and smaller petals.

Spiræa LINN.

Spiræa prunifolia SIEB. et ZUCC. fl. simplici; MATSUM. et HAYATA, Enum. Pl. Formos. p. 119.

HAB. in monte Morrison, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1795); Nantō: Hinokiyama, leg. G. NAKAHARA, Feb. 1907; Toroku: Kūreikiyaku, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1902).

DISTRIB. China throughout, Japan and Korea.

Spiræa sp. Suffrutices nani glabri. Folia alterna subsessilia ovata apice obtusa basi acuta vel cuneata 1½ cm. longa medio sursum denticulata basin versus integra, venis supra impressis subtus prominentibus. Fructus in cymas racemosas terminales dispositi. Carpella 2 mm. longa breve rostrata.

HAB. in monte Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 2233 et 2296).

Rubus LINN.

Rubus corchorifolius LINN. f. var. **glaber** MATSUM. in Tōkyō Bot. Mag. XV. p. 157; MATSUM. et HAYATA, Enum. Pl. Formos. p. 120.

HAB. Taichū: Kashigatani, leg. G. NAKAHARA, Feb. 1907.

DISTRIB. Type: Japan and China.

Rubus elegans HAYATA, (Pl. IV.), in Tōkyō Bot. Mag. XX. p. 74. Caulis humilis herbaceus basi suffruticosus simpliusculus suberectus 1– rarius 2-florus. Folia in totum subradicalia ambitu oblonga vel oblongo-lanceolata cum petiolis 6–7 cm. longa 2 cm. lata, petiolis 15 cm. longis, pinnata 13–15-foliolata, foliolis obovatis 1–1.5 cm. longis ½ cm. latis, terminalibus interdum tri-lobatis, serratis, serris acutis, ad petiolum et costas pinnarum aculeolata, stipulis adnatis subulatis linearibus circ. 1 cm. longis. Flores majusculi, pedunculati, pedunculis 5–6 cm. longis, 1-bracteati, bracteis minutis acutis 2 mm. longis. Flores patentes 22 mm. in diametro æquantes. Calycis lobi ovato-triangulares aculeato-acuminati 8 mm. longi extus pubescentes. Petala late ovata 9 mm. longa apice obtusissima, basi brevissime unguiculata. Stamina numerosa, filamentis planis glabris. Capitulum fructiferum ovato-globosum 1 cm. longum vel longius. Receptaculum ovato-globosum.

HAB. Ganzan, ad 9141 ped. alt., in montibus Morrison, leg. S. NAGASAWA, Oct. 1905, (No. 691); in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1956).

As the original description is drawn from an imperfect specimen, I have taken the liberty of repeating the description of this plant, basing the above account upon the most perfect materials.

Rubus fraxinifolius POIR.; MIQ. Fl. Ind. Bat. I. p. 376; HOOK. f. Fl. Brit. Ind. II. p. 342; MAXIM. in Mél. Biol. VIII. p. 391; MATSUM. in Tōkyō Bot. Mag. XVI. p. 4; MATSUM. et HAYATA, Enum. Pl. Formos. p. 121.

HAB. Tōhosha, ad 2930 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 605).

DISTRIB. Java and the Philippine islands. The occurrence of this *Rubus* in India is a little doubtful.

Rubus pectinellus MAXIM. in Mél. Biol. VIII. p. 374; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 122; HAYATA, in Tōkyō Bot. Mag. XX. p. 55.

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1799).

DISTRIB. Southern part of Japan, and also recently found in Luzon.

Rubus pentalobus HAYATA, sp. nov. Suffrutex scandens in totum villoso-tomentosus. Folia longe petiolata tomentoso-villosa, petiolis 5–10 cm. longis, laminis ambitu cordato-rotundatis 5–7 cm. in diametro æquantibus læviter 5-lobis apice rotundatis basi cordatis, lobis rotundatis irregulariter denticulatis palmatim 5–7 nerviis supra pilosiusculis subtus villoso-tomentosis pallidioribus, venis subtus prominentibus, stipulis laciniatis 13 mm. longis. Flores axillares solitarii vel gemini pedunculati, pedunculis 1 cm. longis, 2–3 bracteolatis, bracteolis minutis laciniatis. Calycis lobi ovati apice laciniati tomentosi 1 cm. longi. Achænia drupacea.

HAB. in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 2123 et 2265); Biōritsu: Hakkeirin, leg. T. KAWAKAMI et U. MORI, Juli. 1906, (No. 1096).

The present *Rubus* is near *R. pectinellus* MAXIM.; but differs from it in having unarmed sepals and five lobed leaves. The leaves are much more tomentose, and somewhat tuberculate on the upper surface.

Rubus Rolfei VIDAL var. **lanatus** HAYATA, n. v. Suffrutices erecti dense lanati demum glabri. Folia 5- rarius 3-loba, ambitu cordato-orbicularia 3–5 cm. in diametro æquantia, lobis rotundatis vel obtusis irregulariter denticulatis, utraque pagine dense lanata supra demum glabra intra venulas prominente tuberculata subtus dense albo- vel ferrugineo-lanata, petiolis 2–3 cm. longis, stipulis ovatis laceratis 12 mm. longis. Flores ad apicem ramulorum 2–3 fasciculati vel subaxillares, ad basin calycis 2–3 bracteati, bracteis majusculis truncatis laceratis 9 mm. longis totidem latis submembranaceis. Calyx turbinatus 1½ cm. longus, lobis ovatis 9 mm. longis acuminatis extus villosis intus pubescentibus crassis. Fructus ignotus.

HAB. Seizan, in montibus Morrison, leg. S. NAGASAWA, Nov. 1905, (No. 574); in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2263).

The present variety differs from the type in having more densely woolly leaves and much larger flowers.

DISTRIB. type: the Philippine islands.

Rubus rosæfolius SM. var. **hirsutus** HAYATA, n. v. Ramuli aculeati pilosi, pilis validiusculis, aculeis parvis falcatis acuminatis. Folia ambitu ovato-acuminata hirsuta cum petiolis 5–6 cm. longa 5-foliolata, foliolis lateralibus subsessilibus vel breve petiolulatis oblongo-ellipticis 1 cm. longis vel longioribus dentatis, dentibus acutis, foliolis terminalibus petiolulatis, petiolulis 5 mm. longis, laminis ovato-lanceolatis duplicato-dentatis, dentibus acuminatis, petiolis et costis aculeatis, stipulis subulatis ciliolatis. Flores terminales vel laterales sæpe solitarii, pedunculati. Calycis lobi ovato-triangulares longe caudati, caudis linearibus 6 mm. longis, extus pubescentes. Petala ovata 11 mm. longa 8 mm. lata apice rotundata basi acuta. Stamina numerosa, filamentis planis. Fructus ignotus.

HAB. in monte Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2264).

The present variety differs from the type in having hirsute leaves and in all respects is much smaller than the type.

DISTRIB. Type: common in the warmer parts of India, China and Japan.

Fragaria LINN.

Fragaria sp. Caulis brevis validiusculus longe stoloniferus. Folia in totum radicalia longe petiolata, petiolis 3–4 cm. longis tomentosis, trifoliolata, foliolis lateralibus rotundatis 13 mm. longis 11 mm. latis apice truncatis basi valde obliquis inferne rotundatis superne acutis et integris, foliolis terminalibus late obovatis 15 mm. longis 14 mm. latis apice rotundatis vel truncatis basi acutis præter basin dentatis, subsessilibus subtus sericeo-pilosis supra pilosiusculis, dentibus rotundato-acutis, venis supra plicato-impressis subtus prominentibus, stipulis membranaceis ad basin petiolorum connatis 11 mm. longis 4 mm. latis aristato-acutis extus pilosis. Pedunculi uniflori tenues piloso-tomentosi 1½ cm–2 cm. longi.

HAB. in monte Morrison, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2236); Tōzan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906.

Mr. T. KAWAKAMI tells me that the fruit of this *Fragaria* is very delicious.

Potentilla LINN.

Potentilla gelida C. A. MEY.; LEDEB. Fl. Ross. II. p. 59; HOOK. f. Fl. Brit. Ind. II. p. 357; DIELS, Fl. Tin ling shan, in ENGL. Bot. Jahrb. XXXVI. Beibl. p. 56; HAYATA, in Tōkyō Bot. Mag. XX. p. 73.

Potentilla grandiflora LINN.; WAGNER, Deut. Fl. ed-3, p. 359; THOMÉ, Fl. Deut. Öst. u. Schw. III. p. 70.

HAB. in monte Morrison, ad 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 683).

DISTRIB. Extends to Europe, North India, central China, Japan, East Siberia, and the Kurile and Aleutian islands.

The species seems to vary over a very wide range, and especially so in the size of flowers.

Potentilla leuconota DON, "Prodr. p. 230"; HOOK. f. Fl. Brit. Ind. II. p. 352; DIELS, Fl. Centr. Chin. p. 403.

var. **morrisonicola** HAYATA, n. v. (Pl. V).

Potentilla leuconota HAYATA, in Tōkyō Bot. Mag. XX. p. 74.

Caulis sericeo-pilosus erectus circ. 15 cm. longus. Folia subradicalia pinnata in ambitu oblanceolata obtusa 10 cm. longa circ. 19-foliolata, foliolis sessilibus obovatis obtusis 1 cm. longis argute dentatis supra pilosiusculis subtus sericeo-pilosis, petiolis appresse pilosis, stipulis majusculis scariosis circ. 3 cm. longis ad basin petiolorum adnatis integris. Folia caulina radicali conformia sed multo minora, pauca sæpe ad medium caulis 1–2. Flores ad apicem caulis 9-8 fasciculati subumbellati 1–2-bracteati, pedicellis 1 cm. longis. Flores patentes 8 mm. in diametro æquantes, bracteolis angustis integris. Calycis lobi ovati acuti sericei. Petala late obovata, basi leviter angusta, apice rotundata. Stamina 10 (—20 ?). Achænia circ. 15 glabra.

HAB. in monte Morrison, ad 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 732); in eodem loco, T. KAWAKAMI et G. NAKAHARA.

DISTRIB. The type is rather of the alpine character, being found in high mountains of Asia such as the Himalayas, and those of Borneo and west central China.

In my former paper above cited, I referred this Formosan species to *Potentilla leuconota* DON. After studying more carefully, I found that there is a little difference between this and that. It is not, however, without hesitation, that I have described it as a new variety. The present plant differs from the type mainly in the absence of whorled leaves at the base of an umbel.

Sibbaldia LINN.

Sibbaldia procumbens LINN. Sp. Pl. ed-2, p. 406; DIELS, Fl. Centr. Chin. p. 404, et Fl. Tsin ling shan, in ENGL. Bot. Jahrb. XXXVI. Beibl. p. 56; THOMÉ, Fl. Deut. Öst. u. Schw. III. p. 60; ASCHERSON et GRÆBN. Syn. Mitt. Fl. VI.-1, p. 661; WAGNER, Deut. Fl. ed-3, p. 361; HAYATA, in Tōkyō Bot. Mag. XX. p. 58; MAKINO, in Tōkyō Bot. Mag. XV. p. 98.

Potentilla Sibbaldi HALLER f. in "Ser. Mus. Helvet. I. p. 51"; HOOK. f. Fl. Brit. Ind. II. p. 345.

Sibbaldia cuneata KUNZE, in Linnæa, XX. p. 59; EDGEW. in Journ. Linn. Soc. XX. p. 44.

HAB. ad verticem montis Morrison, 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 757); in eodem loco, ad 13000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2256).

DISTRIB. This plant having had a wide range in the glacial period is now found here and there in the polar and alpine regions of Europe and Asia.

Rosa LINN.

Rosa sp. Suffrutices spinosissimi, aculeis albidis rectis subulatis, ramis patentibus gracilibus. Folia pinnata 7–11-foliolata glabra ambitu elliptica cum petiolis 5 cm. longa 2½ cm. lata, petiolis gracilibus minutissime aculeolatis, foliolis subsessilibus firmis late obovatis vel subrotundatis 13 cm. longis 7 mm. latis medio denticulatis apicem versus dentatis, dentibus acutis, stipulis petiolo adnatis apice liberis acutis glabris glanduloso-serrulatis, serrulis argutis. Flores secus ramulos quasi racemosi, e gemmis solitarii breviter pedunculati, pedunculis 1½ cm. longis apice in calycis tubo abeuntibus. Calycis tubi post anthesin pyriformes 8 mm. longi apice constricti basi attenuati, lobis integris lanceolatis longe acuminatis intus lanato-pubescentibus extus parce pubescentibus marginibus parcissime glandulosis. Petala ignota. Carpella 4–5 trigona 5 mm. longa apice hirsuta, stylis persistentibus.

HAB. in monte Morrison, leg. S. NAGASAWA, Nov. 1905, (Nos. 572 et 618); eodem loco, ad 11000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2293).

The present *Rosa* is very like *R. xanthina* LINDL. and *R. Willmottiæ* HEMSL. in Bot. Mag. t. 8186; but the serrature of the leaves of this plant is far too acute for those species. My specimen has the spines arranged in opposite position as *R. Willmottiæ*.

Rosa sp.

HAB. Arizan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906.

Saxifragaceæ.

Astilbe HAM.

No species belonging to this genus has been recorded hitherto from the island. The following two species and variety are the first recorded from Formosa, and come from the hilly regions.

Astilbe chinensis FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 144 (var. *japonica*); FRANCHET, Pl. David. p. 121 (var. *Davidi*); FORBES et HEMSL. Ind. Fl. Sin I. p. 265; DIELS, Fl. Centr. Chin. p. 363.

Hoteia chinensis MAXIM. Prim. Fl. Amur. p. 120; WALP. Ann. VII. p. 889.

Astilbe odontophylla MIQ. in Ann. Mus. Bot. Lugd.-Bat. III. p. 96.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 636).

DISTRIB. Amurland, Japan, and central and northern China.

There is a little doubt about this being *A. chinensis* FR. et SAV.

Astilbe chinensis FRANCH. et SAV. var. **longicarpa** HAYATA, n. v. Herba circ. 1 m. alta vel altior erecta, caulibus glabris. Folia radicalia ignota. Folia caulina longe petiolata ternato-bipinnata, foliolis lateralibus ovatis terminalibus acuminato-ovatis duplicato serratis, serris acuminatis, petiolulatis. Racemi 30 cm. longi basi 12 cm. lati pyramidales, racemulis deorsum pedunculatis sursum subsessilibus. Flores brevissime pedicellati basi calycis bracteolati. Calyces 1½ mm. longi, lobis ovatis truncatis. Petala spathulato-obovata vix 1 mm. longa apice minute apiculata margine integra diffusa. Stamina 10 multo exserta, petalum duplo superantia. Carpella 2, distincta. Fructus cylindraceo-ovoidei breve rostrati cum rostris 4 mm. longi.

HAB. Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1743); in monte Morrison, ad 8500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1990).

Very like the type; but the fruits of this variety are much longer than those of the type.

Astilbe macroflora HAYATA, sp. nov. Herba circ. 30 cm. alta, erecta basi squamis membranaceis fuscis late ovatis acuminatis numerosis obvallata, rhizomate crasso fibris numerosissimis obtecto, caulibus petiolisque pilis fuscis parce vestitis. Folia radicalia et caulina ternato-bipinnata, petiolis lamina subæqualibus ad ramificationes parce longe pilosis, foliolis ovatis vel oblongis basi cordatis rarius leviter 3-lobatis 3 cm. longis 2½ cm. latis supra parcissime pilis scabris vestitis subtus ad costas pilosiusculis biserratis, serraturis primariis majusculis patulis breviter acuminatis secundariis minutis seta brevi terminatis, foliolis terminalibus longe, eis lateralibus brevissime petiolulatis, stipulis membranaceis ovatis acuminatis fuscis erectis. Racemi folio florali minuto instructi 10 cm. longi basi 5 cm. lati pyramidales, rhachibus fusco-hirtis, bracteis stipula conformibus erectis. Flores versus apicem racemulorum subpedunculatorum dense congesti, breviter pedicellati. Calyx 3½ mm. longus campanulatus lutescens, lobis ovatis obtusis 3 mm. longis trinerviis crassiusculis tubo multo longioribus. Petala spathulata 4 mm. longa 1 mm. lata valde exserta margine minute ciliato-serrata, utraque latere 2–3 serris, diffusa. Stamina 10 disco calycis inserta. Carpella 2, distincta. Fructus breviter rostrati cum rostro 5 mm. longi, rostris carpello æquilongis. Semina scobiformia oblique fusiformia 1 mm. longa.

HAB. in monte Morrison, leg. G. NAKAHARA (?), Oct. 1906.

Remarkable for the large form of flowers and the capitate racemes.

Chrysosplenium LINN.

Chrysosplenium sp. Herbæ humiles piloso-pubescentes. Folia membranacea longe petiolata, petiolis 1½ cm. longis lamina vix longioribus planis subalatis pilosis basi dilatis, laminis late ovatis vel orbicularibus 1½ cm. longis apice rotundatis basi abrupte acutis vel truncatis brevissime attenuatis in petiolum abeuntibus margine crenatis, crenis emarginatis apice callis crassatis minutis suffultis, supra pilosiusculis, pilis subsetaceis, subtus subglabris. Flores ignoti.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1993).

This is the only *Chrysosplenium* found in the island and must be a very interesting one. In the imperfectness of the specimen, the specifical determination is impossible.

Mitella LINN.

Mitella japonica MIQ. in Ann. Mus. Bot. Lugd.-Bat. III. pp. 96 et 201, et Prol. Fl. Jap. pp. 260 et 365; FRANCH. et SAV. Enum. Pl. Jap. I. p. 147, excl. syn. (non MAXIM.); MAKINO, in Icon. Fl. Jap. Imp. Uni. Tōkyō, I.-2, p. 7, tt. IV. et V.; HAYATA, in Tōkyō Bot. Mag. XX. p. 54.

HAB. in monte Morrison, ad 8000 ped. alt., (No. 2035), et eodem loco, ad 12000 ped. alt., (No. 2131), leg. T. KAWAKAMI et U. MORI, Oct. 1906; Tōzan, in monte Morrison, leg. G. NAKAHARA, Oct. 1906.

DISTRIB. In Japan; very common in the valleys of the lowland hills. The distribution of the genus *Mitella* is rather limited, being found only in North America, Manchuria, East Siberia, Japan and Formosa.

The Morrison specimens are of a form having rather more divaricate and fimbriate petals and less tuberculate seeds. A more diverged form of this species was found in Japan by Mr. T. MAKINO who described it in Tōkyō Bot. Mag. XIX. p. 17 as a new variety *integripetala*. Another species *M. acerina* MAKINO was found also in Japan.

Parnassia LINN.

Parnassia palustris LINN. Sp. Pl. ed-2, p. 391; DC. Prodr. I. p. 320; MAXIM. Ind. Fl. Pek. in Prim. Fl. Amur. p. 469; HOOK. f. Fl. Brit.

Ind. II. p. 401; DRUDE, in Linnæa, XXXIX. p. 307; FORBES et HEMSL. Ind. Fl. Sin. I. p. 272; HAYATA, in Tōkyō Bot. Mag. XX. p. 19.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905; in monte Morrison, ad 9000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2209).

DISTRIB. West Asia to Europe, and eastward to Japan; but not yet found in central China.

Hydrangea LINN.

Hydrangea chinensis MAXIM. Revis. Hydrang. As. or. p. 7; HANCE, in Journ. Bot. (1878) p. 11; FORBES et HEMSL. Ind. Fl. Sin. I. p. 273; HENRY, List Pl. Formos. p. 41; Itō et MATSUM. Tent. Fl. Lutch. p. 461; MATSUM. et HAYATA, Enum. Pl. Formos. p. 131.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2073); Taitō: Bushiseki, leg. T. KAWAKAMI et U. MORI, (No. 2185); Toroku: Nanshikiyakumansha, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1906).

DISTRIB. The Loo-choo islands and south central China.

Hydrangea glabra HAYATA, sp. nov. (Pl. VI.). Frutices ad truncos scandentes, ramis glaberrimis cortice cinereo-fusco tectis. Folia oblonga petiolata, petiolis lamina 3-plo brevioribus, laminis oblongis 11 cm. longis 7 cm. latis apice acutis basi obtusis vel acutis margine serratis, serraturis acutis, utraque pagine glaberrimis. Cymæ corymbosæ ternato-ramosæ, rhachibus tomentosis demum glabris. Flores exteriores steriles, sepalis 4 petaloideis late obovatis nervosis basi breve cuneatis apice rotundatis vel truncatis interdum emarginatis 15 mm. longis 17 mm. latis. Flores interiores fertiles. Capsula depresso-globosa apice truncata latere leviter compressa. Semina oblonga plana ala angusta cincta.

HAB. in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1787).

This new plant is near *H. involucrata* SIEB.; but differs from it in having quite glabrous leaves and more expanded cymes; from *H. Kawakamii*, this differs in having entire sepals of radial flowers and broad wings of seeds.

Hydrangea integra HAYATA, sp. nov. (Pl. VII). Frutices ad truncos scandentes, ramis subglabris cortice fusco-rubro tectis. Folia petiolata oblongo-elliptica 22 cm. longa 8 cm. lata acuta vel cuspidato-acuta basi obtusa vel angusta integra utraque pagine glabra, laminis petiolum 3-plo superantibus, petiolis ferrugineo-rubris. Cymæ corymbosæ umbellato-fasciculatæ terminales 14 cm. longæ 15 cm. in diametro æquantes, rhachibus tomento subfloccoso dense tectis. Flores exteriores steriles, sepalis 2 petaloideis late rotundatis valde nervosis, altero minore 1½ cm. lato altero majore 2 cm. lato. Capsula hemispherica latere compressa 3–4 mm. lata, calycis limbis obscuris, stylis persistentibus apice recurvis. Semina fusiformia longitudinaliter striata.

HAB. in monte Morrison, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1723).

Somewhat resembles *H. integrifolia*, but easily distinguished in having narrowed base of the leaves.

Hydrangea Kawakamii HAYATA, sp. nov. (Pl. VIII). Frutices ad truncos scandentes, ramis tomentoso-pubescentibus demum subglabris, cortice cinereo-fuscente tectis. Folia tomentoso-hirsuta petiolata, petiolis lamina 3-plo brevioribus, laminis oblongo-ovatis circ. 14 cm. longis 7 cm. latis apice acuminatis basi acutis vel rotundatis margine irregulariter subbiserratis, serris aristato-acutis, supra pilis scaberrimis sparce subtus dense tectis. Cymæ corymbosæ umbellato-fasciculatæ terminales circ. 12 cm. longæ 14 cm. in diametro æquantes, rhachibus tomentosis. Flores exteriores steriles, sepalis 4 petaloideis nervosis fere orbicularibus 2 cm. longis totidem latis utraque latere præter basin apicemque serratis, serris acutis; interiores fertiles. Capsula hemispherica apice leviter constricta 10-costata, calycis lobis persistentibus acuminatis, stylis persistentibus valde divaricatis apice leviter recurvis. Semina fusiformia utrinque producta longitudinaliter striata intra strias transversum reticulata.

HAB. in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1875).

Somewhat near *H. involucrata* SIEB.; but differs from that in its scandent habit, and in having serrate sepals of the radial flowers.

Hydrangea longifolia HAYATA, sp. nov. Frutices erecti? ramis tomentosis, cortice cinereo-fusco tectis. Folia breve petiolata, petiolis lamina 10-plo brevioribus, laminis oblongo-lanceolatis acuminatis basi obtusis circ. 20 cm. longis 4½ cm. latis margine remote serrulatis, serraturis acuminatis, supra scabro-pilosis subtus ad costas tomentosis. Cymæ corymbosæ umbellato-fasciculatæ terminales circ. 9 cm. longæ 14 cm. latæ, rhachibus tomentulosis. Flores exteriores steriles, sepalis petaloideis utraque pagine tomentulosis late orbicularibus nervosis apice rotundatis basi brevissime contractis 17 mm. longis totidem latis. Capsula hemispherica tomentulosa latere leviter compressa, stylis persistentibus apice recurvis. Semina fusiformia utrinque producta.

HAB. Taitō: Torokusha, leg. T. KAWAKAMI et G. NAKAHARA, Januar. 1906, (No. 690).

Somewhat resembles *H. Kawakamii* HAYATA; but differs from it in having long lanceolate leaves, hairy capsules and entire hairy sepals of marginal flowers.

Deutzia THUNB.

Deutzia scabra THUNB. Fl. Jap. p. 185 ; DC. Prodr. IV. p. 17 ; MAXIM. Revis. Hydrang. As. or. p. 24 ; MIQ. Prol. Fl. Jap. p. 263 ; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 155 ; HANCE, in Journ. Bot. (1878) p. 11 ; S. MOORE, in Journ. Bot. (1878) p. 138 ; Bot. Mag. t. 38 ; FORBES et HEMSL. Ind. Fl. Sin. I. p. 276 ; HENRY, List Pl. Formos. p. 41 ; ITŌ et MATSUM. Tent. Fl. Lutch. p. 463 ; DIELS, Fl. Centr. Chin. p. 372 ; MATSUM. et HAYATA, Enum. Pl. Formos. p. 132.

Deutzia crenata SIEB. et ZUCC. Fl. Jap. p. 19, t. 6 ; MAXIM. Revis. Hydrang. As. or. pp. 22. et 45.

Deutzia crenata δ taiwanensis MAXIM. l. c.

HAB. in monte Morrison, ad 11000 ped. alt., (No. 2287); ad 9000 ped. alt., (No. 1701), et ad 7500 ped., alt., (No. 1703), in montibus centralibus, (No. 2198), leg. T. KAWAKAMI et U. MORI, Nov. 1906.

DISTRIB. Common in Japan and central China.

It is a little doubtful whether my plant is referable to this species. In the imperfectness of the specimens, the determination is rather conjectural.

Cardiandra SIEB. et ZUCC.

Cardiandra sinensis HEMSL. in Gard. Chronic. Feb. 7, 1902, p. 81.

Cardiandra formosana HAYATA, in Tōkyō Bot. Mag. XX. p. 54 ; MATSUM. et HAYATA, Enum. Pl. Formos. p. 132.

HAB. Taitō : Tōkeizan, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No, 2201) ; Kagi : Kōden, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1735).

DISTRIB. Central China : Kiangsi.

In the year 1902, Mr. W. B. HEMSLEY described a new species of *Cardiandra* from Central China in the foot note of the Gardener's Chronicle above cited. Unfortunately, owing to an error on my part, the description had been carelessly overlooked by myself when I studied the *Cardiandra* from Formosa. I found afterward that my plant is entirely referable to the species described by the above authority. *C. formosana* HAYATA should, therefore, be rendered to a synonym of *C. sinensis* HEMSL.

Ribes LINN.

Ribes formosanum HAYATA, (Pl. IX.), in Tōkyō Bot. Mag. XX. p. 56. Frutices, ramulis angularibus spinis infra-axillaribus ternatis validis patentibus. Folia simplicia vernatione plicata late rotundata basi truncata vel cordata $2\frac{1}{2}$ cm. longa 5–6-lobata, lobis obtusis grosse pauce serratis, petiolata, petiolis pauce glanduloso-setosis laminam æquantibus. Flores subsolitarii, pedicellis 1 cm. longis basi bracteatis medio articulatis 2–4 bracteolatis. Calycis tubus ovoideus ovario adnatus, lobis 5 subpatentibus 1 cm. longis oblongo-ovatis apice rotundatis petalum 3-plo superantibus. Petala 5 calycis fauce inserta oblonga parva squamiformia inclusa 4 mm. longa. Stamina 5, 4 mm. longa, antheris oblongis. Ovarium inferum 1-loculare, ovulis numerosis, placentis 2, parietalibus; styli 2 distincti basi leviter connati, stigmatibus simplicibus. Baccæ globosæ roseæ pulposæ 18 mm. in diametro æquantes, sepalis persistentibus. Semina subangulata, testa extus gelatinosa intus crustacea 3 mm. longa leviter compressa minute reticulata.

HAB. Tōhokei, ad 5907 ped. alt., in montibus Morrison, leg. S. NAGASAWA, Nov. 1905, (No. 592); in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. Mori, Nov. 1906, (Nos. 2141 et 2132).

As the original description is drawn from an imperfect specimen, I have taken the liberty of repeating the description of the plant, basing the above account upon the most perfect material.

Crassulaceæ.

Sedum LINN.

Sedum morrisonense HAYATA, sp. nov. Perennis? erecta humilis circ. 8 cm. alta a basi ramosa glabra, caulibus solitariis interdum subsurculigeris. Folia approximata dense disposita adpresse imbricata crassa carnosa oblongo-lanceolata apice obtusa basi obtusissima ulta insertionem ½ mm. producta 6 mm. longa 1½ mm. lata vel latiora. Cymæ trifidæ pluriflora bracteatæ, bracteis folio conformibus flore brevioribus; floribus ad ramos cymarum sessilibus, parvis 7 mm. longis campanulatis. Sepala oblongo-linearia obtusa petalum ½ æquantia crassiuscula. Petala oblongo-acuta apice obtuse breve carinata 6½ mm. longa; stamina episepala petalum æquantia, epipetala paulo breviora, antheris oblongis; squamis hypogynis minutis late quadratis. Folliculi membranacei basi breviter connati erecto-patuli oblongi in stylos 2-plo breviores attenuati cum stylis 6 mm. longi, stigmatibus punctiformibus. Semina oblonga obscure striata, striis minutissime muriculatis.

HAB. ad summam montis Morrison, ad 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 566); eodem loco, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2281); in montibus centralibus, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1892).

The present plant comes near *S. Roborowskii* MAXIM.; but differs from it in having smaller calcarate leaves and larger sessile flowers.

Sedum sp.

HAB. in monte Morrison, ad 6000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2019).

No fruit, indeterminable.

Kalanchoë ADANS.

Kalanchoë sp.

HAB. in monte Morrison ad 6000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1881); Kagi: Kishirei, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1779).

No flower, indeterminable.

Halorageæ.

Haloragis FORST.

Haloragis micrantha R. BR.; BENTH. Fl. Austral. II. p. 482; CLARKE, in HOOK. f. Fl. Brit. Ind. II. p. 430; HANCE, in Journ. Bot. (1870) p. 276; SIEB. et ZUCC. Fl. Jap. Fam. Nat. I. p.'133; MIQ. Prol. Fl. Jap. p. 264; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 164; FORBES et HEMSL. Ind. Fl. Sin. I. p. 292; ITŌ et MATSUM. Ten. Fl. Lutch. p. 471; DIELS, Fl. Centr. Chin. p. 486; MATSUM. et HAYATA, Enum. Pl. Formos. p. 138.

Gonocarpus micranthus THUNB. Fl. Jap. p. 69 t. 15; DC. Prodr. III. p. 66.

HAB. Ganzan, in montibus Morrison. ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 638).

DISTRIB. India. Malay, Australia, New zealand; China throughout, and Japan.

Myriophyllum LINN.

Myriophyllum spicatum LINN. Sp. Pl. ed.-2, p. 1409; DC. Prodr. III. p. 68; LEDEB. Fl. Ross. II. p. 119; MAXIM. Ind. Fl. Pekin. in Prim. Fl.

Amur. p. 471; CLARKE, in HOOK. f. Fl. Brit. Ind. II. p. 433; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 165; FORBES et HEMSL. Ind. Fl. Sin. I. p. 293; ITŌ et MATSUM. Tent. Fl. Lutch. p. 471; MATSUM. et HAYATA, Enum. Pl. Formos. p. 138.

HAB. Kagi: Rokuryōshō, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1974).

DISTRIB. Generally spread over the cool and temperate regions of the northern hemisphere.

Myrtaceæ.

Eugenia LINN.

Eugenia sinensis HEMSL.? in FORBES et HEMSL. Ind. Fl. Sin. I. p. 298; HENRY, List Pl. Formos. p. 43; MATSUM. in Tōkyō Bot. Mag. XII. p. 64; ITŌ et MATSUM. Tent. Fl. Lutch. p. 481; DIELS, Fl. Centr. Chin. p. 484; MATSUM. et HAYATA, Enum. Pl. Formos. p. 143.

Eugenia Grijsii HANCE, in Journ. Bot. (1871) p. 5, et (1879) p. 10.

Eugenia pyxophylla HANCE, in Journ. Bot. (1871) p. 6.

Syzygium buxifolium HOOK. et ARN. Bot. Beech. Voy. p. 187; WALP. Ann. II. p. 180; BENTH. Fl. Hongk. p. 118.

HAB. Nantō: Shojidaizan, leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1158).

DISTRIB. South central China.

Sp. Hab. Kōshūn: Marihasha leg. T. KAWAKAMI, Juli. 1906, (No. 1631).

Under this family, I have a very interesting plant which it is difficult for me to determine even its genus. The specimen in my hands is only a male and therefore it remains as yet undetermined.

Melastomaceæ.

Osbeckia LINN.

Osbeckia aspera BLUME; WIGHT, Ic. Pl. Ind. or. t. 377; CLARKE, in HOOK. f. Fl. Brit. Ind. II. p. 519; COGN. in DC. Monogr. Phanerog. VII. p. 315; MATSUM. et HAYATA, Enum. Pl. Formos. p. 146.

Melastoma asperum LINN.; DC. Prodr. III. p. 145.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1923).

DISTRIB. Deccan peninsula and Ceylon.

Barthea HOOK. f.

Barthea formosana HAYATA, sp. nov. (Pl. X.). Frutex scandens? ramosus, ramis gracillimis glaberrimis v. partibus novellis sub microscopio glanduloso-lepidotis. Folia breve petiolata, petiolis lamina 10-plo brevioribus laminis subcoriaceis (novellis membranaceis) oblongis circ. 10 cm. longis 3 cm. latis apice oblique caudato-acuminatis, caudis linearibus, basi acutis æqualibus margine subintegris vel remote obscure serrulatis 3–5-nerviis supra sub lente minute sparce setulosis subtus pallidioribus venis prominentibus sub microscopio minute densiuscule lepidotis. Flores ad apicem ramorum terminales 1–3–congesti majusculi patentes 3 cm. in diametro æquantes breve pedicellati, pedicellis 3–4 mm. longis minutissime lepidotis. Calycis tubus glaberrimus obpyramidali-campanulatus 9 mm. longus 4-quetrus, limbus dilatus 4 lobus, lobis brevibus triangularibus apice setoso-carinato-acuminatis. Petala 4, ampla oblique obovata 18 mm. longa 16 mm. lata apice rotundato-apiculata glaberrima margine sub lente ciliato-serrulata. Stamina 8, valde inæqualia; antheræ majores lineari-elongatæ obtusæ 1-porosæ incurvæ. connectivis basi antice longe

2-setosis (setis bi-fidis) postice in calcaria crassa ascendentia productis; antheræ minores breves oblongæ recurvæ, connectivis basi antice 2-setosis (setis simplicibus) postice breve calcaratis. Ovarium calyci adherens (inter ipsum et calycem longitudinaliter 4-canaliculatum) 4-loculare vertice leviter productum; stylus filiformis declinatus ovarium 2-plo superans, stigmate punctiformi. Capsula oblongo-globosa sub-tetragona basi in stipitem abrupte attenuata 7 mm. longa 5 mm. lata 4-valvata. Semina cuneiformia latere compressa, cum alis vix 2 mm. longa, alis subcultriformibus.

HAB. Suihenkiaku? leg. T. KAWAKAMI et G. NAKAHARA, Jan. 1906, (No. 41); Nantō: Mushazan, ad 6000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1148).

Closely resembles *Barthea chinensis* HOOK. f.; but differs from it in having no glandular crown over the ovary and in having subentire leaves.

DISTRIB. The only congener *B. chinensis* HOOK. f. occurs in Hongkong.

Sarcopyramis WALL.

Sarcopyramis nepalensis WALL. "Tent. Fl. Nep. t. 23"; CLARKE, in HOOK. f. Fl. Brit. Ind. II. p. 541; FORBES et HEMSL. Ind. Fl. Sin. I. p. 302; COGN. in DC. Monogr. Phanerog. VII. p. 517.

Sarcopyramis lanceolata WALL.; KURZ, in Journ. Bot. (1873) p. 193; HANCE, in Journ. Bot. (1878) p. 107.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., (No. 652); et Ganzan, in isdem montibus, ad 9141 ped. alt., Oct. 1905. (No. 637); Taitō: Tōkeizan, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 1913).

DISTRIB. India and Malay.

Onagrarieæ.

Epilobium LINN.

Epilobium alpinum LINN.; DC. Prodr. III. p. 41; HOOK. f. Fl. Brit. Ind. II. p. 586; WAGNER, Deut. Fl. ed.-3, p. 480.

HAB. in monte Morrison, ad 11000 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 610); eodem loco, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (Nos. 2118, 2276 et 1893).

DISTRIB. The Himalayas and alpine regions of Europe.

Epilobium roseum SCHREB.; DC. Prodr. III. p. 41; MAXIM. Ind. Fl. Pek. in Prim. Fl. Amur. p. 471; CLARKE, in HOOK. f. Fl. Brit. Ind. II. p. 584; FORBES et HEMSL. Ind. Fl. Sin. I. p. 308.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, (No. 699); in monte Morrison, ad 9000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2067); Nantō: Mushazan, 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, (No. 1130); Taitō: Daironkōsha, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2175).

DISTRIB. Broadly speaking, this species extends from Europe eastward to eastern Asia and North-West America. But not yet found in Japan.

Circæa LINN.

Circæa alpina LINN. Sp. Pl. ed.-2, p. 12; DC. Prodr. III. p. 63; CLARKE, in HOOK. f. Fl. Brit. Ind. II. p. 589; FRANCHET, Pl. David. p. 134; FORBES et HEMSL. Ind. Fl. Sin. I. p. 310; DIELS, Fl. Centr. Chin. p. 485.

HAB. in monte Morrison, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2030).

DISTRIB. Generally spread in the north temperate regions.

Cucurbitaceæ.

Thladiantha Bunge.

Thladiantha formosana Hayata, sp. nov. (Pl. XI.). Herbæ scandentes vel volubiles, ramulis floriferis graciliusculis sulcatis pilosis, pilis longis, cirrhis 2-partitis. Folia longe petiolata, petiolis lamina æquilongis vel brevioribus pilosis, laminis crassiusculis membranaceis angularibus rotundato-cordatis vel ovato-cordatis 10 cm. longis 7 cm. latis acute acuminatis margine minute remoteque denticulatis supra scabridis subtus villoso-pubescentibus. Flores ♂ puberuli racemosi, racemis longis petiolo 2–3-plo longioribus, bracteis parvis cito deciduis. Calycis tubus brevis late campanulatus, lobis ovato-lanceolatis 5 mm. longis. Petala patentia ovato-lanceolata 11 mm. longa. Stamina 5 æqualia, antheris 1-locularibus rectis, filamentis liberis. Ovarii rudimentum globosum. Appendicula brevis petaloidea obtusa discum centrale horizontaliter tegens.

Hab. Tōzan, in montibus Morrison, leg. G. Nakahara, Oct. 1906.

Distrib. An allied species, *T. nudiflora* Hemsl., occurs in central China.

Very much resembles *T. nudiflora* Hemsl.; but differs from it in having peduncled racemes, and smaller flowers which are as half as those of the allied species.

Gynostemma Blume.

Gynostemma pedatum Blume; Walp. Rep. I. p. 98; Miq. Fl. Ind. Bat. I.-1, p. 683; Clarke, in Hook. f. Fl. Brit. Ind. II. p. 633; Cogn. in DC. Monogr. Phanerog. III. p. 913; Franchet, Pl. David. I. p. 136; Forbes et Hemsl. Ind. Fl. Sin. I. p. 320; Itō et Matsum. Tent. Fl. Lutch. p. 519; Diels, Fl. Centr. Chin. p. 604; Hayata, in Tōkyō Bot. Mag. XX. p. 53.

Gynostemma cissoides BENTH. et HOOK. f. Gen. Pl. I. p. 839; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 176.

Enkylia trigyna GRIFFITH.; Miq. Prol. Fl. Jap. pp. 15 et 142.

Pestalozzia pedata ZOLL. et MOR.; WALP. Ann. I. p. 316.

Zanonia cissoides WALL.; WALP. Rep. II. p. 194.

Zanonia pedata MIQ. Fl. Ind. Bat. I.-1, p. 683.

HAB. Arizan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906; in eodem monte, ad 6000 ped. alt., (No. 2001), et ad 6500 ped. alt., (No. 2049), leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. India, Malay archipelago, central and eastern China, Japan and the Loo-choo islands.

Begoniaceæ.

The three species of Begoniaceæ. The specimens are all imperfect and can not be satisfactorily determined.

Umbelliferæ.

Hydrocotyle LINN.

Hydrocotyle javanica THUNB. "Dissertatio p. 415, t. 3"; DC. Prodr. IV. p. 67; MIQ. Fl. Ind. Bat. I.-1, p. 734; HANCE, in Journ. Bot. (1883) p. 321; CLARKE, in HOOK. f. Fl. Brit. Ind. II. p. 667; MAXIM. in Mél. Biol. XII. p. 246; FORBES et HEMSL. Ind. Fl. Sin. I. p. 325; HEMSL. et COLL. in Journ. Linn. Soc. XXVIII. p. 61; HENRY, List Pl. Formos. p. 47; ITŌ et MATSUM. Tent. Fl. Lutch. p. 260; DIELS, Fl. Centr. Chin. p. 490; YABE, Revis. Umbell. Jap. p. 10; MATSUM. et HAYATA, Enum. Pl. Formos. p. 170.

Hydrocotyle nepalensis HOOK.; DC. Prodr. IV. p. 65; MIQ. Fl. Ind. Bat. I.-1, p. 735 (var.); MIQ. Prol. Fl. Jap. p. 243; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 178.

Hydrocotyle polycephala WIGHT et ARN.; WIGHT, Ic. Pl. Ind. or. t. 1003.

Hydrocotyle zeylanica DC. Prodr. IV. p. 67; MIQ. Fl. Ind. Bat. I.-1, p. 734.

Hydrocotyle hirta R. BR. var. *acutiloba* F. MUELL. in BENTH. Fl. Austr. III. p. 340.

HAB. Tappansha, ad 3139 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 719); Tōzan, in montibus Morrison, leg. G. NAKAHARA, Dec. 1906.

DISTRIB. South China and Japan. Tropical Asia to eastern Africa and Australia.

Hydrocotyle rotundifolia ROXB. Fl. Ind. II. p. 88; DC. Prodr. IV. p. 64; WIGHT, Ic. Pl. Ind. or. t. 564; BENTH. Fl. Hongk. p. 134; CLARKE, in HOOK. f. Fl. Brit. Ind. II. p. 668; MAXIM. in Mél. Biol. XII. p. 461; FORBES et HEMSL. Ind. Fl. Sin. I. p. 825; HENRY, List. Pl. Formos. p. 47; ITŌ et MATSUM. Tent. Fl. Lutch. p. 259; DIELS, Fl. Centr. Chin. p. 491; YABE, Revis. Umbell. Jap. p. 12; MATSUM. et HAYATA, Enum. Pl. Formos. p. 171.

Hydrocotyle nitidula RICH.; DC. Prodr. IV. p. 66; MIQ. Prol. Fl. Jap. p. 243.

Hydrocotyle Sibthorpioides LAM.; DC. Prodr. IV. p. 66; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 178.

Hydrocotyle puncticulata MIQ. Fl. Ind. Bat. I.-1, p. 733.

Hydrocotyle Zollingeri MOLKENB.; MIQ. Fl. Ind. Bat. I.-1, p. 733.

Hydrocotyle tenella DON, in DC. Prodr. IV. p. 64.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., Oct. 1905.

DISTRIB. Asia and Africa.

Hydrocotyle setulosa HAYATA, sp. nov. Herba perennis, prostrata ad nodos radicans. Caules prostrati, ramis innovationibus erectis pilosis. Folia longe petiolata, petiolis circ. 2 cm. longis piloso-puberulis, pilis descendentibus, laminis reniformi-cordatis 10 mm. longis 13 mm. latis 7-lobis, lobis obtusis late rotundatis rarius contiguis leviter marginatis crenatis, crenis acutis, supra setulosis subtus piloso-setosis, setis longiusculis; stipulis late rotundatis integris vel bilobis membranaceis. Pedunculi 2–3 cm. longi piloso-pubescentes, pilis descendentibus. Umbellæ simplices multiflores, floribus breve pedicellatis, pedicellis 1 mm. longis, dense capitatis. Fructus late cordato-orbiculati compressi utrinque costati 1 mm. longi $1\frac{1}{2}$ mm. lati.

HAB. Arizan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906.

Somewhat resembles *H. Wilfordi* MAXIM., but differs from it in the fruits and setulose leaves.

Sanicula LINN.

Sanicula petagnioides HAYATA, sp. nov. (Pl. XII.). Herbæ perennes humiles glaberrimæ. Caules erecti circ. 12 cm. alti pauci-ramosi. Folia radicalia longe petiolata, petiolis gracilibus 6 cm. (rarius 12 cm.) longis glabris basi dilatis, laminis ambitu late pentagonis 2–$2\frac{1}{2}$ cm. in diametro æquantibus 5-partitis, segmentis 2–3-lobatis rhomboideis basi cuneatis aristato-serratis albo-lamelligeris breve petiolulatis. Folia caulina sessilia folis radicalibus conformia 3–5-partita, segmentis cuneato-lanceolatis. Umbellæ compositæ ad apicem caulis 2–3, vel axillares solitariæ, longe pedunculatæ, pedunculis 3 cm. longis, 5–7-radiatæ 6 mm. longæ, 10 mm. in diametro æquantes, bracteis paucis setaceo-dentiformibus vel subfoliaceis minutis. Umbellulæ minores $2\frac{1}{2}$ mm. longæ 3 mm. in diametro æquantes basi bracteolatæ, bracteolis 5–6 minutissimis setaceo-dentiformibus, 5–6-floræ, floribus exterioribus masculinis (=sterilibus) longe pedicellatis, centralibus unifloris perfectis fertilibus. Flores ♂: minutissimi circ. $\frac{2}{3}$ mm. in diametro æquantes longe pedicellati, pedicellis $1\frac{1}{2}$ mm. longis; calycis lobis prominulis setaceo-dentiformibus; petalis albis ovatis apice obtuse acutis inflexis; staminibus 5, filamentis petalo duplo longioribus; ovarii rudimentis convexis. Flores ♀: sessiles minuti, florem ♂ in magnitudine 3–plo superantes 2 mm. longi; calycis tubis ellipsoidalibus echinatis, lobis suberectis prominente setaceis; petalis staminibusque iis fl. ♂ conformibus; stylis suberectis leviter recurvis. Fructus obovato-orbiculares $1\frac{2}{3}$ mm. lati valde compressi multicostati secus costam echinati, calycis lobis persistentibus erectis, stylis persistentibus valde reflexis.

HAB. in monte Morrison, ad 7500 ped. alt., (No. 2026), et ad 8000 ped. alt., (No. 1988), leg. T. KAWAKAMI et U. MORI, Oct. 1906: Tōzan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906.

The present plant comes very near *S. satsumana* MAXIM.; but differs from it in having 5-parted leaves, less spined fruits, smaller flowers, and in the presence of cauline leaves; and still more in the structure of the fruits. As seen in the section of the fruit (Pl. XII.), this plant differs greatly from the congener in the position of vittæ. The vittæ in my species are very few, while in the other they are as many as eight. An allied genus, *Petagnia* GUSS., has no vitta in its fruits, in which respect the present plant is the nearest to it.

The five species of the distinct Umbelliferæ. In the absence of the mature fruits, the genera can not be determined with certainty.

Araliaceæ.

Acanthopanax DCNE et PL.

Acanthopanax aculeatum SEEM. in Journ. Bot. (1867) p. 238; HANCE, in Journ. Linn. Soc. XIII. p. 105; FRANCH. Pl. David. p. 146; CLARKE, in HOOK. f. Fl. Brit. Ind. II. p. 726; FORBES et HEMSL. Ind. Fl. Sin. I. p. 339; HENRY, List Pl. Formos. p. 47; DIELS, Fl. Centr. Chin. p. 489; MATSUM. et HAYATA, Enum. Pl. Formos. p. 176.

Panax aculeatum AIT. Hort. Kew. ed-2, V. p. 482; DC. Prodr. IV. p. 252.

Panax Loureirianum DC. Prodr. IV. p. 252.

Zanthoxylum trifoliatum LINN. Sp. Pl. ed-2, p. 1455.

Plectronia chinensis LOUR. Fl. Cochinch. ed-WILLD. p. 201.

HAB. Tappansha, leg. S. NAGASAWA, Oct. 1905, (No. 717); in monte Morrison, ad 6000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2022).

DISTRIB. Eastern India, central China, and Japan.

Fatsia DCNE et PL.

Fatsia polycarpa HAYATA, sp. nov. (Pl. XIII.). Arbor? Ramuli primum valde fulvo-lanati, pilis longiusculis, demum subglabri. Folia (novella fulvo-lanate demum glabra) ampla longe petiolata, petiolis in longitudine laminam æquantibus vel brevioribus basi valde dilatis ciliatis, stipulis intra petiolum parum prominulis, laminis ambitu late orbicularibus 15–30 cm. in diametro æquantibus profunde ad $\frac{2}{3}$ partem laminæ palmatim 7-fidis inter lobos valde sinuatis, lobis oblongo-obovatis apice caudato-acuminatis basi attenuatis margine præter acumen partes basilares et sinuatas dentato-serratis, serraturis mucronato-acuminatis ascendentibus, palmatim 7-nerviis, subtus nervis prominentibus, pallidioribus. Umbellæ paniculatæ. Paniculæ terminales 30–40 cm. longæ dense fulvo-lanatæ, ramis infimis 14 cm. longis umbellis pedunculatis remote instructis; pedunculi umbellarum 1–$\frac{1}{2}$ cm. longi umbellam in longitudine æquantes; bracteæ ad basin umbellarum ovatæ 1–$\frac{1}{2}$ cm. longæ membranaceæ caducissimæ dense lanatæ; bracteolæ minutissimæ lineares. Umbellæ circ. 20-floræ in alabastro globosæ 1 cm. in diametro æquantes indumento lanato obtectæ; umbellæ demum patentes 1½ cm. longæ 2½ cm. in diametro æquantes. Flores patentes longe pedicellati, pedicellis 1 cm. longis gracilibus flore continuis sed basi pedunculo articulatis, majusculi 7 mm. in diametro æquantes. Calycis tubus brevis leviter sulcatus, margine vix prominulo. Petala 5 membranacea valvata revoluta longe triangularia apice mucronato acuta 3½ mm. longa basi vix latiora quam 2 mm. Stamina 5, filamentis filiformibus petalo longioribus horizontaliter patentibus reflexis, antheris oblongis. Discus convexus margine integer. Ovarium 10-loculare, loculis 1-ovulatis. Styli 10 a basi distincti brevissimi ½ mm. longi, stigmatibus terminalibus parvis.

HAB. in monte Morrison, ad 8500 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1868).

DISTRIB. The only congeners we have at present are *F. japonica* DCNE. et PL. and *F. papyrifera* BENTH. et HOOK. f. The former occurs in Japan, and the latter, in Formosa.

The present species is a very interesting addition to the Formosan flora. The plant is by far the most remarkable species in having 10-celled ovaries in which respect it appears to be referable to *Trevesia* VIS. All other characters of the plant, however, quite agree with *Fatsia* DCNE. et PL. I think, therefore, it will be better to refer the new plant to this genus, and at the same time to extend the limit of the generic character.

Helwingia WILLD.

Helwingia rusciflora WILLD. Sp. Pl. IV. p. 716; SIEB. et ZUCC. Fl. Jap. I. p. 164, t. 86; FORBES et HEMSL. Ind. Fl. Sin. I. p. 341; DIELS, Fl. Centr. Chin. p. 505.

Helwingia japonica DIETR.; DC. Prodr. XVI.-2, p. 680; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 195.

Osyris japonica THUNB. Fl. Jap. p. 31, et Ic. Pl. dec. III. t. 1.

DISTRIB. Japan and central China.

Heptapleurum GÆRTN.

Heptapleurum octophyllum BENTH. in BENTH. et HOOK. f. Gen. Pl. I. p. 942; HANCE, in Journ. Linn. Soc. XIII. p. 105; FORBES et HEMSL. Ind. Fl. Sin. I. p. 342; HENRY, List Pl. Formos. p. 48; MATSUM. et HAYATA, Enum. Pl. Eormos. p. 178.

Aralia octophylla LOUR. Fl. Cochinch. ed.-WILLD. p. 233; DC. Prodr. IV. p. 258.

Paratropia cantoniensis HOOK. et ARN. Bot. Beech. Voy. p. 189; WALP. Rep. IV. p. 433; BENTH. Fl. Hongk. p. 136.

Agalma octophyllum SEEM. in Journ. Bot. (1864) p. 298.

HAB. in monte Morrison, ad 9000 ped. alt., leg. T. KAWAKAMI et U. Mori, Nov. 1906, (Nos. 1899 et 1879).

DISTRIB. South China and the Loo-choo islands.

The plant grows usually in the low regions and sometimes ascends to such an elevation almost ten thousand feet high.

Heptapleurum racemosum BEDD. Fl. Sylv. t. 214; CLARKE, in HOOK. f. Fl. Brit. Ind. II. p. 729; HAYATA, in Tōkyō Bot. Mag. XX. p. 53.

Hedera racemosa WIGHT, Ic. Pl. Ind. or. t. 1015.

Agalma racemosum SEEM. "Rev. Heder. p. 24."

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; Arizan, in isdem montibus, leg. G. NAKAHARA, Nov. 1906; in monte Morrison, 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1709).

DISTRIB. The present plant grows in the mountainous districts of southern India such as Nilghiries at elevations of 3000–5000 ft., and also in Ceylon at altitudes of 3000–5000 ft., (after BEDDOME); but not found in Himalaya. It is very remarkable case that such a southern element is found in the high regions of Formosa. No species belonging to this genus has yet been known from central China.

Oreopanax DCNE. et PL.

Oreopanax formosana HAYATA, sp. nov. (Pl. XIV). Arbor? Rami cinereo-stellato-tomentosi et adpresse pilosi. Folia ampla longe petiolata, petiolis primum adpresse stellato-pilosis demum subglabris lamina 1–2-plo longioribus basi dilatis, stipulis parum prominulis acutis ad basin petiolorum connatis, laminis ambitu late orbicularibus 20 cm. longis 23 cm. latis vel minoribus basi late truncatis vel cordato-truncatis margine obsolete 3–5-lobatis vel grosse irregulariter dentatis, dentibus acutis inter dentes sinuatis, 5–7-nerviis, supra subglabris venis impressis, subtus pilis stellatis et simplicibus dense obtectis venis et venulis prominentibus. Florum capitula corymboso-paniculata. Paniculæ terminales 15 cm. longæ petiolum æquantes 13 cm. latæ, pilis stellatis et simplicibus dense obtectæ, ramis alternis angulo obtuso divaricantibus, capitulis florum pedunculatis remote instructis, et ad apicem ramorum capitulis ternatis; bracteæ basi pedunculorum late ovatæ 4 mm. longæ; bracteolæ florum squamelliformes crassiusculæ sub singulo flore 3-næ, 1 subtendente majore late ovata 3 mm. longa, 2 lateralibus minoribus oppositis, pilis longis dense tectis et barbis validis nigris sparce insertis. Capitula florum subglobosa 6–7 mm. in diametro æquantia, circ. 15-flora, pedunculis capitulum 2-plo superantibus. Flores omnio villosi intra bracteas arcte sessiles in alabastro subturbinati 2½ mm. longi. Calycis margo obsolete dentatus. Petala 5 valvata intus glabra ovato-triangularia $1\frac{1}{2}$ mm. longa vel longiora caducissima. Stamina 5, filamentis brevissimis, antheris oblongis; discus explanatus. Ovarium 2-loculare, loculis 1-ovulatis, stylis 2 brevibus distinctis erectis, stigmatibus terminalibus. Fructus late globosi $4\frac{1}{2}$ mm. longi 5 mm. lati læves abortu 1-spermi compressiusculi tomentulosi drupacei, stylis persistentibus valde recurvis. Semina ovoidea subtriquetra 4 mm. longa, albuminibus ruminatis. Embryo hilo proximus minutus.

HAB. Taitō: Bataiankei, ad 6000 ped. alt., leg. N. KONISHI, Juni. 1902, (No. 34, A); Arizan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (Nos. 1871 et 1709); Taitō: in monte Iryokukaku, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 1914.

In "BENTH. et HOOK. f. Gen. Pl. I. p. 939", it is stated that the ovary of the genus *Oreopanax* is 5-celled. But, in "ENGL. und PRANTL, Nat. Pfl.-fam. III.–8, p. 39", the generic character of this genus is a little broadened in such an extent that the ovary is sometimes 2-celled and the flower is usually hermaphrodite. Accepting the latter statement, the present plant which has two celled-ovaries should be referred to *Oreopanax*, on account of capitate and sessile flowers, ruminate albumens, simple leaves, and the existence of three bracts under each flower. The style of this plant is exceptionally short. The occurrence of this genus in the island is very remarkable. So far as I am aware, we have had no representative of this American genus in any other region on the globe.

Hedera LINN.

Hedera Helix LINN. Sp. Pl. ed-2. p. 292; DC. Prodr. IV. p. 261; CLARKE, in HOOK. f. Fl. Brit. Ind. II. p. 739; "HANCE, in Journ. Bot. (1882) p. 6"; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 194; FORBES et HEMSL. Ind. Fl. Sin. I. p. 343; DIELS, Fl. Centr. Chin. p. 487.

Hedera colchica KOCH; SEEM. in Journ. Bot. (1864) p. 307.

Hedera rhombea SIEB. et ZUCC. Fl. Jap. Fam. Nat. I. p. 94.

HAB. Kagi: Tappansha, (No. 1907), in monte Morrison, ad 6000 ped. alt., (No. 2017), et ad 8000 ped. alt., (No. 1889), leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. Western Europe and North Africa eastward to Japan.

Dendropanax DCNE.

Dendropanax sp. Rami glabri cortice cineraceo-flavo tectis. Folia longe petiolata, petiolis lamina 1–2-plo longioribus, basi dilatis stipulis fere obsoletis, laminis profunde 3–lobatis in circumscriptione obtriangularibus 9 cm. longis totidem latis basi abrupte cuneatis apice trilobis, lobis lateralibus terminali conformibus ascendentibus lanceolato-acuminatis, 3–nerviis utraque pagine inter reticula punctatis, interdum laminis simplicibus oblongo-ellipticis cuspidato-acuminatis basi cuneatis. Umbellæ ad apicem ramulorum solitariæ pauciflorae breve pedunculatæ, pedunculis 7 mm. longis, pedicellatæ, pedicellis 8 mm. longis. Flores ignoti. Fructus globosi 4 mm. in diametro æquantes multi-sulcati.

HAB. in monte Morrison, ad 6000 ped. alt., (No. 2056), et in eodem monte, ad 7000 ped. alt., (No. 2041), leg. T. KAWAKAMI et U. MORI, Oct. 1906.

The specimens are wanting of flowers and it is rather questionable whether this belongs to *Dendropanax*.

Cornaceæ.

Marlea Roxb.

Marlea begoniæfolia Roxb. Fl. Ind. ed.-Carey, II. p. 261; DC. Prodr. IV. p. 267; Benth. Fl. Hongk. p. 183; Hook. et Arn. Bot. Beech. Voy. p. 187; Clarke, in Hook. f. Fl. Brit. Ind. II. p. 743; Forbes et Hemsl. Ind. Fl. Sin. I. p. 344.

Stylidium chinense Lour. Fl. Cochinch. ed.-Willd. p. 273.

Hab. Kagi: Murōensha, leg. T. Kawakami et U. Mori, Nov. 1906, (No. 1750).

Distrib. India, Malay, south central China and Japan.

Aucuba Linn.

Aucuba japonica Thunb. Fl. Jap. pp. 4 et 64, tt. 12 et 13; Willd. Sp. Pl. IV. p. 328; Bot. Mag. tt. 1197 et 5512; DC. Prodr. IV. p. 274; Miq. Prol. Fl. Jap. p. 92; Franch. et Savat. Enum. Pl. Jap. p. 197; Henry, List. Pl. Formos. p. 48; Forbes et Hemsl. Ind. Fl. Sin. I. p. 346; Itō et Matsum. Tent. Fl. Lutch. p. 541; Diels, Fl. Centr. Chin. p. 507; Palibin, Conspect. Fl. Koreæ, I. p. 102; Hayata, in Tōkyō Bot. Mag. XX. p. 55.

Aucuba himalaica Hook. f. Fl. Brit. Ind. II. p. 747.

Aucuba chinensis Benth. Fl. Hongk. p. 138.

Hab. in monte Morrison.

Distrib. From middle Himalaya through central China to Japan and the Korean archipelago.

In my specimen, the flowers are much larger, and the leaves are narrower, oblanceolate, and with more diverging veinlets. I think the plant may be regarded as a form of the Japanese species.

Dicotyledones

Gamopetalæ

Caprifoliaceæ.

Lonicera LINN.

Lonicera sp.

HAB. in monte Morrison, (No. 1816).

The four species of *Viburnum*: but not yet determined.

Rubiaceæ.

Ophiorrhiza LINN.

Ophiorrhiza pumila CHAMP.; BENTH. Fl. Hongk. p. 147; WALP. Ann. V. p. 117; FORBES et HEMSL. Ind. Fl. Sin. I. p. 378; HENRY, List Pl. Formos. p. 50; MATSUM. in Tōkyō Bot. Mag. XIV. p. 147; MATSUM. et HAYATA, Enum. Pl. Formos. p. 187.

HAB. Tappansha, ad 3138 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 580); in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1713); Tōzan et Arizan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; Taitō: Busshiseckisha, leg. T. KAWAKAMI et U. MORI. Dec. 1906, (No. 2182).

DISTRIB. South China.

Knoxia LINN.

Knoxia corymbosa WILLD. Sp. Pl. I. p. 582; BENTH. Fl. Hongk. p. 164; HOOK. f. Fl. Brit. Ind. III. p. 128; WIGHT, Ic. Pl. Ind. or. t. 128;

Willd. Sp. Pl. I. p. 582; Miq. Fl. Ind. Bat. II. p. 330; Forbes et Hemsl. Ind. Fl. Sin. I. p. 384; Matsum. in Tōkyō Bot. Mag. XVI. p. 13; Matsum. et Hayata, Enum. Pl. Formos. p. 189.

Spermacoce teres Roxb. Fl. Ind. ed.-Carey, I. p. 367.

Hab. in monte Morrison, ad 6000 ped. alt., leg. T. Kawakami et U. Mori, Oct. 1906. (No. 1945).

Distrib. Malay, North Australia, and South China.

Damnacanthus Gærtn.

Damnacanthus angustifolius Hayata, sp. nov. (Pl. XV.). Frutices glaberrimi dichotome ramosissimi, ramulis cinereo-fulvis nitentibus 4-gonis. Folia opposita brevissime petiolata lanceolata vel lanceolato-linearia 13 cm. longa 1½ cm. lata basi acuta apice acuminata margine integra vel remote minuteque denticulata subtus pallidiora, venis utrinque prominulis, venulis fere transversum divergentibus, stipulis interpetiolaribus multi-dividis minute digitaliformibus. Flores parvi in axillis 5–6 fasciculatim vel umbellatim dispositi, pedicellis gracilibus 2–3 mm. longis. Calycis tubus obovoideus 1 mm. longus limbum in longitudine æquans, limbo campanulato 4-lobo, lobis triangularibus persistentibus. Corolla cylindrico-campanulata 5 mm. longa, tuto fauceque piloso, limbo 4 lobo, lobis valvatis ovato-triangularibus tubo 3-plo brevioribus minute apiculatis. Stamina 4, lobis corollæ alterna fere libera, filamentis longiusculis, antheris oblongis obtusis dorso connectivo lato affixis. Discus pulvinatus. Ovarium 4–loculare loculis 1-ovulatis, ovulis in loculis solitariis ab apice loculi pendulis amphitropis, stylo filiformi, stigmate clavellato 4-fido, ramis latiusculis erecto-patentibus. Drupæ rubræ late globosæ 6 mm. in diametro æquantes 4-pyrenæ, pyrenis dorso rotundatis subtrigonis cartilagineis 1-spermis. Semina subtrigona, testa tenuissima, albumine corneo; embryo parvus, cotylidonibus subplanis crassis, radicula brevi infra.

HAB. in Suizan, in montibus Morrison, ad 7703 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 784); Tōzan et Arizan, in isdem montibus, leg. G. NAKAHARA, Dec. 1906; in monte Morrison, ad 6500 ped. alt., (No. 1794), ad 7500 ped. alt., (No. 2055), et ad 9000 ped. alt., (No. 1926), leg. T. KAWAKAMI et U. MORI, Oct. 1906.

This new species is very remarkable for very small flowers and very narrow leaves.

Damnacanthus indicus GÆRTN. f. "Fruct. III. p. 18, t. 182"; DC. Prodr. IV. p. 473; S. MOORE, in Journ. Bot. (1875) p. 231; HOOK. f. Fl. Brit. Ind. III. p. 158; MAXIM. in Mél. Biol. XI. p. 795; FORBES et HEMSL. Ind. Fl. Sin. I. p. 386.

HAB. Suizan, in montibus Morrison, leg. S. NAGASAWA, Oct. 1905, (No. 658); in monte Morrison, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1704); Nantō: Hinokiyama, leg. G. NAKAHARA, Feb. 1907.

DISTRIB. Eastern India, central China, the Loo-choo islands, and Japan.

It is stated by Mr. W. B. HEMSLEY that *D. macrophyllus* SIEB. is a form of *D. indicus* GÆRTN. f., as he has very many transitional stages between the two species. Mr. T. MAKINO refers also to this interesting species in the Tōkyō Botanical Magazine, XVIII. pp. 12–14, where he mentions that the above two species and *D. major* SIEB. et ZUCC. do not show any specifical distinction and they should be regarded as one and the same species accordingly. He also proposes to make many varieties, α, β, γ, and δ, including various forms. To my opinion, however, the plants do not seem to vary from one to another. At present, I am much inclined to regard the former two as specifically distinct species. The preceding new plant bears much resemblance to *D. macrophyllus* SIEB. from which it differs in having much smaller flowers and more narrowed leaves.

Lasianthus JACK.

Lasianthus formosensis MATSUM. in Tōkyō Bot. Mag. XV. p. 17; MATSUM. et HAYATA, Enum. Pl. Formos. p. 195, t. XV. A.

HAB. Taitō: Dakunsha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2159).

Pæderia LINN.

Pæderia tomentosa BLUME; DC. Prodr. IV. p. 471; HOOK. f. Fl Brit. Ind. III. p. 197; MAXIM. in Mél. Biol. XI. p. 798; MIQ. Fl. Ind. Bat. II. p. 258; FORBES et HEMSL. Ind. Fl. Sin. I. p. 389; MATSUM. in Tōkyō Bot. Mag. XV. p. 38; DIELS, Fl. Centr. Chin. p. 582; PALIBIN, Conspect. Fl. Koreæ, I. p. 106; MATSUM. et HAYATA, Enum. Pl. Formos. p. 197.

Pæderia fœtida THUNB. Fl. Jap. p. 106; HOOK. et ARN. Bot. Beech. Voy. p. 194; BENTH. Fl. Hongk. p. 162; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 210; HANCE, in Journ. Bot. (1874) p. 261.

Pæderia chinensis HANCE, in Journ. Bot. (1878) p. 228, et (1879) p. 12; FRANCHET, Pl. David. p. 155.

HAB. Taitō: Daironkōsha, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2163).

DISTRIB. Eastern India, Malay peninsula and archipelago, China, and Japan.

Nertera BANKS et SOL.

Nertera nigricarpa HAYATA, sp. nov. Herbæ parvæ glaberrimæ exsiccato nigricantes, caulibus repentibus ad nodos radicantibus, internodiis 1–3 cm. longis, ramulis depressis. Folia petiolata, petiolis laminam in longitudine superantibus, laminis late ovatis vel ovato-reniformibus obtusis minute mucronatis basi abrupte attenuatis ad petiolum abeuntibus margine integerrimis 5 mm. latis 4 mm. longis, stipulis interfoliaceis validiusculis triangularibus vel late cuspidatis. Flores quasiterminales sessiles solitarii 2½ mm. longi. Calycis tubus ovoideus, limbo integro annulato. Corolla tubulata 4-loba, lobis integerrimis margine sub microscopio minute cristatis. Stamina 4, filamentis disco insertis, antheris late ovatis brevissime apiculatis. Ovarium 2-loculare, stylis 2 elongatis suberectis intus cristato-stigmatosis. Drupæ nigricantes globosæ 4½ mm. in diametro æquantes carnosæ dicoccæ (rariusmono coccæ), calycis limbo annulari coronatæ, coccis coriaceis ovatis intus plano-concavis extus convexis 1-spermis. Semina ovata plano-convexa circ. 2 mm. longa intus leviter sulcata.

HAB. Tōzan, in montibus Morrison, Oct. 1906; in monte Morrison, leg. S. NAGASAWA, Nov, 1905.

DISTRIB. According to Mr. E. D. MERRILL, an allied Australian species *N. depressa* BANKS et SOL. occurs in the Philippine islands.

Very much like *N. depressa* BANKS et SOL.; but differs from it in having entire lobes of corolla, black colored berries, and cristate stigmas. The occurrence of this Australian genus is very remarkable.

Rubia LINN.

Rubia cordifolia LINN.; DC. Prodr. IV. p. 588; FRANCHET, Pl. David. p. 155; MAXIM. Mél. Biol. IX. p. 266; HOOK. f. Fl. Brit. Ind. III. p. 202; MIQ. Fl. Ind. Bat. II. p. 337; FORBES et HEMSL. Ind. Fl. Sin. I. p. 393; DIELS, Fl. Centr. Chin. p. 583; MATSUM. in Tōkyō Bot. Mag. XV. p. 39; PALIBIN, Conspect. Fl. Koreæ, I. p. 106; MATSUM. et HAYATA, Enum. Pl. Formos. p. 199.

HAB. Toroku: Tōhozan, Nov. 1905, (No. 1827), et in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2058).

DISTRIB. Japan to central China and Dahuria; mountains of India southward to Ceylon and Malacca; tropical Africa.

Rubia lanceolata HAYATA, sp. nov. Herbæ minute aculeolatæ, caulibus elongatis 4-gonis. Folia 4-natim verticillata longe petiolata, petiolis lamina in longitudine 1–2-plo longioribus minute uncinato-aculeolatis, laminis lanceolatis ovato-lanceolatis vel lineari-lanceolatis apice acuminatis basi rotundatis vel leviter cordatis 9 cm. longis 1 cm. latis supra ad nervos hispidulis subtus ad nervos et margines uncinato-asperis trinerviis. Flores minuti in cymas paniculatas circ. 20 cm. longas axillares et terminales dispositi, bracteis angusto-lanceolatis 4-natim verticillatis. Flores ignoti. Fructus didymi 5 mm. lati 3 mm. longi.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 687); in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 1715 et 1989?).

Closely resembles *R. cordifolia* LINN.; but differs from it in having lanceolate and trinerved leaves; from *R. Schumanniana* E. PRITZEL, this differs in having minutely aculeolate stems and uncinately asperous petioles.

Galium LINN.

Galium brachypodium MAXIM. in Mél. Biol. IX. p. 260.

HAB. in monte Morrison, ad 9000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1805).

DISTRIB. Northern part of Japan.

A more species of *Galium*; not yet determined.

Valerianeæ.

Patrinia JUSS.

Patrinia scabiosæfolia FISCH.; DC. Prodr. IV. p. 624; LEDEB. Fl. Ross. II. p. 427; HANCE, in Journ. Bot. (1870) p. 225, et (1883) p. 322; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 216; FRANCHET, Pl. David. p. 158; FORBES et HEMSL. Ind. Fl. Sin. I. p. 397.

Patrinia parviflora SIEB. et ZUCC. Fl. Jap. Fam. Nat. n. 678; MIQ. in Ann. Mus. Bot. Lugd.-Bat. III. p. 115.

HAB. Nantō: Mushazan, ad 6000 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1162).

DISTRIB. Japan through China westward to Dahuria.

Patrinia villosa JUSS.; DC. Prodr. IV. p. 624; FRANCH. et SAVAT. Enum. Pl. Jap. I p. 216; FORBES et HEMSL. Ind. Fl. Sin. I. p. 398; HENRY, List Pl. Formos. p. 51; DIELS, Fl. Centr. Chin. p. 597; PALIBIN, Conspect. Fl. Koreæ, I. p. 108.

Patrinia ovata BUNGE; FRANCHET, Pl. David. p. 157.

Valeriana villosa THUNB. Fl. Jap. p. 32, t. 6.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., Oct. 1905, (No. 672); Toroku: Tōhokei, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1905).

DISTRIB. Japan and China.

Hœckia ENGL. et GRÆBN.

Hœckia Aschersoniana ENGL. et GRÆBN. in DIELS, Fl. Centr. Chin. p. 598; HAYATA, in Tōkyō Bot. Mag. XX. p. 57.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 635); in monte Morrison, ad 11000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2272).

DISTRIB. Central China. This monotypic genus is found in central China and Formosa, but nowhere else.

Dipsaceæ.

Scabiosa LINN.

Scabiosa (Sect. *Sclerostemma*) **lacerifolia** HAYATA, (Pl. XVI.), in Tōkyō Bot. Mag. XX. p. 16. Herbæ perennes pubescentes vel glabriusculæ, caulibus validiusculis 10–20 cm. altis pauci-ramosis. Folia sessilia semi-amplexicaulia linearia oblanceolata obsolete pinnatisecta vel lacerata, segmentis irregulariter serratis, radicalia circ. 12 cm. longa 5–6 mm. lata, caulina opposita breviora minora 4–5 cm. longa apice acuta basi longe attenuata sensim dilata. Capitula terminalia depressa 3.5–4 cm. in diametro æquantia longe pedunculata, pedunculis 5–6 cm. longis vel longioribus. Involucri bracteæ 3-seriatæ herbaceæ liberæ sublanceolatæ plerumque 1-florem gerentes extimæ 15 mm. longæ interiores minores ; receptaculi paleæ spathulatæ 5 mm. longæ. Involucellum 4-costatum 8-foveolatum apice 4-lobatum, lobis obtusis. Calycis limbus in 5 setas radiato-patentes diversus. Flores radiantes involucrum fere excedentes ; corollæ 18 mm. longæ, limbis 5-fidis 2-labiatis. Stamina 4, omnia perfecta. Stylus filiformis. Achænium involucello basi adnatum calycis limbo persistente coronatum obovoideum 3 mm. longum ; setæ breves 1 mm. longæ.

HAB. in monte Morrison, ad 13094 ped. alt., leg. S. NAGASAWA ; in montibus centralibus, ad 11000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1852).

As the original description is based upon an imperfect specimen, I have taken the liberty of repeating the description of the plant, basing the above diagnosis upon a most perfect specimen.

DISTRIB. The present genus is mainly distributed in Europe, West Asia, and Africa. In East Asia, four species are found in the alpine regions of the Himalayas, one species in North China, and also one in Japan. No species has ever been known from either central or southern China.

Compositæ.

Ethulia LINN.

Ethulia conyzoides LINN. DC. Prodr. V. p. 12; CLARKE, Comp. Ind. p. 1; HOOK. f. Fl. Brit. Ind. III. p. 226.

Ethulia ramosa ROXB. Fl. Ind. ed.-CAREY, p. 413.

Ethulia gracilis DELILE; DC. Prodr. V. p. 12.

Ethulia angustifolia BOJER; DC. Prodr. V. p. 12.

HAB. Tikusan, ad 150 ped. alt., leg. S. NAGASAWA, Oct. 1905. (No. 763).

DISTRIB. Tropical Africa and Asia. The Philippine islands and Java.

The present plant does certainly not belong to the mountain flora of the island. As the species is new to the Formosan flora, I have taken this occasion to mention it.

Vernonia SCHREB.

Vernonia Andersoni CLARKE, Comp. Ind. p. 26; HOOK. f. Fl. Brit. Ind. III. p. 241; FORBES. et HEMSL. Ind. Fl. Sin. I. p. 400; HENRY, List Pl. Formos. p. 51; HAYATA, Compos. Formos. p. 4; MATSUM. et HAYATA, Enum. Pl. Formos. p. 201.

HAB. Taichū: Kashigatani, leg. G. NAKAHARA, Feb. 1907.

DISTRIB. South China; Assam, Burma, and Tenasserim.

Vernonia cinerea LESS. in Linnæa, IV. p. 291 et VI. p. 673; DC. Prodr. V. p. 24; MIQ. Fl. Ind. Bat. II. p. 11; BENTH. Fl. Hongk. p. 169;

GRISEBACH, Fl. Brit. W. Ind. Isl. p. 353; BENTH. Fl. Austral. III. p. 459; CLARKE, Comp. Ind. p. 20; OLIVER, Fl. Tropic. Afric. p. 275; HOOK. f. Fl. Brit. Ind. III. p. 233; FORBES et HEMSL. Ind. Fl. Sin. I. p. 401; DIELS, Fl. Centr. Chin. p. 608; HAYATA, Comp. Formos. p. 5; MATSUM. et HAYATA, Enum. Pl. Formos. p. 201.

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906.

DISTRIB. Tropical Asia, Africa and Australia.

Adenostemma FORST.

Adenostemma viscosum FORST; LESS. Synop. Comp. p. 156; DC. Prodr. V. p. 111; SIEB. et ZUCC. Fl. Jap. Fam. Nat. p. 181; BENTH. Fl. Hongk. p. 171, et Fl. Austral. III. p. 462; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 219; CLARKE, Comp. Ind. p. 28; OLIVER, Fl. Tropic. Afric. p. 299; FRANCHET, Pl. David. p. 159; MIQ. Fl. Ind. Bat. II. p. 23; HOOK. f. Fl. Brit. Ind. III. p. 242; FORBES et HEMSL. Ind. Fl. Sin. I. p. 403; DIELS, Fl. Centr. Chin. p. 608; HAYATA, Comp. Formos. p. 7; MATSUM. et HAYATA, Enum. Pl. Formos. p. 202.

Spilanthes tinctorius LOUR. Fl. Cochinch. ed-WILLD. p. 590.

HAB. Toroku: Washa, leg. T. KAWAKAMI et U. MORI, Nov. 1906. (Nos. 1825).

DISTRIB. South China; Tropical Asia, Africa, America, and Australia.

Ageratum LINN.

Ageratum conyzoides LINN. Sp. Pl. ed-2, p. 1175; LESS. Synop. Comp. p. 155; DC. Prodr. V. p. 108; MIQ. Fl. Ind. Bat. II. p. 23; BENTH. Fl. Hongk. p. 171; SONDER, Fl. Capens. III. p. 57; BENTH. Fl. Austr. III. p. 462; GRISEBACH, Fl. Brit. W. Ind. Isl. p. 356; SEEMANN, Fl. Vit. p. 149; CLARKE, Comp. Ind. p. 30; OLIVER, Fl. Tropic. Afric. III. p. 300; HEMSL. Voy. Chall. Bot. I. p. 40, et in Biol. Centr.-Americ. II. p. 81; HOOK f. Fl. Brit. Ind. III. p. 243; FORBES et HEMSL. Ind. Fl. Sin. I. p. 403; HENRY, List Pl. Formos. p. 51; HAYATA, Comp. Formos. p. 7; MATSUM. et HAYATA, Enum. Pl. Formos. p. 202.

HAB. Taitō: Bokusekikaku, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 1831).

DISTRIB. Generally spread over all the warm regions, though often existing only as a colonist. Perhaps, an American origin.

Eupatorium LINN.

Eupatorium formosanum HAYATA, sp. nov. Herbæ basi suffruticosæ præter inflorescentiam subsimplices villoso-pubescentes. Folia opposita tri-partita, segmentis lateralibus subsessilibus lanceolatis basi obliquis vel latere inferiore ad petiolum decurrentibus segmentis terminalibus lanceolatis breve petiolulatis iis lateralibus longioribus, apice acuminata basi acuta serrulata supra scabra subtus pallidiora pubescentia ad costas venulasque villosa, petiolis villoso-pubescentibus segmento terminali 2-plo brevioribus. Capitulum parvulum 7 mm. longum corymbosum 4–5-florum. Involucrum oblongo-campanulatum, bracteis 3-seriatis imbricatis scariosis, intimis oblongo-angustis 5 mm. longis, exterioribus gradatim minoribus, extimis parvissimis ovatis 1½ mm. longis. Receptaculum parvum convexum foveolatum. Corollæ tubulatæ 4 mm. longæ, tubis tenuibus limbis parum ampliatis tubo 2-plo brevioribus breviter 5-dentatis, dentibus triangularibus marginatis. Antheræ appendiculatæ basi obtusæ integræ. Styli basi disco dentato annulari coronati, ramis elongatis obtusis. Achænia 5-angulata apice truncata basi attenuata 2 mm. longa; pappi setæ 1-seriatæ rigidulæ scabræ 3½ mm. longæ.

HAB. in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1961); Arizan in montibus Morrison, leg.

G. NAKAHARA, Nov. 1906 : in montibus centralibus, ad 9000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1898).

The present plant comes near *E. chinensis* LINN. ; and resembles especially its variety, *tripartitum* of MIQUEL ; but differs from them in having distinctly triparted leaves and hairy stems and leaves.

Eupatorium Lindleyanum DC. Prodr. V. p. 180; BENTH. Fl. Hongk. p. 172, et Fl. Austr. III. p. 462 ; FORBES et HEMSL. Ind. Fl. Sin. I. p. 404 ; HENRY, List Pl. Formos. p. 52 ; DIELS, Fl. Centr. Chin. p. 608 ; HAYATA, Comp. Formos. p. 9 ; MATSUM. et HAYATA, Enum. Pl. Formos. p. 203.

HAB. Kagi : Shakkōshō, leg. T. KAWAKAMI et U. MORI, Nov. 1906. (No. 1978) ; Goryō, ad 350 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 760).

DISTRIB. China, Manchuria and Japan.

Eupatorium Tashiroi HAYATA, Compos. Formos. p. 9 ; MATSUM. et HAYATA, Enum. Pl. Formos. p. 203.

HAB. Kōshun : Naibun, leg. G. NAKAHARA, Feb. 1907.

Solidago LINN.

Solidago Virga-aurea LINN. ; THUNB. Fl. Jap. p. 317 ; WILLD. Sp. Pl. p. 2065 ; LESS. Synop. Comp. p. 163 ; DC. Prodr. V. p. 338 ; BENTH. Fl. Hongk. p. 179 ; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 228 ; CLARKE, Comp. Ind. p. 35 ; HOOK. f. Fl. Brit. Ind. III. p. 245 ; FORBES et HEMSL. Ind. Fl. Sin. I. p. 406 ; HENRY, List Pl. Formos. p. 52 ; HAYATA, Comp. Formos. p. 10 ; MATSUM. et HAYATA, Enum. Pl. Formos. p. 203.

Solidago cantoniensis et *S. decurrens* LOUR. Fl. Cochinch. ed-WILLD. p. 612 ; DC. Prodr. V. pp. 341–342.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 662) ; in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2146) : Nantō : Mushazan, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1132); in montibus centralibus, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (Nos. 2208 et 2207).

DISTRIB. Cosmopolitan; North America to Japan, westward to temperate Asia and Europe.

Myriactis LESS.

Myriactis Wightii DC. Prodr. V. p. 308; WIGHT, Ic. Pl. Ind. or. t. 1091; CLARKE, Comp. Ind. p. 38; HOOK. f. Fl. Brit. Ind. III. p. 247; TRIMEN, Fl. Ceyl. III. p. 15.

Myriactis javanica DC. Prodr. V. p. 308; CLARKE, Comp. Ind. p. 38.

HAB. Suizan, ad 7702 ped. alt., in montibus Morrison, Oct. 1905, (No. 657), eodem loco, ad 11579 ped., alt., (No. 620), et Tōzan, in isdem montibus, leg. G. NAGASAWA, Oct. 1906: in isdem montibus, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1790), Taitō: Daironkōsha, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1844).

DISTRIB. The Nilghiry Mountains: at an altitude of 8000 ft.: Ceylon: the central province, at elevations of 5–8000 ft.

According to Sir. J. D. Hooker, this species is very variable. He states that three species belonging to this genus mentioned in "The Flora of British India" are all similar. Accepting his statement, the Formosan plant may be referred to this species.

Aster LINN.

Aster baccharoides STEETZ; BENTH. Fl. Hongk. p. 75; FORBES et HEMSL. Ind. Fl. Sin. p. 409; HENRY, List Pl. Formos. p. 52; DIELS, Fl. Centr. Chin. p. 610; HAYATA, Comp. Formos. p. 13; MATSUM. et HAYATA, Enum. Pl. Formos. p. 204.

HAB. in monte Morrison, ad 8000 ped. alt., Oct. 1906, (No. 1959), et in montibus centralibus, ad 10000 ped. alt., leg. T. KAWA-

KAMI et U. MORI, Nov. 1906, (No. 2206): Nantō: Nankōkei, leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1174).

DISTRIB. South central China.

Aster scaber THUNB. Fl. Jap. p. 316; FORBES et HEMSL. Ind. Fl. Sin. I. p. 415; DIELS, Fl. Centr. Chin. p. 611.

Biotia discolor MAXIM. in Prim. Fl. Amur. p. 146.

Doellingeria scabra NEES; DC. Prodr. V. p. 263; MIQ. in Ann. Mus. Bot. Lugd.-Bat. II. p. 169.

HAB. in montibus centralibus, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1850).

DISTRIB. China, Manchuria eastward to Japan as far as North America.

Aster trinervius ROXB. Fl. Ind. ed.-CAREY, p. 433; BENTH. Fl. Hongk. p. 174; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 222; HOOK. f. Fl. Brit. Ind. III. p. 252; FRANCHET, Pl. David. p. 161; MAXIM. in ENGL. Bot. Jahrb. VI. p. 68; FORBES et HEMSL. Ind. Fl. Sin. I. p. 416; HENRY, List Pl. Formos. p. 52; HAYATA, Comp. Formos. p. 13; MATSUM. et HAYATA, Enum. Pl. Formos. p. 204.

Diplopappus asperrimus DC. Prodr. V. p. 277 (fide HEMSL.).

Aster ageratoides TURCZ; MAXIM. Prim. Fl. Amur. p. 144.

HAB. Ganzan, in monte Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 695); in monte Morrison, ad 7000 ped. alt., (Nos. 1876 et 1960), et ad 8000 ped. alt., (No. 1958), leg. T. KAWAKAMI et U. MORI; Suizan in montibus Morrison, ad 7702 ped. alt., (No. 559), Oct. 1905; Tappansha, ad 3138 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 715); Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; Tōhosha, ad 2930 ped. alt., (Nos. 607 et 606) Nov. 1905, leg. S. NAGASAWA; Nantō: Hinokiyama leg. G. NAKAHARA, Feb. 1907.

DISTRIB. Japan to Manchuria, westward to the mountains of northern India.

This species is, so far as I am aware, exceptionally variable, and many apparently different specimens in my hands are mentioned under a single name.

Erigeron LINN.

Erigeron morrisonensis HAYATA, sp. nov. Herbæ perennes parvæ, caulibus hirsutis subsimplicibus circ. 10 cm. altis erectis. Folia radicalia longe spathulata cum petiolis 6 cm. longa 5 mm. lata apice rotundata vel brevissime apiculata basi longe attenuata in petiolum 3 cm. longum abeuntia, caulina alterna sessilia angusta breviora. Capitula mediocria 13 mm. in diametro æquantia, solitaria heterogama, floribus radialibus ♀, disci ☿, omnibus fertilibus. Involucrum late campanulatum, bracteis sub-3-seriatis angustis linearibus circ. 6 mm. longis apice coloratis margine scariosis numerosis parum inæqualibus extus pilosissimis. Receptaculum convexum nudum. Corollæ ♀ ligulatæ angustissimæ tubis limbo vix brevioribus; ☿ tubulatæ 4 mm. longæ, tubis pilosiusculis, limbis parum ampliatis 4-dentatis. Antheræ basi obscure sagittatæ. Styli fl. ☿ rami complanati, appendicibus triangularibus. Achænia compressa angusta 2 mm. longa pilosa, margine nervio, facie enervia; pappi setæ tenues 1-seriatæ scabriusculæ rufo-albæ 3 mm. longæ.

HAB. in summam montis Morrison, ad 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905; in eodem loco, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2247).

Near *E. Thunbergi* GRAY; but distinguished by the spathulate linear leaves and small ray florets.

Blumea DC.

Blumea chinensis DC. Prodr. V. p. 444; BENTH. Fl. Hongk. p. 177; HOOK. f. Fl. Brit. Ind. III. p. 268; FORBES et HEMSL. Ind. Fl. Sin. I. p. 420; HENRY, List Pl. Formos. p. 53; HAYATA, Comp. Formos. p. 30; MATSUM. et HAYATA, Enum. Pl. Formos. p. 209.

Conyza chinensis LINN. Sp. Pl. ed.-2, p. 1208; MIQ. Fl. Ind. Bat. II. p. 52.

HAB. Washakei, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1823); Kagi: Shitōsha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1979).

DISTRIB. South China, eastern India, and Java.

Laggera SCH.-BIP.

Laggera alata SCH.-BIP.; CLARKE, Comp. Ind. p. 91; HOOK. f. Fl. Brit. Ind. III. p. 271; FORBES et HEMSL. Ind. Fl. Sin. I. p. 422; MATSUM. et HAYATA, Enum. Pl. Formos. p. 210.

Blumea alata DC. Prodr. V. p. 448; BENTH. Fl. Hongk. p. 177; WIGHT, Ic. Pl. Ind. or. t. 1101.

HAB. in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906. (No. 2114).

DISTRIB. Generally found in tropical Asia, Africa, and Madagascar; South China.

It is rather an anomalous case that we have such a tropical species in the high regions of Formosa.

Leontopodium BR.

Leontopodium microphyllum HAYATA, sp. nov. (Pl. XVII). Herbæ suffruticosæ perennes cæspitosæ lanatæ, caulibus ascendentibus erectisve simplicibus 5–6 cm. altis. Folia radicalia caulinis conformia spathulato-angusta integerrima 1 cm. longa 2 mm. lata, supra laxe subtus dense lanata. Capitula parvula 3 mm. longa ad apicem caulis in cymas densas foliis floralibus quasi involueratas 4–5-conferta; foliis floralibus 5–6 in cyma quisque, horizontaliter patentibus dense lanatis linearibus acuminatis 1 cm. longis; fl. ♀ fertilibus in ambitu paucis; fl. ☿ sterilibus in disco paucis. Involucrum campanulatum, bracteis circ. 2-seriatis imbricatis scariosis, intimis angusto-acutis apice lanatis circ. 3 mm. longis, extimis latioribus dorso lanatis. Receptaculum convexum fere epaleaceum foveolatum. Corollæ ♀ filiformes truncatæ; ☿ regulares 2 mm. longæ tubulosæ, limbis ampliatis subcampanulatis apice 5-fidis pauce pilosis. Antheræ basi sagittatæ, auriculis tenuissime caudato-appendiculatis. Stylus breviter 2-fidus, ramis obtusis. Achænia parva oblonga subteretia ecostata glabra; pappi setæ 1-seriatæ tenues breviter valdeque barbellatæ basi subconnatæ.

HAB. in monte Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 246).

Very distinct species having very small leaves.

Anaphalis DC.

Anaphalis margaritacea BENTH. et HOOK. f. Gen. Pl. II. p. 303; CLARKE, Comp. Ind. p. 103; MAXIM. in Mél. Biol. XI. p. 235; FORBES et HEMSL. Ind. Fl. Sin. I. p. 425.

Antennaria margaritacea R. BR.; DC. Prodr. VI. p. 270; LEDEB. Fl. Ross. II. p. 613.

Gnaphalium margaritaceum LINN. Sp. Pl. ed-2, p. 1198; FRANCH. et SAVAT. Enum. Fl. Jap. I. p. 242.

var. **angustifolia** (FRANCH. et SAVAT.).

Gnaphalium margaritaceum LINN. var. *angustifolium* FRANCH. et SAVAT· Enum. Pl. Jap. I. p. 242.

Antennaria japonica MIQ. Prol. Fl. Jap. p. 110.

forma **nana**. Humiles circ. 5 cm. altæ, caulibus simplicibus.

Folia parvissima oblonga vel oblongo-linearia 6 mm. longa 1 mm.–1½ mm. lata apice crassiusculo-apiculata lanata.

HAB. in monte Morrison, ad 10000 ped. alt.

forma **morrisonicola.** Altiores 10–15 cm. altæ, caulibus simplicibus. Folia parviora oblongo-lanceolata vel oblongo-linearia circ. 2½ cm. longa 3 mm. lata aristato-apiculata vel obtusa supra glabra subtus lanata.

HAB. In monte Morrison, ad 5000 ped. alt., leg. R. TORII, 1899; Giyokusan, ad 10634 ped. alt., (No. 711), et Ganzan, ad 9141 ped. alt., (No. 705), in montibus Morrison, leg. S. NAGASAWA, Nov. 1905; Tōzan, in isdem montibus, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 8000 ped. alt., (No. 1797), et ad 10000 ped. alt., (No. 2277), leg. T. KAWAKAMI, et U. MORI, Oct. 1906; in montibus centralibus, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1848); Nantō: Hinokiyama, leg. G. NAKAHARA, Feb. 1907; Mushasan, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1128).

There is a little doubt about identifying the all above plants with *A. margaritacea* var. *angustifolia.* The plant represented by var. *angustifolia* is exceptionally variable. I have examined a considerable number of various forms of this variety collected in Japan and Formosa, and found that they show no specifical distinction though they seem apparently different.

DISTRIB. Type: Japan and China northward to Amurland and Kamtchatka; also in North America and nationalized in Europe.

Anaphalis Nagasawai HAYATA, (Pl. XVIII.), in Tōkyō Bot. Mag. XX. p. 15. Herbæ perennes erectæ lanatæ stoloniferæ 4 cm.–5 cm. altæ tenuiusculæ, radicibus lignescentibus. Folia alterna integerrima decurrentia obovato-spathulata apice rotundata vel obtusa

1 cm.–1½ cm. longa 3 mm.–5 mm. lata lanata. Capitula majuscula ad apicem caulis subsimplicis solitaria 1.5 cm.–2 cm. in diametro æquantia heterogama; floribus ♀ fertilibus in ambitu ∞–seriatis, ☿ in disco sterilibus numerosis. Involucrum late campanulatum, bracteis radiantibus niveis ∞–seriatis imbricatis scariosis, intimis oblongo-lanceolatis 7 mm. longis 1 mm. latis, interioribus oblongis petaloideis patentibus 10 mm. longis 3 mm. latis, exterioribus brevioribus, extimis ovatis dorso lanatis 8 mm. longis 3 mm. latis. Receptaculum convexum epaleaceum. Corollæ fl. ♀ filiformes, 4-dentatæ apice glanduloso-pilosæ; fl. ☿ tubulosæ, limbo ampliato subcampanulato apice 5-fido minuto papilloso-marginato. Antheræ apice appendiculatæ, appendicibus obtusis, basi sagittatæ caudatæ. Styli fl. ♀ filiformes minute 2-lobi; fl. ☿ apice breve 2-lobi, ramis truncatis. Achænia oblonga minutissime hirtello-papillosa subteretia 1 mm. longa ½ mm. in sectione æquantia; pappi setæ tenues 1-seriatæ scabræ liberæ caducæ 6 mm. longæ.

HAB. in monte Morrison, ad 13000 ped. alt., leg. T. KAWAKAMI et U. MORI, (Nos. 2126 et 2239).

In general appearance, this species resembles very much *G. niitakayamense* HAYATA. The difference by which the genera, *Gnaphalium* and *Anaphalis*, are separated from each other is indeed a very slight one. The separation lies on the point whether the disc flowers are stirile or not. So far as my knowledge extends, this does not seem to be a fixed character. I am, therefore, much inclined to think that the separation of *Anaphalis* from *Gnaphalium* is rather artificial.

Gnaphalium LINN.

Gnaphalium hypoleucum DC. Prodr. VI. p. 222; HOOK. f. Fl. Brit.

Ind. III. p. 288; WIGHT, Ic. Pl. Ind. or. t. 1114; FORBES et HEMSL. Ind. Fl. Sin. I. p. 426.

Gnaphalium amogens HANCE, in Journ. Bot. (1868) p. 174, et (1878) p. 108; BENTH. Fl. Hongk. p. 187.

HAB. Ganzan, ad 9141 ped. alt., in montibus Morrison, Oct. 1905, (No. 630), in monte Morrison, ad 11000 ped. alt., (No. 2077), et ad 12000 ped. alt., (No. 2234), leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. South China and Japan; and also in the mountains of India and Abyssinia.

Gnaphalium lineare HAYATA, sp nov. (Pl. XIX.). Herbæ graciles sericeo-lanatæ. Caules erecti tenuissimi simplices 20 cm. alti foliis caulinis remote instructi. Folia radicalia sessilia linearia 7 cm. longa 1½ mm. lata apice obtusa basi decurrentia, caulina radicali conformia alterna breviora basi semi-amplexicaulia exsiccato revoluta supra subglabra subtus sericeo-lanata. Capitula ad apicem caulis in cymas densas foliis floralibus quasi involucratas circ. 10 conferta. Cyma capitulorum depresso-globosa 2½ cm. in diametro æquans, foliis floralibus 5–10, 2-seriatis linearibus circ. 1 cm. longis 1½ mm. latis apice obtusis basin versus dilatis intus subglabris extus plus minus lanatis. Involucrum ovoideum 4 mm. longum 2 mm. latum, bracteis 2–3-seriatis scariosis apice fuscis, interioribus spathulatis integris vel pauce laceratis 4 mm. longis ⅔ mm. latis, exterioribus brevioribus latioribus obovatis dorso lanatis. Receptaculum leviter concavum minute muricatum. Fl. ♀ in ambitu ∞-seriati; corollæ filiformes 3 mm. longæ apice breviter 2–3-fidæ; styli rami elongati recurvi. Fl. ☿ in disco paucissimi 1–4, tubulosi tenues, limbo parum ampliato 5-dentato, dentibus triangularibus marginatis; antheræ basi sagittatæ, auriculis sæpe paucifidis tenuiter caudato-appendiculatis; styli rami subteretes apice subcapitati. Achænia oblonga ½ mm. longa teretiuscula ecostata minute pauceque glanduloso-tuberculata, pappi setis 1-seriatis tenuibus caducis scariosis 3 mm. longis.

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906: in monte Morrison, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1995).

Near *G. japonicum* THUNB.; but easily distinguished from it by the linear leaves; from *G. collinum* LABILL., by the compound heads; from *G. Thomsoni* HOOK. f., by the not papillose achenes and smaller clusters of the heads; and from *G. uliginosum* LINN., by the extremely narrow leaves.

Gnaphalium luteo-album LINN. Sp. Pl. ed-2, p. 1196; LESS. Synop. Comp. p. 331; DC. Prodr. VI. p. 230; MIQ. Fl. Ind. Bat. II. p. 91; BENTH. Fl. Austr. III. p. 653; SONDER, Fl. Capens. III. p. 262; CLARKE, Comp. Ind. p. 114; HEMSL. Biol. Centr.-Americ. II. p. 139; HOOK. f. Fl. Brit. Ind. III. p. 288; HENRY, List Pl. Formos. p. 53; HAYATA. Comp. Formos. p. 32; MATSUM. et HAYATA, Enum. Pl. Formos. p. 210.

HAB. in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 1980 et 2044); Nantō: Mushasan, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1133).

DISTRIB. Himalaya, mountains of Java and Australia.

Gnaphalium niitakayamense HAYATA, in Tōkyō Bot. Mag. XX. p. 14. Herbæ perennes erectæ dense lanatæ 6–7 cm. altæ validiusculæ. Folia alterna integerrima sessilia oblanceolata vel spathulato-obovata 1–1½ cm. longa 5 mm. lata. Capitula parva obovoidea 1 cm.–1½ cm. in diametro æquantia ad apicem caulis 2–3 conferta vel solitaria, floribus in ambitu ♀ ∞-serratis, ☿ paucioribus, omnibus fertilibus. Involucrum obovoideo-campanulatum, bracteis 4–5 seriatis scariosis albis, extimis dorso lanatis, intimis linearibus, interioribus oblongis 8 mm. longis. Receptaculum planum foveolatum. Corollæ ♀ filiformes, minute 4-dentatæ; ☿ regulares tubulosæ tenues, limbo parum ampliato 5-fido. Antheræ apice appendiculatæ basi sagittatæ, auriculis caudato-appendiculatis. Styli fl. ☿ rami subteretes apice subcapitati. Achænia oblongo-obovoidea teretiuscula ecostata glabra minute papillosa ⅞ mm. in sectione æquantia; pappi setæ 1-seriatæ tenues caducissimæ 4 mm. longæ.

HAB. in monte Morrison, ad 13000 ped. alt., (Nos. 2241, 2244 et 2128), et in montibus centralibus, ad 11000 ped. alt., (No. 1853), leg. T. KAWAKAMI et U. MORI, Nov. 1906.

The present plant is remarkable in having general appearance of *Anaphalis*. As the disc flowers are all fertile, however, this should be referred to *Gnaphalium*.

Carpesium LINN.

Carpesium acutum HAYATA, sp. nov. Herbæ rigidæ basi suffruticosæ erectæ ramosæ puberulæ vel tomentosæ 2–3-ped. altæ. Folia alterna ovata vel lanceolata cum petiolis 7 cm. longa apice acuminata basi acuta vel rotundata abrupte attenuata ad petiolum 2 cm. longum abeuntia, vel superiora lanceolata sessilia, margine obscure dentata, dentibus mucronatis, supra pubescentia subtus tomentoso-hirsuta pallidiuscula. Capitula mediocria 8 mm. longa 10 mm. in diametro æquantia cernua ad axillas foliorum longe pedunculata, floribus in ambitu ♀ ∞–seriatis discique ☿ fertilibus. Involucrum campanulato-semiorbiculatum, bracteis sub–4-seriatis, interioribus angustis 4 mm. longis obtusis vel acutis scariosis, extimis 5–6 foliaceis lanceolatis dentatis 2½ cm. longis. Receptaculum planum muricatum. Corollæ fl. ♀ breve tubulosæ 1½ mm. longæ 5-dentatæ; fl. ☿ longiores 3 mm. longæ achænium æquantes, limbo paulo latiore 5-dentato. Antheræ apice appendiculatæ rotundato-truncatæ basi sagittatæ, auriculis caudis setaceo-subramosis appendiculatis. Styli fl. ☿ rami latiores complanati apice rotundati. Achænia elongata teretia circ. 4 mm. longa 10-striata apice in rostrum glanduloso-punctatum longum vel breve contracta, annulo obscuro coronata ; pappus 0.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 694) ; Arizan, in isdem montibus, leg. G. NAKAHARA, Nov. 1906 ; in eodem monte, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1991) : Toroku : Washa, leg. T. KAWAKAMI et U. MORI, Nov. 1906. (No. 1937).

Remarkable for the acute foliose bracts of involucres.

Siegesbeckia LINN.

Siegesbeckia orientalis LINN. Sp. Pl. ed.-2, p. 1269 ; ROXB. Fl. Ind. ed.-CAREY, III. p. 439 ; LOUR. Fl. Cochinch. ed.-WILLD. p. 616 ; DC. Prodr. V. p. 495 ; SIEB. et ZUCC. Fl. Jap. Fam. Nat. p. 185 ; MIQ. Fl. Ind. Bat. II. p. 67 ; BENTH. Fl. Hongk. p. 182, et Fl. Austr. III. p. 535 ; SONDER, Fl. Capens. III. p. 132 ; SEEMANN, Fl. Vit. p. 142 ; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 231 ; CLARKE, Comp. Ind. p. 133 ; OLIVER, Fl. Tropic. Afric. III. p. 372 ; HOOK. f. Fl. Brit. Ind. III. p. 304 ; FRANCHET, Pl. David. p. 164 ; FORBES et HEMSL. Ind. Fl. Sin. I. p. 433 ; HENRY, List Pl. Formos. p. 54 ; DIELS, Fl. Centr. Chin. p. 615 ; HAYATA, Comp. Formos. p. 17 ; MATSUM. et HAYATA, Enum. Pl. Formos. p. 205.

HAB. Toroku : Kureikiaku, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1818).

DISTRIB. Cosmopolitan in the warm and temperate regions.

Spilanthes LINN.

Spilanthes Acmella LINN. ; THUNB. Fl. Jap. p. 321 ; DC. Prodr. V. p. 623 ; MIQ. Fl. Ind. Bat. II. p. 79 ; CLARKE, Comp. Ind. p. 138 ; OLIVER, Fl. Tropic. Afric. III. p. 384 ; HOOK. f. Fl. Brit. Ind. III. p. 307 ; HENRY, List Pl. Formos. p. 54; HAYATA, Comp. Formos. p. 20; MATSUM. et HAYATA, Enum. Pl. Formos. p. 205.

HAB. Kōdenshō: ad 2623 ped. alt., leg. S. NAGASAWA, Oct. 1905; Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1761).

DISTRIB. India throughout, and extends to all warm countries.

Chrysanthemum LINN.

Chrysanthemum indicum LINN. Sp. Pl. ed.-2, p. 1253; THUNB. Fl. Jap. p. 320; FORBES et HEMSL. Ind. Fl. Sin. I. p. 437; DIELS, Fl. Centr. Chin. p. 617.

Pyrethrum idicum CASS.; MAXIM. in Mél. Biol. VIII. p. 516.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 734); in monte Morrison, ad 7500 ped. alt., Oct. 1906, (No. 1814), et in montibus centralibus, Nov. 1906, (No. 1885), leg. T. KAWAKAMI et U. MORI; Toroku: Tōhozan, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1828).

DISTRIB. China and Japan.

The Formosan plant appears at first sight to be different from the Japanese species. But, after comparing various forms of the plants from both regions, I have found that they do not show any specifical distinction, and thought it better to regard them as the same species.

Artemisia LINN.

Artemisia japonica THUNB. Fl. Jap. p. 310; DC. Prodr. VI. p. 100; BENTH. Fl. Hongk. p. 186; FRANCHET, Pl. David. p. 168; MAXIM. in Mél. Biol. VIII. p. 526, (varietates *japonica* et *desertorum*); FORBES et HEMSL. Ind. Fl. Sin. I. p. 443.

Artemisia parviflora BUCH. ex ROXB. Fl. Ind. ed.-CAREY, III. p. 420; HOOK. f. Fl. Brit. Ind. III. p. 322.

Artemisia cuneifolia DC. Prodr. VI. p. 126.

HAB. Tappansha, ad 3138 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 786); Kagi: Kōdenshō, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1740); Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906.

DISTRIB. Japan and China; westward to North India, from Kashmir to Khasia, Pulney mountains in the Madras Peninsula (after HEMSL.); also in North America.

Artemisia niitakayamensis HAYATA, (Pl. XX.), in Tōkyō Bot. Mag. XX. p. 16. Herbæ perennes basi suffruticosæ hirsutæ odoratæ multicaules, caulibus simplicibus 10 cm.–16 cm. altis. Folia alterna ambitu obovata 2 cm. longa 1 cm. lata basi longe angusta decurrentia semi-amplexicaulia bipinnatisecta, segmentis utrinque 2–3 obovatis 2–3 lobatis, lobis ovato-acutis. Capitula majuscula 1 cm. in diametro æquantia erecta rarius cernua racemosa longe pedicellata, pedicellis 2 cm. longis. Involucrum late campanulatum, bracteis 3-seriatis margine scariosis, intimis 5 mm. longis spathulatis, interioribus oblongis margine denticulatis, exterioribus gradatim minoribus ovato-acutis. Receptaculum semiorbiculatum sparce pilosum. Fl. ♀ in ambitu 1-seriati fertiles; corollæ tenues tubulosæ apice breviter 4-fidæ. Fl. ☿ fertiles; corollæ teretes limbis parum ampliatis basi limbi constrictis apice 5-fidis. Antheræ apice appendiculatæ basi obtusæ. Styli rami apice truncati dilati penicillati. Achænia obovoidea compressa 2 mm. longa 1 mm. in sectione æquantia leviter incurva apice truncata facie dorsali sæpe ecostata ventrali prominente 4-costata.

HAB. in monte Morrison, ad 13000 ped. alt., (Nos. 2282 et 2130.), et in montibus centralibus, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2195).

As the original description is drawn from an imperfect specimen, I have repeated the description basing it upon a most perfect specimen.

Artemisia oligocarpa HAYATA, sp. nov. (Pl. XXI.). Herbæ perennes basi suffruticosæ. Caules erectæ glabrescentes 15 cm.–30 cm. alti. Folia radicalia caulino conformia ambitu obovata basi longe attenuata 3 cm. longa 1 cm.–1½ cm. lata bipinnatisecta, segmentis linearibus 3–5–lobis vel -sectis, lobis linearibus apice obtusis vel acutis, primum pubescentia demum glabra. Capitula parviora 4 mm. in diametro æquantia erecta racemosa vel paniculata pedicellata, pedicellis ½ cm.—1 cm. longis. Involucrum late campanulatum, bracteis 2-seriatis margine scariosis obovatis apice rotundatis basi constrictis 3 mm. longis 2 mm. latis. Receptaculum semiorbiculatum 1⅓ mm. in diametro aequans nudum. Flores ♀ in ambitu 1-seriati 15–20, fertiles; corollæ breve tubulosæ 1 mm. longæ apice 2–3–fidæ; styli rami elongati recurvati. Fl. ☿ steriles; numerosi; corollæ tubuloso-campanulatæ 2½ mm. longæ, limbis longe ampliatis tubum in longitudine æquantibus apice 5-fidis, lobis triangularibus acutis marginatis; antheræ apice appendiculatæ apiculatæ cuspidato-acuminatæ, basi leviter brevissime caudatæ; stylus indivisus apice peltato-dilatus minute et longiuscule papillosus. Achænia oblique obovoidea obscure reticulato-striata 1½ mm. longa.

HAB. in monte Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (Nos. 2280 et 2140).

The present plant is somewhat near *A. salsoloides* WILLD.; but differs from it in having narrowly pinnatisected leaves. As stated by BENTHAM, in the Genera Plantarum Vol. II. p. 551, the anthers of the genus *Artemisia* are wanting of any tail. Nevertheless, I have observed in this species that there is in almost all cases a very small tail at the base of anthers. Moreover, the group to which this plant belongs is far different from other groups in having flowers, which are perfect and sterile, and even more different in having simple peltate stigmata. Upon considering the above cases, I am much inclined to raise this group to a genus separated from *Artemisia*.

Artemisia scoparia WALDST. et KIT.; DC. Prodr. VI. p. 99; MAXIM. in Mél. Biol. VIII. p. 523; FRANCHET, Pl. David. p. 167; HOOK. f. Fl. Brit. Ind. III. p. 323; FORBES et HEMSL. Ind. Fl. Sin. I. p. 445.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905. (No. 631); Tōzan, in montibus Morrison, leg. G. NAKAHARA (Nov. 1906); in monte Morrison, ad 11000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2043).

DISTRIB. Japan and China, northward to Kamtchatka and North America; westward to North India and extends to central Europe.

Petasites GÆRTN.

Petasites tricholobus FRANCHET, Pl. David. p. 173; DIELS, Fl. Centr. Chin. p. 618; FORBES et HEMSL. Ind. Fl. Sin. I. p. 447.

HAB. in monte Morrison, ad 8000 ped. alt., (Nos. 1880 et 2078), et in montibus centralibus, leg. T. KAWAKAMI et U. MORI, Nov. 1906.

DISTRIB. Central China.

Gynura CASS.

Gynura flava HAYATA, sp. nov. Herbæ sparce hirtellæ vel subglabræ. Caules validiusculi sulcati pauci-ramosi 2–3 ped. alti. Folia alterna in ambitu oblonga vel oblongo-ovata 18 cm. longa 6 cm. lata grosse irregulariter dentata vel infra medium profunde dissecta, lobis argute dentatis, apice acuta basi angusta in petiolum

2 cm. longum sensim attenuata, auriculis basin petioli distinctis oblongis dentatis, utraque pagine sparce hirtella ad costas et venulas hirsuta subtus pallidiora. Capitula mediocria 1½ cm. longa ad apicem ramorum corymbosa, pedicellis 1 cm.—2 cm. longis hirsutis, bracteis ad basin pedicelli linearibus 1 cm. longis, homogama, floribus omnibus ☿ fertilibus. Involucrum campanulatum, bracteis 1–seriatis angustis æqualibus 11 mm. longis 2 mm. latis margine scariosis plus minus cohærentibus, additis nonnullis exterioribus parvis linearibus 5 mm. longis ciliolatis. Receptaculum planum foveolatum. Corollæ flavæ tenuiter tubulosæ 13 mm. longæ, limbis parum ampliatis tubo in longitudine 2-plo brevioribus apice breviter 5-fidis, lobis oblongo-triangularibus. Antheræ subexsertæ, elongatæ 2½ mm. longæ basi integræ. Styli exserti cum ramis 17 mm. longi, ramis elongatis erecto-patentibus 5 mm. longis in appendices longas tereti-subulatas hirtellas desinentibus. Achænia glabra angusta 10-striata; pappi setis copiosis tenuibus 10 mm. longis albis.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 562); in monte Morrison, ad 6500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2012); Toroku: Gunkei, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1951).

Senecio LINN.

Senecio monanthus DIELS, Fl. Centr. Chin. p. 621.

HAB. in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2133); eodem loco, et G. NAKAHARA, Nov. 1905.

DISTRIB. Central China.

Senecio scandens HAM.; HOOK. f. Fl. Brit. Ind. III. p. 352; FORBES et HEMSL. Ind. Fl. Sin. I. p. 457; DIELS, Fl. Centr. Chin. p. 620.

Senecio campylodes DC. Prodr. VI. p. 370;

Senecio stipulatus WALL.; DC. Prodr. VI. p. 370.

Senecio Wightianus DC.; WIGHT, Ic. Pl. Ind. or. t. 1136.

Senecio chinensis DC. Prodr. VI. p. 363; BENTH. Fl. Hongk. p. 190; MAXIM. in Mél. Biol. VIII. p. 16.

Senecio intermedius WIGHT, Ic. Pl. Ind. or. t. 1135.

Cineraria repanda LOUR. Fl. Cochinch. ed-WILLD. p. 613.

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 8000 ped. alt., (No. 1877), et ad 7000 ped. alt., (No. 2081), leg. T. KAWAKAMI et U. MORI, Nov. 1906; Toroku: Hōōsan, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1927); Tōhosha, leg. S. NAGASAWA, Nov. 1905, (No. 608).

DISTRIB. South China and southern part of Japan; north and south India, and Ceylon.

Echinops LINN.

Echinops dahuricus FISCH.; DC. Prodr. VI. p. 523; FRANCHET, Pl. David. p. 176; HENRY, List Pl. Formos. p. 55; FORBES et HEMSL. Ind. Fl. Sin. I. p. 459; HAYATA, Comp. Formos. p. 33; MATSUM. et HAYATA, Enum. Pl· Formos. p. 221.

Echinops Gmelini LEDEB. Fl. Ross. II. p. 653; MAXIM. Prim. Fl. Amur. p. 167.

Echinops sphærocephalus MIQ. in Ann. Mus. Bot. Lugd.-Bat. II. p. 182; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 253.

HAB. Taitō: Bokusekikaku, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 1832); Arōkonsha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1741).

DISTRIB. Siberia to Japan and China.

Cnicus LINN.

Cnicus Wallichii DC. Prodr. VI. p. 643; HOOK. f. Fl. Brit. Ind. III. p. 363.

Cirsium Wallichii DC.; DIELS, Fl. Centr. Chin. p. 627.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., Oct. 1905, (No. 778), in monte Morrison, ad 12000 ped. alt., (No. 2245), et in eodem monte, ad 10000 ped. alt., (No. 2279), leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. South China to the Philippine islands, and Himalaya.

Saussurea DC.

Saussurea japonica DC. in Prodr. VI. p. 536; BENTH. Fl. Hongk. p. 167; MAXIM. in Mél. Biol. IX. p. 337; HANCE, in Journ. Linn. Soc. XIII. p. 108; FRANCHET, Pl. David. p. 181; FORBES et HEMSL. Ind. Fl. Sin. I. p. 464; DIELS, Fl. Centr. Chin. p. 627.

var. **longicephala** HAYATA, n. v. Capitula longiuscula ovoidea, squamis involucri apice appendicula petaloidea rotundata instructis.

HAB. loco non indicato.

DISTRIB. Type: China, Japan, and Manchuria to North America.

The type of *Saussurea japonica* DC. has a globose head, while the present variety has a oblong head. Besides, the bracts of the involucres of the variety which are crowned with a petaloidal appendage, are slightly different from those of the type.*

Saussurea sp.

HAB. Taitō: Bushisekisha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2158).

Ainsliæa DC.

Ainsliæa macroclinidioides HAYATA, sp. nov. (Pl. XXII.). Herbæ

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* After completing this manuscript, I have had the opportunity of examining a Chinese specimen named *S. japonica* DC. collected by Dr. HENRY. The specimen is exactly the same as the Formosan one, and is certainly not the type of *S. japonica* DC.

perennes basi suffruticosæ pilosiusculæ elatiores 60 cm. altæ. Folia alterna ad medium caulis conferta pilosiuscula longe petiolata, petiolis lamina 3-plo brevioribus 4 cm. longis, laminis ovatis vel ovato-lanceolatis circ. 9 cm. longis 3½ cm. latis acuminatis basi rotundatis truncatis vel cordatis margine remote aristato-serrulatis albo-lamelligeris 3-nerviis subglabratis ad costas breve pilosiusculis, subtus pallidioribus. Capitula angusta mediocria 2 cm. longa 2–3-flora secus caulem subspicata. Involucrum angustum circ. 1 cm. longum, bracteis 3–4-seriatis valde inæqualibus unicostatis rigidis scariosis intimis oblanceolatis acutis 1 cm. longis 2 mm. latis, exterioribus gradatim brevioribus, extimis brevissimis late ovatis 1½ mm. longis. Receptaculum parvum nudum. Flores normales ignoti. Flores cleistogami: corollæ tubulosæ pappi setis 2-plo breviores, apice 5-fidæ; antheræ basi longe sagittatæ, auriculis in caudas longas 2-fidas productis; styli rami obtusi basi incrassati. Achænia oblongo-obovoidea subcompressa 7 mm. longa apice contracta 10-costata pilosa, stipitibus parvis persistentibus; pappi setæ 1-seriatæ plumosæ 8 mm. longæ rufo-albæ.

HAB. Suizan, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 665); Kagi: Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1971).

Remarkable for the fascicled leaves at the middle of the stem just like those of *Macroclinidium robustum* MAXIM.

Ainsliæa morrisonicola HAYATA, n. n. (Pl. XXIII).

Ainsliæa elegans HAYATA, (non HEMSL.) in Tōkyō Bot. Mag. XX. p. 14. Herbæ laxe pilosæ, caulibus erectis 5–6 cm. altis simplicibus aphyllis. Folia omnia radicalia oblanceolata 15 mm.–20 mm. longa 8 mm. lata apice apiculato-acuta basi subito angusta ad petiolum attenuata vel basi rotundata margine remote ciliatoaristata, petiolis 10 mm. longis basi dilatis. Capitula 3–4-flora secus caulem spicata sessilia demum pendula. Involucrum angustum 3–4 mm. longum, bracteis 3-seriatis rigidis subpaleaceis aristato-acutis, interioribus elongatis, exterioribus gradatim brevioribus, intimis longissimis $\frac{1}{2}$ cm. longis. Receptaculum nudum. Flores normales ignoti. Flores cleistogami: corollæ tubulosæ pappi setis breviores circ. 4 mm. longæ, apice leviter 5-fidæ clausæ: antheræ basi sagittatæ, auriculis in caudas longas productis: styli basi dilati, ramis angustis, complanatis apice rotundatis. Achænia obovoideo-oblonga subteretia 5 mm. longa 1 mm. in sectione æquantia 10-costata apice truncata glabra; pappi setæ 1-seriatæ plumosæ $5\frac{1}{2}$ mm. longæ rufo-albæ.

HAB. Seizan, in montibus Morrison, ad 11707 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 628); Tōzan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906.

The plant is originally named *Ainsliæa elegans*, which name is, however, found afterward in the Chinese plants. As it is not desirable to maitain one and the same name for two different plants, I have taken this occasion to change the name of the Formosan plant to a new name, *A. morrisonicola* HAYATA.

Ainsliæa reflexa MERRILL. in Philipp. Journ. Sci. I. Suppl. Bot. p. 242.

HAB. Nantō: Mushazan, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1138); Hinokiyama, leg. G. NAKAHARA, Feb. 1907.

DISTRIB. The Philippine islands.

Picris LINN.

Picris hieracioides LINN. Sp. Pl. ed.-2. p. 1115; DC. Prodr. VII. p.

128; HOOK. f. Fl. Brit. Ind. III. p. 393; FRANCHET, Pl. David. p. 185; FORBES et HEMSL. Ind. Fl. Sin. I. p. 474.

Picris japonica THUNB. Fl. Jap. p. 299; DC. Prodr. VII. p. 130.

HAB. in monte Morrison, ad 10000 ped. alt., Nov. 1906, (No. 2294), et in montibus centralibus, ad 10000 ped. alt., Dec. 1906, (No. 2204), leg. T. KAWAKAMI et U. MORI.

DISTRIB. Japan and central China; eastward to America and western Europe; northward to Kamtchatka; also in Australia and New zealand.

Lactuca LINN.

Lactuca versicolor SCH.-BIP.; MAXIM. in Mél. Biol. IX. p. 362; BAKER et MOORE, in Journ. Linn. Soc. XVII. p. 383; FRANCHET, Pl. David. p. 188; FORBES et HEMSL. Ind. Fl. Sin. I. p. 485; DIELS, Fl. Centr. Chin. p. 631; HAYATA, Comp. Formos. p. 39; MATSUM. et HAYATA, Enum. Pl. Formos. p. 212.

Ixeris versicolor DC. Prodr. VII. p. 151; BENTH. Fl. Hongk. p. 193; MIQ. in Ann. Mus. Bot. Lugd.-Bat. II. p. 191; LEDEB. Fl. Ross. II. p. 817.

Prenanthes chinensis THUNB. Fl. Jap. p. 301.

Youngia chinensis DC. Prodr. VII. p. 194.

HAB. Tappansha, ad 3138 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 775); Taitō: Daironkōsha, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2220).

DISTRIB. Japan and China northward to Dahuria; also in North America.

Campanulaceæ

Pratia GAUD.

Pratia begonifolia LINDL.; CLARKE, in HOOK. f. Fl. Brit. Ind. III. p.

422; FORBES et HEMSL. Ind. Fl. Sin. II. p. 2; HENRY, List Pl. Formos. p. 56; DIELS, Fl. Centr. Chin. p. 607; MATSUM. et HAYATA, Enum. Pl. Formos. p. 213.

Piddingtonia Nummularia DC. Prodr. VII. p. 341; BENTH. Fl. Hongk. p. 196.

Lobelia Horsfieldiana MIQ. Fl. Ind. Bat. II. p. 577.

HAB. Kōdenshō, ad 2623 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 742).

DISTRIB. South China, Malay, and eastern India.

Lobelia LINN.

Lobelia affinis WALL. in DC. Prodr. VII. p. 360; BENTH. Fl. Hongk. p. 197, (in nota sub *L. trigona*); CLARKE, in HOOK. f. Fl. Brit. Ind. III. p. 424; HANCE in Journ. Linn. Soc. XIII. p. 109; FORBES et HEMSL. Ind. Fl. Sin. II. p. 2.

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1983).

DISTRIB. Widely diffused in India, Ceylon, and Malay; South China.

Lobelia pyramidalis WALL.; DC. Prodr. VII. p. 381; CLARKE, in HOOK. f. Fl. Brit. Ind. III. p. 426; Bot. Mag. t. 2387; FORBES et HEMSL. Ind. Fl. Sin. II. p. 3.

Lobelia Davidi FRANCHET, Pl. David. p. 191.

HAB. Taitō: Bunshisekisha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 1911).

DISTRIB. Mountains of North and East India, and Burma; South China.

Wahlenbergia SCHRAD.

Wahlenbergia gracilis A. DC. "Monogr. Camp. p. 142." et Prodr.

VII. p. 433; BENTH. Fl. Austral. IV. p. 137; CLARKE, in HOOK. f. Fl. Brit. Ind. III. p. 429; FRANCHET, Pl. David. p. 192; HENRY, List Pl. Formos. p. 56; FORBES et HEMSL. Ind. Fl. Sin. II. p. 4; MATSUM. in Tōkyō Bot Mag. XIV. p. 58; DIELS, Fl. Centr. Chin. p. 606; MATSUM. et HAYATA, Enum. Pl. Formos. p. 215.

Wahlenbergia agrestis A. DC. Prodr. VII. p. 434; BENTH. Fl. Hongk. p. 197.

Wahlenbergia marginata A. DC. Prodr. VII. p. 433; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 277.

Wahlenbergia dehiscens A. DC., *W. Sieberi* A. DC., *W. lavandulæfolia* A. DC. et *W. quadrifida* A. DC., ex CLARKE, in HOOK. f. Fl. Brit. Ind. III. p. 429.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 729); in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2063).

DISTRIB. South China and southern part of Japan; India throughout; Australia, and also found in New Zealand and South Africa.

Codonopsis WALL.

Codonopsis sp. nov.?

HAB. in monte Morrison, leg. T. KAWAKAMI et G. NAKAHARA, Nov. 1905.

Remarkable for small leaves and seeds.

Campanumœa BL.

Campanumœa axillaris OLIV. in HOOK. Ic. Plant. XVIII. t. 1775; FORBES et HEMSL. Ind. Fl. Sin. II. p. 7.

Codonopsis truncata WALL. DC. Prodr. VII. p. 423.

Cyclocodon truncatus HOOK. f. et THOMS. in Journ. Linn. Soc. II. p. 18.

HAB. Kagi: Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1780); Taitō: Bunshisekisha, leg. T. Kawakami et U. Mori, Dec. 1906, (No. 2162).

Distrib. The Loo-choo islands, westward to central and southern China, and Burma.

Campanumœa javanica Blume; DC. Prodr. VII. p. 423; Clarke, in Hook. f. Fl. Brit. Ind. III. p. 435; Forbes et Hemsl. Ind. Fl. Sin. II. p. 8.

Codonopsis cordata Hook. f. Bot. Mag. t. 5372.

Campanumœa japonica Maxim. in Mél. Biol. VI. p. 268.

Hab. Taitō: Rokurō, leg. G. Nakahara, Jan. 1906, (No. 752).

Distrib. Frequently found in Japan and central China; also in mountains of East Burma and Java.

Peracarpa Hook. f. et Thoms.

Peracarpa carnosa Hook. f. et Thoms. in Journ. Linn. Soc. II. p. 26; Clarke, in Hook. f. Fl. Brit. Ind. III. p. 437.

Peracarpa circæoides H. Feer, in Engl. Bot. Jahrb. XII. p. 621.

Campanula carnosa Wall. "in Roxb. Fl. Ind. II. p. 102"; DC. Prodr. VII. p. 474.

Campanula circæoides F. Schmidt. Reis. in Amur. pp. 154 et 222, t. III. fig. 14-19; Miq. in Ann. Mus. Bot. Lugd.-Bat. III. pp. 195 et 204; Franch. et Savat. Enum. Pl. Jap. I. p. 278; Forbes et Hemsl. Ind. Fl. Sin. II. p. 9.

Hab. in monte Morrison, leg. T. Kawakami, 1905; Tōzan, in montibus Morrison, leg. G. Nakahara, Oct. 1906.

Distrib. Japan, Manchuria, Saghalien; westward to central China as far as Himalaya.

Upon considering the various forms of this species, I am much inclined to think that the Indian *Peracarpa* is quite identical with the Japanese one, and in this Mr. T. Makino concurs.

Adenophora Fisch.

***Adenophora verticillata** Fisch.; DC. Prodr. VII. p. 492; Herder, Pl. Radd. IV.-1, p. 28; Franch. et Savat. Enum. Pl. Jap. II. p. 422; Hance, in Journ. Bot. (1885), p. 325; Forbes et Hemsl. Ind. Fl. Sin. II. p. 14.

Hab. Suizan, in montibus Morrison, ad 7702 ped. alt., Oct. 1905, (No. 650).

Distrib. Type: Japan and China; Manchuria to Dahuria.

var. **linearis** Hayata, v. n. Folia opposita vel 4-natim verticillata linearia 6 cm. longa 2 mm. lata subglabra integra.

Hab. Nantō: Mushasan, ad 7500 ped. alt., leg. T. Kawakami et U. Mori, Aug. 1906, (No. 1131).

Adenophora polymorpha Ledeb. var. **Lamarckii** Trautv.; Herder, Pl. Radd. IV.-1, p. 27.

Hab. in monte Morrison, ad 13000 ped. alt., leg. T. Kawakami et U. Mori, Oct. 1906, (No. 2266).

Adenophora polymorpha Ledeb. var. **coronopifolia** Trautv.; Herder, Pl. Radd. IV.-1, p. 27.

Hab. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. Nagasawa, Oct. 1905, (No. 733); in montibus Morrison, ad 8000–10000 ped. alt., leg. T. Kawakami et U. Mori, (Nos. 2290, 1942, 1943, et 2290.)

Distrib. Type: China, Japan, and North America.

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* It seems to me that the plant is extremely variable, although I am not sure about the habit of this plant in Formosa, as I have never stayed so long in the island as to study the living state of the plant. As I have observed in Japan, the range of the variation of this plant is very wide. In ordinary condition, the leaves are disposed in whorls, but on the branches shooting out from a stump after the stem is cut they are arranged alternately. Mr. T. Makino also refers to this point in Tōkyō Bot. Mag. XX. p. 39, where he expresses his opinion that *A. verticillata* Fisch. γ. *alternifolia* Franch. et Savat. is nothing but a sport of the type.

Vacciniaceæ.

Vaccinium LINN.

Vaccinium emarginatum HAYATA, sp. nov. Frutices ramosi cortice cinereo vestiti, ramulis glabris in exsiccato rufescentibus. Folia oblonga vel oblongo-obovata circ. 5 cm. longa 2 cm. lata margine integerrima revoluta apice emarginata basi sensim attenuata crasse coriacea nitida pallida subtus pallidiora breve petiolata, petiolis 4 mm. longis. Flores in racemos breves axillares folio 2-plo breviores fasciculatim dispositi, bracteis 2 subulatis. Calycis tubus globosus, limbo 5-lobo, lobis longe triangularibus. Corollæ ignotæ. Baccæ oblongo-globosæ 8 mm. longæ 10-loculares, loculis polyspermis. Semina minuta ovoidea 1½ mm. longa 1 mm. lata compressa angulata testa coriacea reticulata.

HAB. Tōzan, in monte Morrison, leg. G. NAKAHARA, Oct. 1906; eodem loco, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1947); Nantō: Mushasan, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (Nos. 71461, 1178 et 1143); Taitō: Iryokukakusha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2166).

Vaccinium Merrillianum HAYATA, sp. nov. (Pl. XXIV.). Frutices ramosissimi, ramulis ad innovationem squamatis rufescentibus hispido-tomentosis. Folia parvula approximata obovata circ. 8 mm. longa 5 mm. lata apice rotundata emarginata basi cuneata breve petiolata, petiolis 1 mm.–2 mm. longis, integerrima margine albo-lamelligera supra nitida in exsiccato profunde rugosa subtus lævia pallidiora crasse coriacea. Flores in racemos terminales dispositi. Calycis lobi 5, lobis late triangularibus. Baccæ globosæ, circ. 1 cm. in diametro æquantes 10-loculares, loculis oligospermis. Semina minuta obovoidea compressa testa coriacea minute reticulata 1½ mm. longa 1 mm. lata.

HAB. Seizan, in montibus Morrison, ad 11707 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 573); Tōzan, in isdem montibus, leg. G. NAKAHARA, Oct. 1906; in eodem monte, ad 10000 ped. alt., (No. 2286), et ad 6000 ped. alt., (No. 1730), leg. T. KAWAKAMI et U. MORI, Oct. 1906.

Ericaceæ.

Gaultheria LINN.

Gaultheria Cumingiana VIDAL, Phanerog. Cuming. p. 184, et Rev. Pl. Vascul. Filip. p. 170; HAYATA, in Tōkyō Bot. Mag. XX. p. 72.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 738); in eodem monte, ad 7500 ped. alt., (No. 1714), et ad 9000 ped. alt., (No. 1554), leg. T. KAWAKAMI et U. MORI, Nov. 1906.

DISTRIB. The Philippine islands.

Gaultheria Itōana HAYATA, (Pl. XXV.), in Tōkyō Bot. Mag. XX. p. 74. *Gaultheria repens* HAYATA, in Tōkyō Bot. Mag. XX. p. 18. Suffrutices decumbentes v. erecti 10-15 cm. alti sparce pubescentes. Folia coriacea brevissime petiolata oblonga 1 cm. longa 3 mm. lata utrinque acuta serrulata, supra glabra venis impressis subtus minute setulosa venis prominentibus. Flores parvi in racemos terminales dispositi cernui rosei? Recemi 2 cm. longi, pedicellis 6 mm.–7 mm. longis apicem versus glanduloso-ciliatis bracteatis bracteolatisque, bracteolis ovatis 2–3 mm. longis acutis marginibus scariosis alternis persistentibus. Calyx 5-partitus 2 mm. longus, lobis acutis. Corolla lata globosa urceolata 6 mm. in diametro æquans 4 mm. longa apice 5-loba, lobis brevissimis 0.5 mm. longis erectis recurvis. Stamina 10 basi tubi corollæ adherentia inclusa, filamentis glabris supra basin dilatis quam anthera longioribus, antheris 2-locularibus, loculis in tubos recurvos apice furcatos productis. Discus non conspicuus. Ovarum 5-loculare 5-lobum leviter pubescens, stylo columnari 4 mm. longo apice truncato. Calyx fructifer accrescens persistens carnosus depresso-globosus 6 mm.–7 mm. in diametro æquans. Capsulæ sparce pubescentes intra calycem inclusæ, loculicide 5-valvatæ polyspermæ. Semina minuta 0.5 mm. longa obtuse angulata, testis crustaceis minute reticulatis.

HAB. Seizan, in montibus Morrison, ad 11707 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 625); Tōzan, in isdem montibus, leg. G. NAKAHARA, Nov. 1906; in monte Morrison, ad 12000 ped. alt., Oct. 1906, (No. 2134), ad 9000 ped. alt., (No. 1727), et in montibus centralibus, Nov. 1906, (No. 1887), leg. T. KAWAKAMI et U. MORI.

As the original description is based on an imperfect specimen, it would not be superfluous if I have repeated the description, basing it upon the most perfect material.

Pieris DON.

Pieris formosa D. DON.; DC. Prodr. VII. p. 599; CLARKE, in HOOK. f. Fl. Brit Ind. III. p. 461; WIGHT, Ic. Pl. Ind. or. t. 1200; FORBES et HEMSL. Ind. Fl. Sin. II. p. 16; MATSUM. in Tōkyō Bot. Mag. XIV. p. 59; MATSUM. et HAYATA, Enum. Pl. Formos. p. 219.

HAB. Suizan, in monte Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 735); in eodem monte, ad 10000 ped alt., (Nos. 1890, 2136 et 2068), leg. T. KAWAKAMI et U. MORI, Nov. 1906; Taitō: Daironsan, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No.

2184); Nantō: Mushazan, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1145).

DISTRIB. South China; North and East India.

Pieris ovalifolia D. DON.; DC. Prodr. VII. p. 599; CLARKE, in HOOK. f. Fl. Brit. Ind. III. p. 460; FORBES et HEMSL. Ind. Fl. Sin. II. p. 17; DIELS, Fl. Centr. Chin. p. 515; MATSUM. et HAYATA, Enum. Pl. Formos. p. 219.

Andromeda ovalifolia WALL.; MAXIM. in Mél. Biol. VIII. p. 620; WIGHT, Ic. Pl. Ind. or. t. 1199.

Andromeda elliptica SIEB. et ZUCC. Fl. Jap. Fam. Nat. n. 433.

HAB. Nantō: Shojōdaizan, ad 6000 ped alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1124).

DISTRIB. Japan and China; common in North India, extending from Kashimir to the Khasia mountains and Burma.

Rhododendron LINN.

Rhododendron brachycarpum G. DON.; DC. Prodr. VII. p. 723; A. GRAY, Bot. Jap. p. 400; MAXIM. Rhod. As. or. p. 22.

HAB. in monte Morrison? leg. T. KAWAKAMI? 1907.

DISTRIB. Manchuria and Japan.

Rhododendron ellipticum MAXIM. in Mél. Biol. XII. p. 742; FORBES et HEMSL. Ind. Fl. Sin. II. p. 22; TASHIRO, in Tōkyō Bot. Mag. III. p. 201; MAKINO, in Tōkyō Bot. Mag. XVIII. p. 47, et Icones Floræ Japonic. I.-3, p. 15, t. 9.

HAB. Akō, ad 8000 ped. alt., leg. T. KAWAKAMI? 1907; Biōritsu: Bahozan, leg. T. KAWAKAMI et U. MORI, Juli. 1906, (No. 1112).

DISTRIB. South China and the Loo-choo islands.

The specimens here mentioned have not so long a bract as the Loo-choo plant which is excellently figured by MR. T. MAKINO in the Icones above cited.

Rhododendron Nakaharai Hayata, sp. nov.

Rhododendron serpyllifolium Hayata, in Tōkyō Bot. Mag. XX. p. 72.

Frutices humiles ramosi, ramis divaricantibus cinereo-fuscis novellis badio-strigosis. Folia in apices ramulorum conferta obovata vel oblonga 1 cm. longa 5 mm. lata apiculata basi attenuata breve petiolata supra adpresse strigosa subtus ad costas et margines dense longeque strigosa. Flores ad apices ramulorum lateralium brevissimorum 2–3–nati, pedunculis 7 mm. longis strigosis basi squamis ovatis apiculatis circumvallatis. Sepala obovata spathulata 4 mm. longa extus et margine longe strigoso-ciliata. Corolla campanulata $2\frac{1}{2}$ cm. longa 5-fida, lobis obovatis apice rotundatis tubo brevioribus. Stamina 10, corollam superantia, filamentis $2\frac{1}{2}$ cm. longis infra medium pilosiusculis, antheris obovoideis apice truncatis 2-porosis. Ovarium longe et dense setosum. Capsula ignota.

Hab. Monte Shichiri, leg. G. Nakahara, Juli. 1905.

In my paper above cited, I make an error of identifying the present plant with *R. serpyllifolium* Miq. In sterile specimens, the two come so closely that it is difficult to distinguish one from the other. On comparing flowers, I have found that both plants entirely differ from each other. The new species differs from the other in having much larger flowers, long hairy sepals, and in the number of stamens.

Rhododendron Oldhami Maxim. Rhod. As. or. p. 34; Forbes et Hemsl. Ind. Fl. Sin. II. p. 28; Henry, List Pl. Formos. p. 57; Matsum. et Hayata, Enum. Pl. Formos. p. 218.

Hab. Toroku: Kasōgi, leg. T. Kawakami et U. Mori, Nov. 1906, (No. 1821).

Distrib. An endemic plant.

Rhododendron Oldhami Maxim. var. **glandulosum** Hayata n. v.

Rami in totum pilis longis mollissimi atque pubibus teneribus brevioribus glandulosis badio-villosi. Folia crasse membranacea breve petiolata oblonga vel ovato-oblonga utrinque acuta apice mucrone longiusculo glanduloso apiculata obscure 7–8–nervia. Flores ad apices ramorum 3–4–nati basi squamis circumvallati 4-bracteati, bracteis lanceolatis vel ovatis 5 mm. longis pilosis vel glabris, pedunculis corollam ½ æquantibus glanduloso-villosis. Calyx 5-partitus, lobis lanceolatis longissime acuminatis 5 mm.–15 mm. longis. Corolla campanulato-infundibuliformis 4 cm. longa, tubo lobum in longitudine æquante. Stamina 10, corollam subæquantia, filamentis basin versus pubescentibus, antheris oblongis apice truncatis 2-porosis. Ovarium glanduloso-setosum.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA? Oct. 1905, (No. 668); in monte Morrison, ad 8000 ped. alt., (No. 2219), ad 9000 ped. alt., Oct. 1906, (No. 1807), et in montibus centralibus, ad 10000 ped. alt., Nov. 1906, (No. 1860), leg. T. KAWAKAMI et U. MORI.

The present plant is very like *R. Oldhami* MAXIM. The veins of leaves and the proportion of sepals to peduncles are the principal points in which the new variety is separated from the type.

Rhododendron pseudo-chrysanthum HAYATA, sp. nov. (Pl. XXVI.). Frutices humiles dichotome ramosi, cortice cinereo obtecti. Folia in tertium annum persistentia oblonga crasse apiculata basi attenuata 6 cm. longa 2 cm. lata glabra rigide coriacea, supra costis et venulis reticulatis profunde impressis, subtus ad costas prominentes floccoso-tomentosa cæterum glabra, margine integerrima leviter revoluta, petiolis 5–7 mm. longis. Gemma florifera terminalis strobiliformis, squamis multiseriatis imbricatis, exterioribus sensim brevioribus late ovatis apiculatis, interioribus sensim angustis, intimis linearibus. Flores ad apices ramorum corymbosi, pedunculis glanduloso-tomentosis circ. 2 cm. longis florem in longitudine æquantibus. Calycis lobi acuti. Corolla rotato-campanulata, lobis rotundatis leviter emarginatis. Stamina 10, antheris oblongis apice truncatis, filamentis inæqualibus basi leviter dilatis pubescentibus. Ovarium ovoideum 5-loculare 5-sulcatum pubescens, styo corollam vix superanti basi glanduloso-piloso declinato, stigmate capitato 5-lobo. Capsula oblonga 1 cm. longa vel longiora lignosa 5-locularis apice septicede dehiscens. Semina scobiformia 1½ mm. longa, nucleis parvis oblongis, testis reticulatis utrinque in appendiculam laceram productis.

HAB. in monte Morrison, ad 13000 ped. alt., (Nos. 2144 et 2240), leg. T. KAWAKAMI et U. MORI, Nov. 1906; Nantō: Mushazan, ad 6000 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1144).

Near *R. chrysanthum* PALL; but differs from it in having conspicuously 5-lobed calyces and apiculate leaves.

Pyrola LINN.

Pyrola morrisonensis HAYATA, n. n.

Pyrola elliptica NUTT. var. *morrisonensis* HAYATA, in Tōkyō Bot. Mag. XX. p. 18.

Folia late ovata 2 cm. longa totidem lata apice obtusa vel acuta basi truncata vel rotundata coriacea glanduloso-serrulata longe peteolata, petiolis 3–5 cm. longis supra impresso-reticulata subtus prominente venosa glaberrima. Racemi 15 cm. longi. Flores ignoti. Capsula depresso-globosa cernua 5–6 mm. in diametro æquans. Semina minutissima ¼ mm. longa angusta reticulata.

HAB. in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2273); in montibus centralibus ad

10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1896).

The present plant is originally described by myself as a variety of *P. elliptica* NUTT. On examining carefully the leaves with impressed veins and most minute seeds, I have thought it better to regard the plant as specifically distinct from that species.

Pyrola rotundifolia LINN. Sp. Pl. ed-2, p. 567; DC. Prodr. VII. p. 772; MAXIM. Mél. Biol. VIII. p. 622; CLARKE, in HOOK. f. Fl. Brit. Ind. III. p. 475; HANCE, in Journ. Bot. (1878) p. 109; FRANCHET, Pl. David. p. 197; FORBES et HEMSL. Ind. Fl. Sin. II. p. 33.

HAB. in monte Morrison, leg. T. KAWAKAMI, Oct. 1906.

DISTRIB. In the temperate and cold regions all around the North Hemisphere. Japan and China.

Diapensiaceæ.

Shortia TORR. et GR.

Shortia rotundifolia (MAXIM.) MAKINO, in Tōkyō Bot. Mag. XV. p. 149.

Schizocodon rotundifolius MAXIM. in Mél. Biol. XII. p. 743; FORBES et HEMSL. Ind. Fl. Sin. II. p. 34.

HAB. in monte Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2283); Nantō: Mushasan, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1150); Shintiku: Karesan, leg. T. KAWAKAMI et U. MORI, Juli. 1906, (No. 1422).

DISTRIB. The Loo-choo islands.

It is no matter of dispute that the plant should be referred to *Shortia*, as stated by Mr. T. MAKINO.

Primulaceæ.

Primula LINN.

Primula sp. Herbæ annuæ. Folia radicalia spathulata circ. 13 cm. longa 2½ cm. lata apice rotundata ad medium deorsum sensim attenuata basi leviter dilata sursum argute denticulata deorsum subintegra. Scapi elongati 30 cm. longi. Flores in verticillos 2–3 superpositos dispositi, bracteis linearibus, pedicellis 3 cm. longis. Capsula obconica 7 mm. longa.

HAB. in monte Morrison.

This very interesting, if not new, rare *Primula* is the only species found in the island. The plant resembles very much *P. Cockburniana* HEMSL. (in Gard. Chronic. May 27, 1905, p. 331 Fig. 137) in having two or three whorls of flowers towards the top of the scape.

Lysimachia LINN.

Sysimachia sikokiana MIQ. in Ann. Mus. Bot. Lugd.-Bat. III. p. 121, et Prol. Fl. Jap. p. 285; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 302; MATSUM. in Tōkyō Bot. Mag. XIV. p. 84; ENGL. Bot. Jahrb. VI. p. 64; FORBES et HEMSL. Ind. Fl. Sin. II. p. 57; MATSUM. et HAYATA, Enum. Pl. Formos. p. 223.

HAB. Taitō: Tōkeisha, leg. T. KAWAKAMI et U. MORI, Dec. 1905, (No. 1929).

DISTRIB. Japan.

Myrsineæ.

There is three distinct species belonging to *Ardisia* and two species to *Mæsa*; but they are not yet determined.

Styraceæ.

Symplocos LINN.

Symplocos confusa BRAND. in ENGL. Pfl-reich, IV.-242, Symploc. p. 88.

HAB. in monte Morrison, ad 7000 ped. alt., Oct. 1906, (No. 2006), et ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1785).

DISTRIB. The Philippine islands.

The above cited description of Mr. BRAND is not very clear and even wanting of any account about fruits. It is, therefore, most desirable to give some additional account about this plant.

Frutices? ramulis pubescentibus badio-fuscis. Folia ad apices ramorum approximata alterna breve petiolata ovata vel oblonga utrinque obtusa vel apice obtuse acuminata 7 cm. longa 3 cm. lata margine integra rarius obscure crenata supra costis impressis venulis obscuris, subtus prominentibus petiolis circ. 5 mm. longis intus basi hirtellis. Flores ad axillas foliorum ramulorum superiorum solitarii vel 2–3 racemoso-fasciculati breve pedicellati, bracteis minutis. Calyx per anthesin campanulatus basi pedicellum abeuns pubescens 3 mm. longus obscure 5-lobus, lobis latis truncatis. Corolla cylindraceo-campanulata 1 cm. longa 5-loba, lobis patentibus oblongis apice rotundatis crassiusculis. Stamina numerosa ∞-seriata corollæ tubo adnata, exterioribus longioribus filamentis complanatis apice abrupte angustis fere usque ad medium in tubum coalitis, antheris brevibus facie dorsoque minute papillosis, loculis parallelis longitudinaliter dehiscentibus. Ovarium apice pilosum semi-inferius 2-loculare, loculis 2-ovulatis, ovulis pendulis ex angulo superiore, stylo filiformi pilosissimo, stigmate capitato. Fructus (immaturi ?) carnosi cylindracei apice truncati.

Symplocos modesta BRAND, in ENGL. Pfl.-reich, IV. 242 Symploc. p. 66.

Symplocos myrtacea HEMSL. in FORBES et HEMSL. Ind. Fl. Sin. II. p. 73; MATSUM. et HAYATA, Enum. Pl. Formos. p. 230.

HAB. Taitō: Iryokukakusha, Dec. 1906, (No. 2151), in monte Morrison, ad 6500 ped. et ad 7000 ped. alt., (Nos. 2020 et 1712), leg. T. KAWAKAMI et U. MORI, Oct. 1906; Arizan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906.

DISTRIB. An endemic plant.

As the original description of Mr. BRAND seems to have been drawn from an imperfect specimen, a complete account relating to flowers is much desirable. The following description is, therefore, may properly be added here.

Frutices arborescentes glaberrimi, ramulis gracillimis. Folia chartacea oblonga longe cuspidato-acuminata vel abrupte ad acumen 2½ cm. longum attenuata 7 cm. longa 2 cm. lata basi cuneata, supra costis impressis venulis leviter prominentibus, subtus costis et venulis prominentibus. Racemi ad axillas foliorum inferiorum ramulorum novellorum solitarii laxiflori vel densiflori folio breviores gracillimi. Flores longe pedicellati, pedicellis 1–2 cm. longis basi pedicelli 2-bracteatis, bracteis parvis ciliatis triangularibus costatis. Calyx longe campanulatus glaber viridis 3 mm. longus, lobis 5 rotundatis margine ciliatis. Corolla patens 5½ mm. longa, tubo brevissimo, 5-loba, lobis ovatis apice rotundatis margine obscure ciliolatis imbricatis. Stamina numerosa ∞-seriata, exterioribus longioribus corollam excedentibus, ad basin corollæ adnata basi connata, filamentis subcomplanatis. Ovarium inferius 3-loculare, loculis 2-ovulatis, stylo filiformi, stagmate truncato. Fructus ignoti.

Symplocos morrisonicola HAYATA, sp. nov. (Pl. XXVII). Frutices ramosi, ramis pubescentibus cinereo-fuscis, ramulis novellis badio-villosis. Folia parviora alterna coriacea breve petiolata ovata vel oblonga 3½ cm. longa 1½ cm. lata apice aristato-acuta vel abrupte acuminata basi acuta vel rotundata margine obscure serrulata vel subintegra supra nitida venis et venulis prominentibus subtus obscure venosa, petiolis brevissimis 2 mm. longis. Racemi pauciflori axillares folio 2-plo brevioribes pubescentes, bracteis ovatis parvis ½ mm. longis. Calyx campanulatus 2 mm. longus, tubo ovario adnato, limbo 5–lobo, lobis imbricatis latis subtruncatis extus et margine pubescentibus. Corolla campanulata 5 mm. longa 5-loba, lobis ovatis apice rotundatis imbricatis. Stamina circ. 20, sub–2–seriata ad basin corollæ adnata exterioribus longioribus, filamentis complanatis basi connatis corollam excedentibus, antheris brevibus, loculis parallelis longitudinaliter dehiscentibus. Ovarium inferius 3-loculare, loculis 2-ovulatis, ovulis pendulis ex angulo superiore, stylo filiformi, stigmate capitato obscure 3-lobato. Fructus ignoti.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 737); Tōzan, in isdem montibus, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1702).

Near *S. modesta* BRAND; but differs from it in having shorter racemes, subentire leaves and pubescent branchlets.

Symplocos spicata ROXB. Fl. Ind. ed.-CAREY, II. p. 541; A. DC. Prodr. VIII. p. 254; BENTH. Fl. Hongk. p. 212; CLARKE, in HOOK. f. Fl. Brit. Ind. III. p. 573; FORBES. et HEMSL. Ind. Fl. Sin. II. p. 75; HENRY, List Pl. Formos. p. 58; MATSUM. in Tōkyō Bot. Mag. XV. p. 77; DIELS, Fl. Centr. Chin. p. 528; MATSUM. et HAYATA, Enum. Pl. Formos. p. 231.

Lodhra spicata MIERS, in Journ. LINN. Soc. XVII. p. 298.

HAB. Taichū: Kashigatani, leg. G. NAKAHARA, Feb. 1907.
DISTRIB. Japan, south central China, and North and East India.

Oleaceæ.

Osmanthus LOUR.

Osmanthus sp. nov.? Folia alterna rigide coriacea lanceolata 10 cm. longa 2½ cm. lata longe acuminata basi acuta petiolata, petiolis 1 cm. longis. Flores ad axillas foliorum circ. 20-fasciculati, fasciculis squamis 2–3 ovatis acutis coriaceis 5 mm. longis instructis, pedicellis 1 cm. longis. Calyx brevis late 4-lobus. Corolla subcampanulata 4 mm. longa 4 loba, lobis 2½ mm. longis late ovatis subclausis. Stamina 2 ad medium tubi corollæ affixa, antheris suborbicularibus, connectivis latis apiculatis. Ovarium conicum, stylo ovario longiore, stigmate peltato crasso 2-lobo. Fructus ignoti.

HAB. Tōzan, in monte Morrison, leg. G. NAKAHARA, Oct. 1906.

Osmanthus sp. nov.? Folia alterna oblonga 5 cm. longa 2 cm. lata apice aristato-acuta basi obtusa rigide coriacea supra (exsiccato) reticulato-rugosa subtus obscure venosa, petiolata, petiolis 1 cm. longis. Flores ad axillas foliorum circ. 10 fasciculati, fasciculis squamis 2–3 late ovatis minutis 1 mm. longis instructis, pedicellis 1 cm. longis. Calyx brevis 1 mm. longus 4 lobus, lobis late ovatis. Corolla late campanulata 4 mm. longa, tubo brevissimo, limbo 4 lobo lobis late ovatis obtusis. Stamina 2 supra basin corollæ affixa, filamentis brevibus, antheris oblongis apiculatis. Ovarium conicum, stylo brevi, stigmate conico 2-lobo. Fructus ignoti.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2003).

Asclepiadeæ.

Dischidia R. Br.

Dischidia formosana Maxim. in Mél. Biol. IX. p. 822; Forbes et Hemsl. Ind. Fl. Sin. II. p. 116; Matsum. et Hayata, Enum. Pl. Formos. p. 240.

Hab. Tappansha, ad 3138 ped. alt., leg. S. Nagasawa, Oct. 1905, (No. 581).

Distrib. An endemic plant.

Loganiaceæ.

Logania R. Br.

Logania dentata Hayata, n. n. (Pl. XXVIII.).

Nertera dentata Elmer, in Leafl. Philipp. Bot. I.–1, p. 15.

Herbæ humiles repentes in totum hispidae, ramis ad nodos ascendentibus 7-8 cm. longis superiore proliferis. Corpora ad axillas foliorum solitaria squamis teretibus glabris crassiusculis ∞-seriatis instructa 3–4 mm. longa stipitata, stipitibus ½ cm.-1 cm. longis. Folia opposita petiolata late ovata vel orbicularia circ. 10 mm. longa 13 mm. lata apice obtusa basi rotundata truncata margine serrata, serraturis crassiuscule mucronatis, supra setuloso-hispida subtus sparce hispida, petiolis lamina 2-plo brevioribus 6 mm. longis, internodiis circ. 1 cm. longis, stipulis 0. Flores parvissimi 3 mm. longi axillares solitarii breve pedicellati, pedicellis 1 mm. longis glabratis. Calyx 3 mm. longus 4-partitus, segmentis lanceolatis extus glabratis, intus et margine sericeo-setulosis crassiusculis. Corollæ tubus urceolatus, limbo 4-lobo, lobis patentibus rotundatis.

Stamina 4 infra faucem tubi affixa, filamentis brevibus, antheris oblongis. Ovarium globosum 2-lobum stylum subæquans 2-loculare, loculis ∞-ovulatis. Capsula globosa 6 mm. in diametro æquans rubra 4 valvis dehiscens. Semina numerosa ovoidea $\frac{1}{2}$ mm. longa lævia minute reticulata.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 639); in isdem montibus, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 8000 ped. alt., Oct. 1906, (No. 1803), et in montibus centralibus, ad 10000 ped. alt., Nov. 1906, (No. 1847), leg. T. KAWAKAMI et U. MORI.

It is not without hesitation that I have identified the present plant with ELMER's *Nertera dentata*, transferring it to the genus *Logania*. There is a little doubt about this being similar to Mr. ELMER's. In his diagnosis, the fruits are described as follows: "berries shining vermilion red, 2 lin. in diameter; globose, frequently with a short persistent style...." But, in my specimens, they are decidedly capsules, 5 mm. in diameter, opening with two valves, each valve being afterward divided into two. After considering his description and my specimens, I have wondered if he had not made an error of regarding the fruits as "berries." Mr. E. D. MERRILL affirmed me that my plant is exactly the same as the Philippine plant. In superficial observation, it appears very much to be a rubiaceous plant as Mr. ELMER writes in his paper. Nevertheless, the plant has superior ovaries, by which character it should not be regarded as belonging to Rubiaceæ, but must be referred to Loganiaceæ. This species is greatly different from any other species of *Logania* known to us, and it is perhaps the smallest of all the plants belonging to this genus. The plant agrees with the generic characters of *Logania* in its floral structure, inflorescence and habit, and it is somewhat like the

Australian *L. pusilla* R. Br. It also bears some resemblance to *Polypremum* Linn., but differs from the latter in the absence of glands and in having entirely superior ovaries. This new *Logania* is very remarkable in its prostrate habit and in having strikingly deformed flowers. The occurrence of this Australian genus in Formosa and the Philippines is exceptionally interesting. So far as I am aware, no representative of this genus has ever been known from any other regions on the North Hemisphere.*

Gentianaceæ.

Crawfurdia Wall.

Crawfurdia fasciculata Wall.; DC. Prodr. IX. p. 120; Clarke, in Hook. f. Fl. Brit. Ind. IV. p. 107; S. Moore, in Journ. Bot. (1875) p. 231; Bot. Mag. t. 4838; Forbes et Hemsl. Ind. Fl. Sin. II. p. 122; Henry, List Pl. Formos. p. 61; Diels, Fl. Centr. Chin. p. 538; Matsum. et Hayata, Enum. Pl. Formos. p. 243.

Crawfurdia japonica Sieb. et Zucc. Fl. Jap. Fam. Nat. II. p. 36, n. 546; Franch. et Savat. Enum. Pl. Jap. I. p.324; Maxim. in Mél. Biol. IX. p. 399; S. Moore, in Journ. Bot. (1880), p. 4.

Golowninia japonica Maxim. "in Bull. Acad. Imp. Sc. Pétersb. IV. p. 251."

Hab. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. Nagasawa, Oct. 1905, (No. 660).

Distrib. Japan, China, and the mountains of North East India.

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* After completing this manuscript, I am informed by Mr. E. D. Merrill who have just returned to Manila from his trip, that he thinks the Philippine plant *Nertera dentata* Elmer to be referable to *Hemiphragma heterophylla* Wall. of the Himalayas. The Formosan species in my hands does, however, not agree with the description of that genus. In *Hemiphragma*, the corolla is 5-lobed, and stamens are affixed to the base of the tube, while in my plant, corolla is 4-lobed and stamens are affixed to the middle of the tube. Accordingly, the Formosan plant is, I think, not identical with the Himalayan species, though the latter may be the same as the Philippine one. It remains still questionable whether the Formosan plant should be referred to *Logania* or *Hemiphragma*.

Gentiana LINN.

Gentiana (§ *Chondrophylla*) **cæspitosa** HAYATA, sp. nov. Herbæ humillimæ perennes rigidiusculæ glabræ cæspitosæ, caulibus ascendentibus 4 cm. altis simplicibus multifoliatis. Folia approximata opposita plicata leviter recurva prominente costata ovata 5 mm. longa 2½ mm. lata aristato-acuta basi truncata, vaginis interpetiolaribus 1 mm. longis hyalinis, crasse cartilagineæ margine albo-lamellata apicem versus obscure basin argute denticulata. Flores terminales solitarii 17 mm. longi. Calyx campanulato-tubuliformis 7 mm. longus 5-lobus, lobis 3 mm. longis angustis acutis crassiusculis, sinibus inter lobos acutis. Corolla tubulosa campanulata 17 mm. longa 5-loba, lobis 3 mm. longis late ovatis, sinibus inter lobos plicatis, appendiculatis triangularibus. Stamina 5 inclusa, filamentis ad medium adnatis. Capsulæ compresso-obovatæ 6 mm. longæ ad suturas 2-valvis dehiscentes, valvis margine denticulatis, stipitibus longis capsulam in longitudine 2-plo superantibus, stylis persistentibus 2-fidis 2 mm. longis spiraliter recurvis. Semina oblonga angulata 1 mm. longa longitudinaliter reticulata.

HAB. in monte Morrison, ad 12500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2242).

Very near *G. micans* CLARKE (in HOOK. f. Fl. Brit. Ind. IV. p. 112); but differs from it in having undivided folds of corollas.

Gentiana (§ *Pneumonanthe*) **fasciculata** HAYATA, sp. nov. Herbæ humiles glabræ, caulibus repentibus apice ascendentibus gracilibus 8–10 cm. longis, foliis basin versus remote apicem versus approximate dispositis. Folia caulina remota opposita sessilia uninervia lanceolato-linearia obtusa 1.5 cm.–2 cm. longa 3 mm. lata vaginis interpetiolaribus 3 mm. longis; folia floralia ad basin fasciculi florum conferta folio caulino conformia sed 3-plo majora. Flores terminales sessiles erecti 5-fasciculati ebracteati. Calyx tubuliformis 12 mm. longus 5-lobatus, lobis linearibus 3 mm. longis, sinibus latis truncatis. Corolla campanulato-tubuliformis 2.5 cm. longa, fauce tubi nuda 5-loba, lobis patentibus contortis rotundato-acutis, sinibus plicatis, appendiculis 0. Stamina 5 tubo corollæ affixa inclusa; antheris linearibus, connectivis apiculatis. Ovarium stipitatum 1-loculare apice in stylum brevem pubescens 2-divisum attenuatum, stigmatibus lamellatis revolutis. Capsulæ oblongæ cum stylo stipiteque 22 mm. longæ, stipite capsula breviore 6 mm. longo, ad suturas 2-valvis revolutis dehiscentes. Semina ovoidea compressiuscula $\frac{2}{3}$ mm. longa elegante reticulata.

HAB. Seizan, in montibus Morrison, ad 11707 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 624); ibidem, leg. T. KAWAKAMI et G. NAKAHARA.

Gentiana (§ *Chondrophylla*) **flavescens** HAYATA, sp. nov. Herbæ annuæ minute scabriusculæ vel glabratæ, caulibus gracilibus. Folia opposita angusto-obovata 8-mm. longa $2\frac{1}{2}$ mm. lata apice aristato-acuta basi confluentia, vaginis interpetiolaribus 1 mm. longis, margine obscure albo-lamellata integra basin versus minute ciliato-denticulata crassiuscula. Flores ad apices ramorum solitarii. Calyx campanulatus $4\frac{1}{2}$ mm. longus 5-lobatus, lobis $1\frac{1}{2}$ mm. longis cuspidato-acuminatis. Corolla tubuloso-campanulata 12 mm. longa, lobis primariis 5, $2\frac{1}{2}$ mm. longis triangularibus, lobis secundariis 5 ad sinus plicatos lobo primario æquilongis cuspidato-acutis tenuissimis. Stamina 5 tubo corollæ affixa, filamentis ad medium adnatis, antheris oblongis 1 mm. longis basi sagittatis apice emarginatis. Capsulæ obovatæ 6 mm. longæ longe stipitatæ corollam excedentes, stipitibus 12 mm. longis, stylis linearibus 2-divisis complanatis pilosiusculis spiraliter revolutis. Semina oblonga angulata $\frac{2}{3}$ mm. longa minute longitudinaliter reticulato-striata.

Hab. Suizan, in montibus Morrison, ad 7702 ped. alt., (No. 646), et Ganzan, in isdem montibus, ad 9141 ped. alt., leg. S. Nagasawa, Oct. 1905.

Gentiana formosana Hayata, in Matsum. et Hayata, Enum. Pl. Formos. p. 242.

Hab. in monte Shichiseitonzan, leg. B. Hayata, Aug. 1900; ibidem, leg. G. Nakahara, 1905. (No. 5.)

Gentiana humilis Stev.; Clarke, in Hook. f. Fl. Brit. Ind. IV. p. 111. *Gentiana aquatica* Pall. Fl. Ross. II. t. 97, fig. 2 (non Linn.).

Hab. Tōzan, montibus Morrison, leg. S. Nagasawa, Nov. 1905.

Distrib. Western Tibet.

Gentiana (§ *Chondrophylla*) **tenuissima** Hayata, sp. nov. Herbæ humillimæ 6 cm. altæ glabræ tenues. Folia radicalia conferta lanceolato-ovata 1 cm. longa 5 mm. lata apice acuta basi abrupte angusta sessilia margine minutissime denticulata; folia caulina paucissima; folia floralia radicali conformia minora. Flores paniculato-cymosi. Calyx tubuliformis 3 mm. longus 5-lobatus, lobis circ. 1 mm. longis late ovatis aristato-acutis, sinibus inter lobos latis truncatis. Corolla tubuloso-campanulata 5 mm. longa 5-lobata, lobis 1 mm. longis rotundato-acutis, sinibus plicatis obscure lobatis. Stamina 5 tubo corollæ affixa inclusa, filamentis supra medium liberis. Ovarium stipitatum oblongo-obovoideum cum stipitibus 3 mm. longum, stylo brevi $\frac{1}{2}$ mm. longo stigmate 2-lamellato recurvo. Capsulæ obovatæ 3 mm. longæ longe stipitatæ, stipitibus capsulam 2-plo in longitudine superantibus, ad suturas 2-valvis dehiscentes, valvis patento-revolutis marginibus minute serratis. Semina oblonga ½ mm. longa longitudinaliter reticulata utrinque attenuata.

HAB. Taitō: Gozenjō, leg. T. KAWAKAMI.

Neer *G. aquatica* LINN. and *G. delicata* HANCE, but differs from them in having much smaller flowers and reticulated seeds.

Gentiana scabrida HAYATA, sp. nov. Herbæ annuæ paucifoliatæ scabriusculæ, caulibus 20 cm. longis atropurpureis pauciramosis. Folia radicalia caulino conformina oblongo-lanceolata 11 mm. longa 4 mm. lata apice aristato-acuta, vaginis interpetiolaribus 2 mm. longis, margine et ad costam subtus scaberrima albo-lamellata, supra minute scaberrima subtus præter costas glabra. Flores ad apices ramorum solitarii pedunculati, pedunculis ½ cm. longis. Calyx campanulatus obscure 5-costatus, costis scaberrimis, 1 cm. longus 5-lobatus, lobis spathulatis supra basin leviter constrictis basi paullo dilatis 5 mm. longis 2 mm. latis 1-costatis, costis serrulatis, margine albo-lamellatis intus minute scaberrimis. Corolla campanulata 2 cm. longa 5-lobata, lobis late ovatis 4 mm. longis aristato-acutis, sinibus plicatis, appendiculis triangularibus 3 mm. longis. Stamina 5, supra medium tubi corollæ affixa, filamentis ad insertionem dorso dilatis, antheris angustis basi sagittatis apice obtusis. Capsulæ ovatæ 7 mm. longæ longe stipitatæ, stipitibus 20 mm. longis capsulam 3-plo superantibus, stigmatibus lamellatis revolutis. Semina oblonga 1 mm. longa longitudinaliter minute reticulato-striata.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905, (Nos. 701 et 702); in monte Morrison, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2275).

Swertia LINN.

Swertia alata HAYATA, sp. nov. Herbæ annuæ 2–3 ped. altæ glabræ, caulibus tetragonis tetrapteris, alis 2 mm. latis. Folia opposita sessilia membranacea oblongo-lanceolata 7 cm. longa 2 cm. lata apice breve obtuse acuminata basi angusta ad insertionem dilata 6 mm. lata trinervia supra nervis impressis subtus prominentibus. Flores paniculato-racemosi, ramis oppositis, pedicellis oppositis per anthesin ½ cm. longis bracteis lanceolatis. Calyx 4-partitus, lobis lanceolatis 5 mm. longis trinerviis. Corollæ tubus brevis, limbo 4-partito, lobis laciniatis oblongis 7 mm. longis apice obscure serratis prope basin foveolatis, foveolis glandulosis margine ciliato-fimbriatis supra foveolam squamulis fimbriatis. Stamina 4 basi corollæ affixa, filamentis complanato-filiformibus basi dilatis, antheris subsagittatis apiculatis. Ovarium ovoideum apice attenuatum, stylo subnullo, stigmate 2-lamellato, lobis brevissimis latisque leviter recurvis. Capsulæ oblongo-ovatæ circ. 1 cm. longæ ad suturas 2-valvis dehiscentes. Semina parvissima ½ mm. longa compressa ovata reticulato-muricata.

Hab. Arizan, in montibus Morrison, leg. G. Nakahara, Oct. 1906.

Near *S. tetraptera* Maxim., but differs from it in having mostly 3-nerved and sessile leaves and paniculate racemes; from *S. pulchella* Hance, in having prominent wings and much smaller petals.

Swertia sp. Herbæ basi suffruticosæ circ. 1 ped. altæ. Folia oblonga 3 cm. longa apice obtusa basi angusta ad petiolum attenuata. Flores paniculato-racemosi. Capsulæ 6 mm. longæ.

Hab. Ganzan, in montibus Morrison, ad 9140 ped. alt., leg. S. Nagasawa, Oct. 1905, (No. 642); Tōzan, in isdem montibus, leg. G. Nakahara, Nov. 1906.

Hydrophyllaceæ.

Ellisiophyllum MAXIM.

Ellisiophyllum pinnatum MAKINO, in Tōkyō Bot. Mag. XX. p. 92.

Hornemannia pinnata BENTH. in DC. Prodr. X. p. 428.

Sibthorpia pinnata BENTH. in BENTH. et HOOK. f. Gen. Pl. II. p. 959; HOOK. f. Fl. Brit. Ind. IV. p. 288.

Moseleya pinnata HEMSL. in HOOK. Ic. Pl. XXVI. t. 2592.

Ellisiophyllum reptans MAXIM. in Mél. Biol. VIII. p. 18; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 329.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1781).

DISTRIB. Japan, China and the Philippines, westward to the Himalayas.

As stated by Mr. T. MAKINO, the plant should properly be called *E. pinnatum* MAKINO, assuming that *Moseleya pinnata* HEMSL. is the same as *Ellisiophyllum reptans* MAXIM.; for *Ellisiophyllum* is older name than *Moseleya*, and the specific name *pinnata* is much so than *reptans*.

Boragineæ.

Cynoglossum LINN.

Cynoglossum micranthum DESF.; DC. Prodr. X. p. 149; MAXIM. in Mél. Biol. VIII. p. 555; MIQ. Fl. Ind. Bat. II. p. 931; FRANCHET, Pl. David. p. 215; CLARKE, in HOOK. f. Fl. Brit. Ind. IV. p. 156; FORBES et HEMSL. Ind. Fl. Sin. II. p. 150; HENRY, List Pl. Formos. p. 63; MATSUM. in Tōkyō Bot. Mag. XII. p. 108; DIELS, Fl. Centr. Chin. p. 546; MATSUM. et HAYATA, Enum. Pl. Formos. p. 257.

Cynoglossum racemosum ROXB. Fl. Ind. I. ed.-CAREY, p. 456.

Cynoglossum furcatum WALL.; WIGHT, Ic. Pl. Ind. or. t. 1395.

HAB. Kagi: Shakkōshō, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1746).

DISTRIB. South China; widely spread in India Malay and also found in East Africa.

Trigonotis STEV.

Trigonotis formosana HAYATA, sp. nov. Herbæ perennes pilosæ scaberrimæ, caulibus ascendentibus 10 cm. longis stoloniferis. Folia radicalia et inferiora longe petiolata, petiolis 5 cm. longis laminam æquantibus setuloso-pilosis, laminis oblongis vel spathulatis 7 cm. longis 2½—3 cm. latis apice truncato- vel retuso-mucronatis basi acuminatis membranaceis crassiusculis margine integris repandis supra pilis setulosis brevissimis scaberrimis subtus hispidulis pallidioribus, venis transversis primariis utrinque obscure 5–6 ad margines arcuatis 2–3–seriatim anastomosantibus. Folia superiora inferioribus conformia sed minora. Flores in cymas scorpioidales ramosas vel simplices racemosas elongatas dispositi, breve pedicellati pedicellis 1 mm. longis. Calyx 5-fidus, lobis obovatis 1½ mm. longis obtusis intus et extus pilosiusculis, fructifer vix auctus. Corolla rotata 2½ mm. longa, tubo brevi 1 mm. longo fauce squamis brevibus crassis subfornicatis subclausis instructo, lobis 5 imbricatis patentibus late orbicularibus basi breve angustis 1½ mm. longis. Stamina 5 supra medium tubi affixa inclusa, filamentis brevibus, antheris oblongis obtusis. Ovarium depresso-globosum ¼ mm. longum ½ mm. latum 4-lobatum, lobis distinctis, stylo brevi ½ mm. longo, stigmate capitato. Nuculæ 4, obpyramidales ad angulas costatæ 1 mm. longæ vel vix longiores erectæ læves facie superiore planæ truncatæ pauce setulosæ, cæterum glabræ.

HAB. Sanchōki, ad 4000 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 724); Kagi: Kishirei, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1969) ; Taitō : Dakunsha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2230).

Solanaceæ

Solanum LINN.

Solanum sp. Herbæ tenues scandentes pubescentes ad nodos radicantes. Folia ovata 5 cm. longa 3 cm. lata petiolata, petiolis lamina 2-plo brevioribus, apice obtusa acuta basi rotundata subito attenuata ad petiolum abeuntia membranacea utrinque ad costas pubescentia cæterum glabra. Flores axillares longe pedunculati, solitarii, pedunculis petiolum vix superantibus. Bacca globosa 1 cm. in diametro aequans.

HAB. Nantō : Rakurakusha, leg. G. NAKAHARA, Aug. 1905. (No. 466) ; Kagi : Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1737).

Very interesting plant, on account of its intermediate form between *Solanum* and *Capsicum*. It may constitute a new genus when the floral structures are fully known.

Scrophularineæ.

Scrophularia LINN.

Scrophularia alata A. GRAY, Bot. Jap. p. 401 ; MIQ. Prol. Fl. Jap. p. 47 ; DIELS, Fl. Centr. Chin. p. 565 ; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 342.

var. **duplicato-serrata** MIQ. Prol. Fl. Jap. p. 47 ; FRANCH. et SAVAT. Enum. Pl. Jap. I. 343.

HAB. in monte Morrison, leg. G. NAKAHARA, Nov. 1905.

DISTRIB. Type : Central China and Japan.

Mazus LOUR.

Mazus rugosus LOUR. Fl. Cochinch. ed.-WILLD. p. 468; BENTH. in DC. Prodr. X. p. 375, et Fl. Hongk. p. 247; MAXIM. Prim. Fl. Amur. pp. 205 et 475, et in Mél. Biol. IX. p. 402; FORBES et HEMSL. Ind. Fl. Sin. II. p. 183; FRANCHET, Pl. David. p. 222; HENRY, List Pl. Formos. p. 67; DIELS, Fl. Centr. Chin. p. 566; PALIBIN, Conspect. Fl. Koreæ, II. p. 20; MATSUM. et HAYATA, Enum. Pl. Formos. p. 275.

Mazus vandellioides HANCE, in WALP. Ann. III. p. 193.

Lindernia japonica THUNB. Fl. Jap. p. 253.

Mazus japonica O. KUNTZE, "Revis. Gen. Pl. II. (1891) p. 462"; MAKINO, in Tōkyō Bot. Mag. XIV. p. 170;

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906.

DISTRIB. South China and Japan; Afghanistan to Manchuria; and also in the Malay archipelago.

Here we do not follow O. KUNTZE, for *M. rugosa* LOUR. is too commonly used to be suppressed.

Torenia LINN.

Torenia peduncularis BENTH.; HOOK. f. Fl. Brit. Ind. IV. p. 276; FORBES et HEMSL. Ind. Fl. Sin. II. p. 188; HENRY, List Pl. Formos. p. 67. DIELS, Fl. Centr. Chin. p. 567; MATSUM. et HAYATA, Enum. Pl. Formos. p. 278.

Torenia edentula BENTH. in DC. Prodr. X. p. 410; Bot. Mag. t. 4229.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 670).

DISTRIB. South central China, India and Malay.

Bonnaya LINK. et OTTO.

Bonnaya veronicæfolia SPRENG.; BENTH. in DC. Prodr. X. p. 421, et Fl. Hongk. p. 252; MIQ. Fl. Ind. Bat. II. p. 696; MAXIM. in Mél. Biol. IX. p. 421; HOOK. f. Fl. Brit. Ind. IV. p. 285; WIGHT, Ic. Pl. Ind. or. t. 1411;

FORBES et HEMSL. Ind. Fl. Sin. II. p. 192; HENRY, List Pl. Formos. p. 68; MATSUM. et HAYATA, Enum. Pl. Formos. p. 281.

HAB. Tappansha, ad 3139 ped. alt., leg. S. NAGASAWA, Oct, 1905, (No. 718).

DISTRIB. South China, India throughout, Ceylon and Malay.

Rehmannia LIBOSCH.

Rehmannia Oldhami HEMSL. in Ann. Bot. IX. p. 154, et in FORBES et HEMSL. Ind. Fl. Sin. II. p. 194; HENRY, List Pl. Formos. p. 68; MATSUM. et HAYATA, Enum. Pl. Formos. p. 282.

HAB. Sanchōki, ad 4000 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 723); Kagi: Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1745).

DISTRIB. An endemic plant.

Veronica LINN.

Veronica morrisonicola HAYATA, sp. nov. (Pl. XXIX). Herbæ validæ basi suffruticosæ repentes ad nodos radicantes, ramis ascendentibus 10–20 cm. longis præter inflorescentiam simplicibus hispidulis demum glabratis. Folia opposita spathulato-lanceolata sessilia 2 cm. longa 6 mm. lata apice acuta basi sensim attenuata margine sursum serrata deorsum integra subtus costis prominentibus venulis inconspicuis. Racemi pubescentes ad axillas foliorum superiorum ramorum siti, longe pedunculati ramos excedentes, pedunculis 5 cm. longis partem florigeram æquantibus, bracteis angustis 4 mm. longis pedicello vix longioribus. Calyx 5-partitus, lobis angustis acutis 4 mm. longis. Corolla rotata circ. 5 mm. longa, tubo brevissimo limbo 4–lobato, lobo postico majore late ovato obtuso, lobis lateralibus mediocribus, lobo antico minore. Stamina 2 tubo ad latere lobi postici affixa, filamentis exsertis, antheris loculis divergentibus obtusis apice confluentibus. Ovarium pilosum. Capsulæ compressæ apice emarginatæ bisulcatæ 6 mm. longæ totidem latæ loculicide dehiscentes, valvis columna placentifera adherentibus. Semina numerosa ovata 1 mm. longa facie interna plano-cymliformi affixa. dorso rugulosa.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., (Nos. 704 et 633), Seizan, in isdem montibus, ad 11579 ped. alt., (No. 634), et Suizan, in isdem montibus, ad 7702 ped. alt., Oct. 1905, (No. 736), leg. S. NAGASAWA; in monte Morrison, ad 9000 ped. alt.. Oct. 1906, (No. 2278), et in montibus centralibus, ad 10000 ped. alt.. leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2213).

Very like *V. serpyllifolia* LINN.; but differs from that species in having long pedunculate racemes and very small bracts. The habit of this plant is like that of *V. Onoei* FRANCH. et SAVAT., but differs from it in having obovate lanceolate leaves.

Veronica spuria LINN. Sp. Pl. ed.-2, p. 13; LEDEB. Fl. Ross. III. p. 236 (var.); FORBES et HEMSL. Ind. Fl. Sin. II. p. 200; PALIBIN, Conspect. Fl. Koreæ, II. p. 21; DIELS, Fl. Centr. Chin. p. 267; HAYATA, in Tōkyō Bot. Mag. XX. p. 72.

Veronica angustifolia FISCH.; HANCE, in Journ. Linn. Soc. XIII. p. 84.

Veronica paniculata LINN.; BENTH. in DC. Prodr. X. p. 465; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 348.

HAB. in monte Morrison, ad 8500 ped. alt., (Nos. 1809, 2080 et 1811), et eodem monte, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2295); Tikuzan, ad 150 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 764).

DISTRIB. Japan to central Asia, and westward to central Europe.

Sopubia HAM.

Sopubia formosana HAYATA, sp. nov. Herbæ annuæ erectæ circ.

30 cm. altæ pubescentes siccitate nigricantes, caulibus ramosis vel simplicibus tetragonis sulcatis. Folia opposita sessilia oblonga 2 cm. longa 8 mm. lata dentata deorsum integra apice acuta vel obtusa basi acuta vel cuneata supra exsiccato nigricantia subtus pallidiora distincte nervosa. Flores ad apices ramorum dense subspicati, ad axillas bractearum solitarii, bracteis lanceolatis dentatis calycem 2-plo superantibus, pedicellis 1 mm. longis 2-bracteolatis, bracteolis linearibus calycem æquantibus. Calyx campanulato-semiorbiculatus 7 mm. longus 10-nervatus breviter 5-lobus, lobis valvatis triangularibus acuminatis. Corolla ignota. Stamina 4 didynamia subinclusa: 2 longiora, antheris majoribus coherentibus, filamentis longe barbatis; 2 breviora, antheris parvioribus liberis, filamentis glabris; loculis antherarum omnibus ovatis basi muticis. Stylus apice stigmatoso-incrassatus sublinguiformis obtusus. Capsulæ depresso-globosæ 5 mm. in diametro æquantes apice retusæ, loculicide dehiscentes, valvis demum 2-fidis columnam placentiferam liberantibus. Semina numerosa minutissima angusta 1 mm. longa truncata testa laxiuscula.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (Nos. 661 et 673); Kagi: Kōdenshō, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1739).

DISTRIB. An allied species *S. trifida* HAM. occurs in India and Ceylon; and is also found in Kwangtung in the opposit continent.

Near *S trifida* HAM.; but differs from it in having ovato-lanceolate leaves.

Phtheirospermum BUNGE.

Phtheirospermum chinense BUNGE; BENTH. in DC. Prodr. X. p. 391; MAXIM. Prim. Fl. Amur. p. 208; HANCE, "in Journ. Bot. (1882), p. 292"; FRANCHET, Pl. David. p. 225; FORBES et HEMSL. Ind. Fl. Sin. II. p. 204; DIELS, Fl. Centr. Chin. p. 570.

Phtheirospermum japonicum KANITZ, "Anthoph. Jap. p. 12"; MAKINO, in Tōkyō Bot. Mag. XV. p. 72.

Gerardia japonica THUNB. Fl. Jap. p. 251, et Icn. Pl. Jap. Decas-5, t. X; WILLD. Sp. Pl. III. p. 224: BENTH. in DC. Prodr. X. p. 519.

HAB. Toroku: Tōhozan, (No. 2082); Taitō: Dakunsha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2169).

DISTRIB. Japan and China northward to Manchuria; and also in North America.

Here we do not follow Mr. T. MAKINO, for *P. chinense* BUNGE is too generally used to be supressed.

Euphrasia LINN.

Euphrasia borneensis STAPF in "Trans. Linn. Soc. II. 4, (1794) 210, t. 16, f. 1-16"; MERRILL, in Philipp. Journ. Scie. I. Suppl. Bot. p. 236.

HAB. Nanto: Mushazan, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1129).

DISTRIB. The Philippine islands and also in Borneo.

Euphrasia petiolaris WETTST. Monogr. Gatt. Euphras. p. 199, t. IV. Figs. 321-325, et t. XI. Fig. 8.

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906; in monte Morrison, ad 8000 ped. (No. 1728), et eodem monte, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI. Oct. 1906. (Nos. 1894 et 2274).

DISTRIB. in Himalaya.

Orobanchaceæ.

Orobanche LINN.

Orobanche cœrulescens STEPH.; WILLD. Sp. Pl. III. p. 349; DC. Prodr. XI. p. 34; LEDEB. Fl. Ross. III. p. 322; PALIBIN. Conspect. Fl.

Koreæ, II. p. 22 ; Biblioth. Bot. IV. p. 138 ; MATSUM. et HAYATA, Enum. Pl. Formos. p. 285.

HAB. in montibus Morrison, ad 9000 ped. alt., (No. 2238), et ad 8000 ped. alt., (No. 2071), leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. Asia, Europe, and North America.

Gesneraceæ.

Lysionotus DON.

Lysionotus pauciflorus MAXIM. in Mél. Biol. IX. p. 366 ; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 327 ; S. MOORE, in Journ. Bot. (1875) p. 231 ; CLARKE, in DC. Monogr. Phanerog. V. p. 59 ; FORBES et HEMSL. Ind. Fl. Sin. II. p. 225 ; HENRY, List Pl. Formos. p. 68 ; MATSUM. et HAYATA, Enum. Pl. Formos. p. 287.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 556) ; Arizan, in isdem montibus, leg. G. NAKAHARA, Oct. 1906 ; in monte Morrison, ad 6000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1719).

DISTRIB. Japan and central China.

Rhynchoglossum BLUME.

Rhynchoglossum obliquum BLUME ; DC. Prodr. IX. p. 274 ; CLARKE, in HOOK. f. Fl. Brit. Ind. IV. p. 367.

Rhynchoglossum Blumei DC. Prodr. IX. p. 274.

HAB. Kōdenshō : ad 2623 ped. alt., leg. S. NAGASAWA, Oct. 1906, (No. 745) ; Kagi : Kishirei, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1777).

DISTRIB. The Philippine islands throughout, and the other islands of the Malay archipelago.

Chirita HAM.

Chirita anachorata HANCE; DC. in DC. Monogr. Phanerog. V.–1, p. 115; MAXIM. in Mél. Biol. IX. p. 370; FORBES et HEMSL. Ind. Fl. Sin. II. p. 231; HENRY, List Pl. Formos. p. 68; MATSUM. et HAYATA, Enum. Pl. Formos. p. 288.

HAB. in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2048).

DISTRIB. South China.

Conandron SIEB. et ZUCC.

Conandron ramondioides SIEB. et ZUCC. Fl. Jap. Fam. Nat. II. p. 730, t. 3, f. 1; MIQ. Prol. Fl. Jap. p. 55; MAXIM. Mél. Biol. IX. p. 370; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 328; Bot. Mag. t. 6484.

HAB. Biyōritsu: Banahōzan, leg. T. KAWAKAMI et U. MORI, Juli. 1906, (No. 1093).

DISTRIB. Japan.

Acanthaceæ.

Strobilanthes BLUME.

Strobilanthes flaccidifolius NEES, in DC. Prodr. XI. p. 194; T. ANDERS. in Journ. Linn. Soc. IX. p. 481; HANCE, in Journ. Linn. Soc. XIII. p. 116; CLARKE, in HOOK. f. Fl. Brit. Ind. IV. p. 468; Bot. Mag. t. 6947; FORBES et HEMSL. Ind. Fl. Sin. II. p. 239; MATSUM. et HAYATA, Enum. Pl. Formos. p. 291.

Strobilanthes Championi T. ANDERS.; BENTH. Fl. Hongk. p. 261.

Goldfussia Cusia NEES, in DC. Prodr. XI. p. 175.

HAB. Kōdenshō, ad 2623 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 727); in monte Morrison, ad 5000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2061).

DISTRIB. South China, Burma and eastern India.

Codonacanthus NEES.

Codonacanthus pauciflorus NEES, in DC. Prodr. XI. p. 103; CLARKE, in HOOK. f. Fl. Brit. Ind. IV. p. 500; BENTH. Fl. Hongk. p. 267; FORBES et HEMSL. Ind. Fl. Sin. II. p. 244; HENRY, List Pl. Formos. p. 69; MATSUM. et HAYATA, Enum. Pl. Formos. p. 292.

HAB. Tappansha, ad 3138 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 787); Taitō: Inikufukusha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2156).

DISTRIB. South China and eastern India.

Justicia LINN.

Justicia procumbens LINN.; HANCE, in Journ. Linn. Soc. XIII. p. 116; CLARKE, in HOOK. f. Fl. Brit. Ind. IV. p. 539; FORBES et HEMSL. Ind. Fl. Sin. II. p. 246; HENRY, List Pl. Formos. p. 69; DIELS, Fl. Centr. Chin. p. 579; MATSUM. et HAYATA, Enum. Pl. Formos. p. 293.

Rostellularia procumbens NEES, in DC. Prodr. XI. p. 371; BENTH. Fl. Hongk. p. 265; Wight, Ic. Pl. Ind. or. t. 1539; FRANCHET, Pl. David. p. 230.

HAB. in monte Morrison, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1886).

DISTRIB. China and Japan; Malay, India, Ceylon, and also in Australia.

Rungia NEES.

Rungia parviflora NEES, in DC. Prodr. XI. p. 469; CLARKE, in HOOK. f. Fl. Brit. Ind. IV. p. 550; FORBES et HEMSL. Ind. Fl. Sin. II. p. 247.

var. **pectinata** CLARKE, in HOOK. f. Fl. Brit. Ind. IV. p. 550; MATSUM. et HAYATA, Enum. Pl. Formos. p. 294.

Rungia pectinata NEES, in DC. Prodr. XI. p. 470; WIGHT. Ic. Pl. Ind. or. t. 1547; T. ANDERS. in Journ. Linn. Soc. IX. p. 517.

Rungia polygonoides NEES, in DC. Prodr. XI. p 471.

HAB. Kagi: Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1967).

DISTRIB. South China; East and South India and Ceylon.

Hypœstes R. BR.

Hypœstes purpurea R. BR.; NEES, in DC. Prodr. XI. p. 509; MIQ. Fl. Ind. Bat. II. p. 851; BENTH. Fl. Hongk. p. 265; FORBES et HEMSL. Ind. Fl. Sin. II. p. 249; HENRY, List Pl. Formos. p. 70; MATSUM. et HAYATA, Enum. Pl. Formos. p. 295.

HAB. Tappansha, ad 3138 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 577); Kagi: Kishirei, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1768).

DISTRIB. South China and in the Philippine islands.

Labiatæ

Mesona BLUME.

Mesona elegans HAYATA, in MATSUM. et HAYATA, Enum. Pl. Formos. p. 306, t. 16.

HAB. in monte Morrison, ad 6000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. An endemic plant.

Mesona procumbens HEMSL. in Ann. Bot. IX. p. 155; HENRY, List Pl. Formos. p. 72; MATSUM. et HAYATA, Enum. Pl. Formos. p. 306.

HAB. Tappansha, ad 3138 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 777); Taitō: Tabari, leg. G. NAKAHARA, Jan. 1906, (No. 736); in monte Morrison, ad 6000 ped. alt., (No. 2211), et ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2212).

DISTRIB. An endemic plant.

Origanum LINN.

Origanum vulgare LINN. Sp. Pl. ed.-2, p. 824; BENTH. in DC. Prodr. XII. p. 193 (varietates); HANCE, in Journ. Bot. (1880) p. 300; FRANCHET, Pl. David. p. 235; HOOK. f. Fl. Brit. Ind. IV. p. 648; FORBES et HEMSL. Ind. Fl. Sin. II. p. 282; DIELS, Fl. Centr. Chin. p. 559.

Origanum heracleoticum et *O. creticum* LOUR. Fl. Cochinch. ed-.WILLD. p. 453.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 632); in monte Morrison, ad 8000 ped. alt., (No. 1957), et eodem monte, ad 11000 ped. alt., (No. 2292), leg. T. KAWAKAMI et U. MORI.

DISTRIB. Central China to Manchuria; from North Africa to West Europe.

This species has dimorphic flowers; the larger flowers are bisexual, and the smaller ones are female which are one third long as the perfect flowers.

Salvia LINN.

Salvia scapiformis HANCE, in Journ. Bot. (1885) p. 368; Bot. Mag. t. 6980; FORBES et HEMSL. Ind. Fl. Sin. II. p. 287; HENRY, List Pl. Formos. p. 73; DIELS, Fl. Centr. Chin. p. 559.

HAB. Taitō: Dakunsha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 1934).

var. **pinnata** HAYATA, in MATSUM. et HAYATA, Enum. Pl. Formos. p. 312, t. 17.

HAB. Suizan, in monte Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 663); in montibus centralibus, ad 9000 ped. alt., (No. 2194), et Toroku: Gunkei, (No. 1820), leg. T. KAWAKAMI et U. MORI, Nov. 1906.

forma **hirsuta**. caules basi subglabri, inflorescentiæ hirsutæ. Folia hirsuta.

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Nov. 1906; Taitō: Shūkoranzan, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1884).

forma **gracilis.** Folia minora, foliolis rhomboideis acutis dentatis, dentibus acutis vel obtusis.

HAB. Tōzan, et Arizan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2050).

DISTRIB. Type: Central China.

Scutellaria LINN.

Scutellaria luzonica ROLFE, in Journ. Linn. Soc. XXI. p. 315; FORBES et HEMSL. Ind. Fl. Sin. II. p. 296; HENRY, List Pl. Formos. p. 73; MATSUM. et HAYATA, Enum. Pl. Formos. p. 314.

HAB. in montibus centralibus, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1862).

DISTRIB. The Philippine islands.

Anisomeles R. BR.

Anisomeles ovata R. BR. AIT. Hort. Kew. ed.-2. II. p. 364; MIQ. Fl. Ind. Bat. II. p. 975; BENTH. in DC. Prodr. XII. p. 455, et Fl. Hongk. p. 278; HOOK. f. Fl. Brit. Ind. IV. p. 672; FORBES et HEMSL. Ind. Fl. Sin. II. p. 299; HENRY, List Pl. Formos. p. 73; MATSUM. et HAYATA, Enum. Pl. Formos. p. 315.

HAB. Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1770).

DISTRIB. South China, tropical and subtropical India.

Leucas R. BR.

Leucas javanica BENTH. in DC. Prodr. XII. p. 528; FORBES et HEMSL. Ind. Fl. Sin. II. p. 304; MATSUM. et HAYATA, Enum. Pl. Formos. p. 317.

HAB. Taitō: Hinansha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 1835).

DISTRIB. Java and the Philippines.

Dicotyledones

Monochlamydeæ

Polygonaceæ

Polygonum LINN.

Polygonum biconvexum HAYATA, sp. nov. Herbæ graciles decumbentes 15 cm.–20 cm. altæ inæqualiter angulatæ retrorsum aculeatæ. Folia alterna hastato-triloba 3 cm. longa basi 2.5 cm. lata apice caudato-acuminata pilis setulosis atque pilis stellatis brevissimis sparce tecta margine integra dense setulosis, petiolis lamina 2-plo brevioribus aculeolatis, ochreis truncatis hirsutis ciliatis. Flores ignoti. Achænia biconvexa, ovata 3½ mm. longa 2½ mm. lata lævia.

HAB. in monte Morrison, leg. G. NAKAHARA, 1905.

This is very near *P. Thunbergii* S. et Z.; differs from it in having biconvex seeds.

Polygonum chinense LINN. Sp. Pl. ed.-2, p. 520; MEISN. in DC. Prodr. XIV. p. 130; MIQ. Fl. Ind. Bat. I.-1, p. 1008; LINN. Fl. Cochinch. ed.-WILLD. p. 297; HOOK. f. Fl. Brit. Ind. V. p. 44; BENTH. Fl. Hongk. p. 289; ROXB. Fl. Ind. ed.-CAREY, p. 289; Bot. Mag. t. 5238; WIGHT. Ic. Pl. Ind. or. t. 1806; HOOK. et ARN. Bot. Beech. Voy. p. 208; FRANCH. et SAVAT. Enum. Pl. Formos. I. p. 398, et II. p. 480; FORBES et HEMSL. Ind. Fl. Sin. II. p. 335; DIELS, Fl. Centr. Chin. p. 314; MATSUM. et HAYATA, Enum. Pl. Formos. p. 334.

Polygonum sinense HOOK. et ARN. Bot. Beech. Voy. p. 269.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S.

NAGASAWA, Oct. 1905, (No. 653); in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1789).

DISTRIB. Japan, south central China, the Philippines, India throughout, and Malay to Ceylon.

Polygonum cuspidatum SIEB. et ZUCC. Fl. Jap. Fam. Nat. n. 731; MEISN. in DC. Prodr. XIV. p. 136; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 402, et II. p. 481; S. MOORE, in Journ. Bot. (1875) p. 231; FRANCHET, Pl. David. p. 256; Bot. Mag. t. 6503; FORBES. et HEMSL. Ind. Fl. Sin. II. p. 336.

HAB. Suizan, in monte Morrison, ad 11707 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 575); in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2071).

DISTRIB. Japan and North China.

Polygonum minutum HAYATA, sp. nov. (Pl. XXX.). Herbæ perennes? minutæ scandentes ramosæ, caulibus glabratis. Folia parva ovato-triangularia 4½ mm. longa 4 mm. lata apice acuta vel obtusa utraque pagine breve setulosa integra, petiolis 1 mm.–2 mm. longis, ochreis 1½ mm. longis setulosis laceratis. Flores 3–4 conferti, pedicellis 1 mm. longis, bracteolis hyalinis connatis 2–3–fidis. Perianthium late campanulatum 1⅓ mm. latum tubo brevissimo, limbo 5 lobato, lobis ovatis obtusis glandulis sparce punctatis, discis basi perianthii connatis. Stamina 8 subæqualia. Achænia ovato-trigona ad angulas prominente costata 2½ mm. longa 1½ mm. lata, styli ramis brevissimis.

HAB. in monte Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2267).

Polygonum morrisonense HAYATA, sp. nov. (Pl. XXXI.). Herbæ annuæ? caulibus erectis vel adscendentibus pauciramosis ad nodos retrorsum pilosis cæterum glabris, ochreis pilosis truncatis 7 mm. longis. Folia obcuneata 4 cm. longa 2 cm. lata apice cuneato-acuminata basi abrupte angusta ad petiolum 1 cm. longum attenuata rarius infra medium profunde sinuata, folia superiora subsessilia obcuneato-cordata, margine albo-lamellata sursum integra deorsum ciliata utraque pagine glandulis subpellucidis punctata. Flores dense spicato-capitati, capitulis subovoideis 8 mm. longis 6 mm. latis ad apices ramorum vel axillas foliorum superiorum solitariis pedunculatis, pedunculis 1 cm. longis apice glanduloso-hispidulis, bracteis scariosis ovato-acutis 3½ mm. longis 2 mm. latis. Flores 2 ad axillas bractearum siti, bracteolis subconnatis hyalinis, pedicellis brevissimis. Perianthium urceolato-campanulatum 4 mm. longum corollinum, 5-lobum segmentis subæqualibus oblongis 2½ mm. longis. Stamina 8, inæqualia; 3 longiora prope basin perianthii affixa, filamentis basi utrinque glandulosis; 5 breviora tubo perianthii affixa, filamentis basi non-glandulosis. Styli rami 3. Achænia ovato-globosa subtrigona vix 2 mm. longa.

HAB. in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2074).

Somewhat near *P. alatum* HAM.; but differs from it in having no involucral leaf; from *P. miorocephalum* DON, in having no auricled leaf.

Polygonum Posumbu HAM.; MIQ. Fl. Ind. Bat. I. p. 1000; HOOK. f. Fl. Brit. Ind. V. p. 38; FRANCHET. Pl. David. p. 258; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 394, et II. p. 473; FORBES et HEMSL. Ind. Fl. Sin. II. p. 345; HENRY, List Pl. Formos. p. 76. DIELS, Fl. Centr. Chin. p. 312; MATSUM. et HAYATA, Enum. Pl. Formos. p. 340.

HAB. in monte Morrison, ad 8500 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1872).

DISTRIB. Japan and China; Java to East Himalaya and Khasia.

Aristolochiaceæ.

Asarum LINN.

Asarum macranthum HOOK. f. in Bot. Mag. t. 7022; HEMSL. in Gard. Chron. 3rd. Ser. VII. p. 421; FORBES et HEMSL. Ind. Fl. Sin. II. p. 359; MATSUM. et HAYATA, Enum. Pl. Formos. p. 343.

HAB. Taitō: Daironkōsha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2186).

DISTRIB. An endemic plant.

Piperaceæ.

Piper LINN.

Piper Futokadsura SIEB. et ZUCC. Fl. Jap. Fam. Nat. II. p. 231, n. 811; MIQ. in Ann. Mus. Bot. Lugd.-Bat. III. p. 139; C.DC. in DC. Prodr. XVI-1, p. 346; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 443; MAXIM. in Mél. Biol. XII. p. 532; FORBES et HEMSL. Ind. Fl. Sin. II. p. 365; HENRY, List Pl. Formos. p. 77; MATSUM. et HAYATA, Enum. Pl. Formos. p. 346.

HAB. Taitō: Tōkeisha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 1910).

DISTRIB. Japan.

Peperomia R. et PAV.

Peperomia dindygulensis MIQ.; C.DC. in DC. Prodr. XVI.-1, p. 442; HOOK. f. Fl. Brit Ind. V. p. 98; WIGHT, Ic. Pl. Ind. or. t. 1921; FORBES et HEMSL. Ind. Fl. Sin. II. p. 366; HENRY, List Pl. Formos. p. 77; MATSUM. et HAYATA, Enum. Pl. Formos. p. 346.

Hab. Suizan, in montibus Morrison, leg. S. Nagasawa, Oct. 1905, (No. 558); in monte Morrison, ad 6000 ped. alt., leg. T. Kawakami et U. Mori, Oct. 1906, (No. 2045).

Distrib. South China, and the western peninsula of India.

Peperomia Nakaharai Hayata, sp. nov. (XXXII.). Herbæ perennes ramosissimæ glabræ procumbentes, ramis ascendentibus 8–9 cm. longis glaberrimis. Folia opposita rarius 3–4 verticillata cuneato-obovata apice profunde emarginata basi obtusa, circ. 1 cm. longa 6 mm. lata integerrima crassiuscula obscure marginata subtus pallidiora. Flores ♀ spicati, spicis clavatim incrassatis $1\frac{1}{2}$ cm. longis. Ovarium sessile ovoideum, bracteis peltatis glanduloso-punctatis.

Hab. in monte Arizan, in montibus Morrison, leg. G. Nakahara, Nov. 1906; in monte Morrison, ad 8000 ped. alt., T. Kawakami et U. Mori, Oct. 1906, (No. 1997).

Peperomia reflexa A. Dietr.; Miq. Fl. Ind. Bat. I.-2, p. 436; Wight, Ic. Pl. Ind. or. t. 1923; Hook. f. Fl. Brit. Ind. V. p. 99; DC. Prodr. XVI.-1, p. 451; Forbes et Hemsl. Ind. Fl. Sin. II. p. 366; Matsum. et Hayata, Enum. Pl. Formos. p. 347.

Hab. in monte Morrison, ad 6000 ped. alt., leg. T. Kawakami et U. Mori, Oct. 1906, (No. 2033).

Distrib. Subtropical Asia, Africa, America, and Australia, South China.

Chloranthaceæ.

Chloranthus Sw.

Chlorantus serratus Roem. et Schult.; Solms, in DC. Prodr. XVI.-1. p. 475; Miq. Fl. Ind. Bat. I.-1. p. 802; Franch. et Savat. Enum.

Pl. Jap. I. p. 444; FORBES et HEMSL. Ind. Fl. Sin. II. p. 369; DIELS, Fl. Centr. Chin. p. 273; MATSUM. et HAYATA, Enum. Pl. Formos. p. 348.

HAB. Kagi: Kōdenshō, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1774).

DISTRIB. Japan and central China.

Laurineæ.

Cinnamomum BURMAN.

Cinnamomum Camphora NEES et EBERM.; MEISN. in DC. Prodr. XV.-1. p. 24; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 411; MIQ. Fl. Ind. Bat. I.-1, p. 892; FORBES et HEMSL. Ind. Fl. Sin. II. p. 371; DIELS, Fl. Centr. Chin. p. 347; MATSUM. et HAYATA, Enum. Pl. Formos. p. 349.

Laurus Camphora LINN. Sp. Pl. ed.-2, p. 528; THUNB. Fl. Jap. p. 172.

HAB. in montibus Morrison.

DISTRIB. Japan and China.

Proteaceæ.

Helicia LOUR.

Helicia formosana HEMSL. in Ann. Bot. IX. p. 156, et in FORBES et HEMSL. Ind. Fl. Sin. II. p. 394; HENRY, List Pl. Formos. p. 80; MATSUM. et HAYATA, Enum. Pl. Formos. p. 354.

forma **subintegra,** foliis subintegris.

HAB. Kōshun; Botansha, leg. G. NAKAHARA, 1905.

forma **acuminata,** foliis apice abrupte acuminatis.

HAB. Nantō: Shichikwaikutsuzan, leg. N. KONISHI, (No. 39); in monte Morrison, ad 6500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2013).

DISTRIB. An endemic plant.

Thymelæaceæ.

Daphne LINN.

Daphne Championi BENTH. Fl. Hongk. p. 296; FORBES et HEMSL. Ind. Fl. Sin. II. p. 395; MATSUM. et HAYATA, Enum. Pl. Formos. p. 355.

HAB. Taitō: Shinrōzan, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 1836).

DISTRIB. Hongkong.

Stellera LINN.

Stellera Chamæjasme LINN.; MEISN. in DC. Prodr. XIV. p. 549; MAXIM. Ind. Fl. Pek. in Prim. Fl. Amur. p. 476; HOOK. f. Fl. Brit. Ind. V. p. 196; "LEDEB. Ic. Pl. Ross. t. 374"; FORBES et HEMSL. Ind. Fl. Sin. II. p. 401.

HAB. in monte Morrison, ad 8000 ped. alt., Oct. 1906, (No. 1708), et eodem monte, ad 7500 ped. alt., (No. 1999), leg. T. KAWAKAMI et U. MORI.

DISTRIB. Caucasus through central Asia eastward to North India, Malay, and central China.

Elæagnaceæ.

Elæagnus LINN.

Elæagnus umbellata THUNB. Fl. Jap. p. 66, t. 14; SCHLECHT. in DC. Prodr. XIV. p. 614; MAXIM. in Mél. Biol. VII. p. 559; HOOK. f. Fl. Brit Ind. V. p. 201; S. MOORE, in Journ. Bot. (1878), p. 138; FORBES et HEMSL. Ind. Fl. Sin. II. p. 404.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 675); Arizan et Tōzan, in isdem montibus, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 9000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 1952 et 1891); in montibus centralibus, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1856).

DISTRIB. China to Japan, North India westward to Afghanistan.

Loranthaceæ.

Loranthus LINN.

Loranthus Yadoriki SIEB. in SIEB. et ZUCC. Fl. Jap. Fam. Nat. n. 398; FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 481; FORBES et HEMSL. Ind. Fl. Sin. II. p. 407; MAXIM. in Mél. Biol. IX. p. 609; HENRY, List Pl. Formos. p. 80; DIELS, Fl. Centr. Chin. p. 305; MATSUM. et HAYATA, Enum. Pl. Formos. p. 357.

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 7500 ped. alt., (Nos. 2038, 1786 et 2007), leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. Japan and south central China.

Loranthus Owatarii HAYATA, in MATSUM. et HAYATA, Enum. Pl. Formos. p. 357.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1948): in montibus centralibus, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 1865).

Viscum LINN.

Viscum articulatum BURM.; MIQ. Fl. Ind. Bat. I.-1, p. 806; DC. Prodr. IV. p. 284; HOOK. f. Fl. Brit. Ind. V. p. 226; FORBES et HEMSL. Ind. Fl. Sin. II. p. 407; HENRY, List Pl. Formos. p. 81; DIELS, Fl. Centr. Chin. p. 305; MATSUM. et HAYATA, Enum Pl. Formos. p. 358.

HAB. Suizan, in montibus Morrison, ad 7700 ped. alt., leg. S.

NAGASAWA, Oct. 1905, (No. 751): in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2014).

DISTRIB. Widely spread in India and Malay.

Viscum orientale WILLD. var. **multinerve** HAYATA, in Tōkyō Bot. Mag. XX. p. 72.

HAB. Jitsugetsutan, leg. G. NAKAHARA, Aug. 1905.

DISTRIB. Type: Java.

Balanophoreæ.

Balanophora FORST.

Balanophora spicata HAYATA, sp. nov. (Pl. XXXIII). Planta ♀ gracilis 7 cm. alta. Pedunculus per partem inferiorem bracteatus, bracteis sæpius suboppositis. Inflorescentia ovata 1½ cm. longa. Flores ♀ brevissime stipitati circa stipites graciles spadicellorum capitatorum apiculatorum dispositi, stylis gracillimis quam ovario circ. 2-plo longioribus. Planta ♂ graciliuscula circ. 14 cm. alta. Pedunculus infra medium bracteatus, bracteis sub-oppositis. Inflorescentia incrassata circ. 5 cm. longa. Flores ♂ sessiles laxiuscule spicati. Perianthium crassiusculum, segmentis 6 inæqualibus, postice et antice latissimis apice truncatis, lateralibus ovatis obtusis minoribus. Antherarum loculi circ. 15, 2-seriatim dispositi.

HAB. Kishirei, ad 4000 ped. alt., leg. S. NAGASAWA, Nov. 1905.

The present plant is very like *B. laxiflora* HEMSL. in its habit; but differs from it in having multi-locular anthers and in the segments of perianths.

Balanophora parvior HAYATA, sp. nov. (Pl. XXXIV). Planta ♀ parvior 7 cm. alta. Pedunculus per totam fere longitudinem bracteatus, bracteis ovatis. Inflorescentia oblongo-cylindracea 3½ cm. longa. Flores ♀ brevissime stipitati, circa stipites graciles spadicellorum clavato-capitatorum dispositi, stylis gracillimis quam ovario 3-plo longioribus. Planta ♂ gracilis circ. 14 cm. alta. Pedunculus fere per totam partem bracteatus, bracteis suboppositis. Inflorescentia incrassata circ. 4 cm. longa. Flores ♂ sessiles, laxiuscule spicati. Perianthium crassiusculum, segmentis 6 inæqualibus, postice et antice majoribus ovatis truncatis, lateralibus parvioribus, oblongo-ovatis acutis. Antherarum loculi circ. 20, irregulariter dispositi.

HAB. in monte Morrison, ad 6000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2227).

This differs from the preceding species in the shape of the segments and the cells of the anthers.

Euphorbiaceæ.

Buxus LINN.

Buxus sempervirens LINN.; MUELL. ARG. in DC. Prodr. XVI.-I, p. 18; HOOK. f. Fl. Brit. Ind. V. p. 267; BENTH. Fl. Hongk. p. 315, (excl. syn. *B. sinensis* LINK.); FORBES et HEMSL. Ind. Fl. Sin. II. p. 418.

Buxus japonica MUELL. ARG. in DC. Prodr. XVI.-1. p. 20; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 428.

Buxus sempervirens LINN. var. *japonica* MAKINO, in Tōkyō Bot. Mag. IX. p. 281, et XV. p. 169; HAYATA, Revis. Euphorb. et Bux. Jap. in Journ. Scie. Coll. XX.-3. p. 82.

HAB. loco non indicata.

DISTRIB. This plant extends from Japan and China through North Africa and Europe to the Canary islands.

The plant presents a great range of variation. Although my plant does not exactly agree with this species, still I think it may be regarded as a form of it.

Glochidion FORST.

Glochidion formosanum HAYATA, in Journ. Scie. Coll. XX.-3. p. 20, t. 2, G.; MATSUM. et HAYATA, Enum. Pl. Formos. p. 360.

HAB. loco non indicato.

Glochidion zeylanicum A. JUSS.; MUELL. ARG. in Linnæa, XXXII. p. 60, et in DC. Prodr. XV.-2. p. 281; HOOK. f. Fl. Brit. Ind. V. p. 311 MATSUM. et HAYATA, Enum. Pl. Formos. p. 360.

DISTRIB. Malay archipelago and Deccan Peninsula.

Aleurites FORST.

Aleurites cordata STEUD.; MUELL. ARG. in DC. Prodr. XV.-2, p. 724; FORBES et HEMSL. Ind. Fl. Sin. II. p. 433; DIELS, Fl. Centr. Chin. p. 430; HAYATA, in Journ. Scie. Coll. XX.-3, p. 55; MATSUM. et HAYATA, Enum. Pl. Formos. p. 366.

HAB. Kagi: Tappansha, leg. T. KAWAKAMI et U. Mori, Oct. 1906, (No. 1757).

DISTRIB. Japan and south central China.

Mercurialis LINN.

Mercurialis leiocarpa SIEB. et ZUCC. Fl. Jap. Fam. Nat. I. p. 145, n. 78; MUELL. ARG. in DC. Prodr. XV.-2, p. 795; MIQ. Prol. Fl. Jap. p. 291; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 425; FORBES et HEMSL. Ind. Fl. Sin. II. p. 436; DIELS, Fl. Centr. Chin. p. 428; PALIBIN, Conspect. Fl. Koreæ, II. p. 43; HAYATA, in Journ. Scie. Coll. XX.-3, p. 38, t. 3, D; MATSUM. et HAYATA, Enum. Pl. Formos. p. 363.

HAB. Tōzan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906; in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1716).

DISTRIB. Japan and south central China.

Mallotus LOUR.

Mallotus cochinchinensis LOUR. Fl. Cochinch. ed.-WILLD. p. 635; MUELL. ARG. in Linnaea, XXXIV. p. 189; HOOK. f. Fl. Brit. Ind. V. p. 430; FORBES et HEMSL. Ind. Fl. Sin. II. p. 439; HENRY, List Pl. Formos. p. 84; HAYATA, in Journ. Scie. Coll. XX.-3, p. 45, t. 3, J; MATSUM. et HAYATA, Enum. Pl. Formos. p. 364.

HAB. Tappansha, ad 3138 ped. alt., leg. S. NAGASAWA, Oct. 1906, (No. 713).

DISTRIB. South China. Malay peninsula and archipelago.

Urticaceæ.

Fatoua GAUD.

Fatoua pilosa GAUD.; BUREAU, in DC. Prodr. XVII. p. 256; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 434; FORBES et HEMSL. Ind. Fl. Sin. II. p. 454.

Fatoua japonica BLUME, in Muss. Bot. Lugd.-Bat. II.-1, p. 38; HANCE, in Journ. Bot. (1878) p. 232.

HAB. in monte Morrison, ad 9000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2065).

DISTRIB. Japan, South China, and Malay archipelago.

Morus LINN.

Morus alba LINN. Sp. Pl. ed.-2. p. 1398; BUREAU, in DC. Prodr. XVII. p. 238; FRANCHET, Pl. David. p. 270; HOOK. f. Fl. Brit. Ind. V. p. 492; FORBES. et HEMSL. Ind. Fl. Sin. II. p. 455; DIELS, Fl. Centr. Chin. p. 297; PALIBIN, Conspect. Fl. Koreæ, II. p. 45; MATSUM. et HAYATA, Enum. Pl. Formos. p. 373.

HAB. Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1778); Taichū: Kashigatani, leg. G. NAKAHARA. Feb. 1907.

DISTRIB. China and Japan: temperate and subtropical Asia.

[*]*Ficus* LINN.

The plants belonging to this genus are very few in the flora of the hilly regions. The specimens brought to me are all wanting of receptacles and therefore they are not determinable.

Urtica LINN.

Urtica Thunbergiana SIEB. in SIEB. et ZUCC. Fl. Jap. Fam. Nat. II. p. 214, n. 756; DC. Prodr. XVI.–1. p. 55; FORBES et HEMSL. Ind. Fl. Sin. II. p. 472; DIELS, Fl. Centr. Chin. p. 301; MATSUM. et HAYATA, Enum. Pl. Formos. p. 390.

Urtica dioica THUNB. Fl. Jap. p. 69.

HAB. Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1747).

DISTRIB. Japan and central China.

Girardinia GAUD.

Girardinia heterophylla DCNE.; DC. Prodr. XVI.–1, p. 100; BLUME, Mus. Bot. Lugd.-Bat. II. p. 158; HOOK. f. Fl. Brit. Ind. V. p. 550.

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[*] The following *Ficus* was found on the sea shore in the island of Kōtō. As the plant is very remarkable for the smallest size of receptacles and the full description of the species was not previously made, I take this occasion to give the following description of the plant.

Ficus vaccinioides HEMSL. et KING. (Pl. XXXV.), in Ann. Bot. Gard. Calc. I.–2, p. 126, t. 159, A; FORBES et HEMSL. Ind. Fl. Sin. II. p. 468; MATSUM. et HAYATA, Enum. Pl. Formos. p. 379. Suffrutices. Rami reptantes vel scandentes graciles ferrugineo-tomentoso-pubescentes remote foliati teretes. Folia subrhombea vel obovata obtusa vel acuta basi rotunda vel subcordata $1\frac{1}{5}$–2 cm. longa 1 cm.–8 mm. lata 1–nervia, venis primariis lateralibus utrinque 3–4 sub angulo 60° egressis, venulis reticulatis inconspicuis, margine minute serrulata, petiolis 2–3 mm. longis, stipulis subulatis 1–nerviis caducis scariosis ferrugineis 3 mm. longis. Receptacula axillaria solitaria breve stipitata globosa apice leviter contracta basi rotundata rarius leviter attenuata hirsuta, ore rotundo concavo extus bracteis latioribus clausis et intus bracteis triangularibus vel lanceolatis instructo, basi bracteis 3–4 late ovatis acutis. Fl. ♂: sessiles, perianthia 4–5 partita, segmentis linearibus, purpureo-fuscentibus; stamina 3–4, filamentis brevioribus. Fl. galliferi sæpe longe pedicellati; ovarium stipitatum. Fl. ♀: breve pedicellati; perianthia 4–6–partita, segmentis purpureo-fuscentibus, subulato-linearibus; ovarium obovoideum basi contractum, stylo laterali filiformi.

HAB. Kōtōshō, leg. T. KAWAKAMI et U. MORI, 1907, (No. 2461); ibidem, G. NAKAHARA, 1905, (No. 974).

DISTRIB. An endemic, and very local plant.

This curious and beautiful *Ficus* was found creeping on the walls or rocks along the sea shore. It is very remarkable for its smallest form of the receptacles. Gall and male flowers are found mixed in one receptacle, while female flowers are in a different receptacle.

Urtica heterophylla VAHL; WIGHT. Ic. Pl. Ind. or. t. 687.

Girardinia palmata GAUD.; FORBES et HEMSL. Ind. Fl. Sin. II. p. 475.

HAB. Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1769).

DISTRIB. Java, Ceylon, and Himalaya.

Pilea LINDL.

Pilea stipulosa MIQ.; HOOK. f. Fl. Brit. Ind. V. p. 555; MIQ. Fl. Ind. Bat. I.-2, p. 236; FORBES et HEMSL. Ind. Fl. Sin. II. p. 478; DIELS, Fl. Centr. Chin. p. 303; MATSUM. et HAYATA, Enum. Pl. Formos. p. 383.

Pilea angulata BLUME, Mus. Bot Lugd.-Bat. II. p. 55; WEDD. in DC. Prodr. XVI.-1, p. 131; MAXIM. in Mél. Biol. IX. p. 631.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1985).

DISTRIB. Central China, North India, Ceylon, and Java.

Pilea Wattersii HANCE, in Journ. Bot. (1885) p. 327; FORBES et HEMSL. Ind. Fl. Sin. II. p. 479; MATSUM. et HAYATA, Enum. Pl. Formos. p. 383.

HAB. Tappansha, ad 3108 ped. alt., (No. 590), et Sanchōki, ad 4000 ped. alt., leg. S. NAGASAWA, Oct. 1905.

DISTRIB. An endemic plant.

Lecanthus WEDD.

Lecanthus Wightii WEDD.; MIQ. Fl. Ind. Bat. I.-2, p. 238; HOOK. f. Fl. Brit. Ind. V. p. 559; FORBES et HEMSL. Ind. Fl. Sin. II. p. 480.

Lecanthus peduncularis WEDD. in DC. Prodr. XVI.-1, p. 164.

Lecanthus Wallichii WEDD. in DC. Prodr. XVI.-1, p. 164; FORBES et HEMSL. Ind. Fl. Sin. II. p. 480.

Lecanthus major WEDD. in DC. Prodr. XVI.-1, p. 164.

Elatostema ovatum WIGHT, Ic. Pl. Ind. or. t. 1985.

HAB. Arizan, leg. G. NAKAHARA, Nov. 1906.

DISTRIB. Central China: Szechuen and Yunnan. The Himalayas, Java, and Tropical Africa.

Very small form of the specis.

Elatostema FORST.

Elatostema minutum HAYATA, sp. nov. (Pl. XXXVI.). Herbæ parvissimæ, caulibus decumbentibus basi ad nodos radicantibus tomentosis. Folia alterna obovata 14 mm. longa 7 mm. lata valde obliqua apice obtusa basi inferiore latere rotundata superiore latere angusta, petiolis 1–2 mm. longis, utraque pagina pilis minutissimis dense atque pilis setulosis sparce obtecta margine serrata, serraturis acutis setulosis, viridissima, stipulis lanceolatis. Flores in receptaculo campanulato fasciculati. Receptacula in axillis foliorum solitaria sessilia, bracteis parvis. Achaenia ovata minuta punctata.

HAB. in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1986).

Elatostema sessile FORST.; WEDD. in DC. Prodr. XVI.-1, p. 172; HOOK. f. Fl. Brit. Ind. V. p. 563; FORBES et HEMSL. Ind. Fl. Sin. II. p. 483.

Procris sessilis HOOK. et ARN. Bot. Beech. Voy. p. 70.

var. **cuspidatum** WEDD. in DC. Prodr. XVI.-1, p. 173; HOOK. f. Fl. Brit. Ind. V. p. 564; MAXIM. in Mél. Biol. IX. p. 634; FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 495.

HAB. in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1987).

DISTRIB. Type: central China through Japan to the Pacific islands and also in Malay.

Procris JUSS.

Procris lævigata BLUME; MIQ. Fl. Ind. Bat. I.-2, p. 248; WEDD. in DC. Prodr. XVI.-1, p. 192; HOOK. f. Fl. Brit. Ind. V. p. 575; FORBES et HEMSL.

Ind. Fl. Sin. II. p. 484; HOOK. Ic. Pl. Ind. or. t. 1295; MATSUM. et HAYATA, Enum. Pl. Formos. p. 385.

HAB. Tappansha, ad 3138 ped. alt., leg. S. NAGASAWA, Oct. 1905. (No. 591).

DISTRIB. South China, India throughout, and extending from Java to the Comoro islands.

Juglandaceæ.

Juglans LINN.

Juglans sp.

HAB. Tōhosha, ad 2930 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 604).

Engelhardtia LESCH.

Engelhardtia spicata BLUME, Fl. Jav. Jugland. p. 8, t. 1, et t. 5, A; DC. Prodr. XVI-2. p. 140; MIQ. Fl. Ind. Bat. I.-1. p. 842; HOOK. f. Fl. Brit. Ind. V. p. 595; MERRILL, in Philipp. Journ. Scie. I. Supp. Bot. p. 41.

var. **formosana** HAYATA, n. v. Bracteæ fructiferæ parviores 2½ cm. longæ 3-lobatæ, lobis lateralibus 1½ cm. longis, terminale 2½ cm. longo lineari-oblongo, scariosis reticulatis.

HAB. Kusshaku, (Nov. 6), et Bunsanho, (No. 25), leg. N. KONISHI, Sept. 1902; Giran: Chūrei, leg. T. KAWAKAMI et U. MORI, Juni. 1906, (No. 1359). Nantō; Nankōkei, leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1173).

DISTRIB. Type: Java, Cochinchina, subtropical Himalaya.

Cupuliferæ.

Alnus GÆRTN.

Alnus maritima NUTT. var. **formosana** BURKILL, in FORBES et HEMSL. Ind. Fl. Sin. II. p. 500; HENRY, List Pl. Formos. p. 90; MATSUM. Revis.

Aln. Jap. in Journ. Scie. Coll. XVI.-5, p. 8; MATSUM. et HAYATA, Enum. Pl. Formos. p. 391.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 1731, 1926 et 1047).

DISTRIB. Type: Japan, North China, Manchuria, and extending to North America.

Carpinus LINN.

Carpinus sp.

HAB. in monte Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1998).

Quercus LINN.

Quercus amygdalifolia SKAN, in FORBES et HEMSL. Ind. Fl. Sin. II. p. 506; MATSUM. et HAYATA, Enum. Pl. Formos. p. 393.

HAB. Nantō: Mushazan, ad 6000 ped. alt., leg. T. KAWAKAMI et U. MORI, Aug. 1906, (Nos. 1139 et 1194).

Quercus dentata THUNB. Fl. Jap. p. 177, et Ic. Pl. Jap. Dec.-V. t. 6; DC. Prodr. XVI.-2, p. 13; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 445; FORBES et HEMSL. Ind. Fl. Sin. II. p. 511; DIELS, Fl. Centr. Chin p. 288; PALIBIN, Conspect. Fl. Koreæ, II. p. 51; MATSUM. et HAYATA, Enum. Pl. Formos. p. 393.

Quercus obovata BUNGE; DC. Prodr. XVI.-2, p. 13.

HAB. Taichū: Dainankō, leg. T. KAWAKAMI et U. MORI, Aug. 1906, (No. 1220).

DISTRIB. China and Japan.

Quercus formosana SKAN, in FORBES et HEMSL. Ind. Fl. Sin. II. p. 513; MATSUM. et HAYATA, Enum. Pl. Formos. p. 393.

HAB. Kōshūn: Kōbutsuzan, leg. N. KONISHI, April. 1898.

Quercus glauca THUNB. Fl. Jap. p. 175; HOOK. f. Fl. Brit. Ind. V.

p. 604; FORBES et HEMSL. Ind. Fl. Sin. II. p. 515; DIELS, Fl. Centr. Chin. p. 293; MATSUM. et HAYATA, Enum. Pl. Formos. p. 392.

HAB. Nantō: Nankōkei, (No. 1172), et Kwantōzan, (No. 1120), leg. T. KAWAKAMI et U. MORI, Aug. 1906.

DISTRIB. Japan, China, and Himalaya.

Quercus (*Pasania*) **Kawakamii** HAYATA, sp. nov. Ramuli validiusculi sulcati cinereo-flavescentes. Folia oblongo-obovata 13–15 cm. longa 6–7 cm. lata apice abrupte obtuse acuminata basi attenuata integra apicem versus obscure undulato-serrata coriacea supra nitida, costis planis leviter sulcatis, subtus pallidiora, costis valde prominentibus venis primariis lateralibus utrinque 13 prominulis sub angulo 50° egressis prope margines curvatis anastomosantibus tenuibus obscuris, petiolis semiteretibus supra leviter sulcatis basin versus incrassatis circ. 3 cm. longis. Flores ignoti. Fructus juniore ternatim aggregati sed proventu solitarii ad pedunculum incrassatum remote dispositi. Cupula subpatelliformis 2½ cm. in diametro 7 mm. longa intus margine depressa medio convexa extus squamis adpressis latis apice cuspidatis pubescentibus 7–8 seriatis suffulta. Glans depresso-globosa breve apiculata 2 cm. longa 2¼ cm. in diametro, cicatrici depressa.

HAB. in monte Morrison, leg. T. KAWAKAMI et U. MORI, Oct. 1906.

The present *Quercus* bears some resemblance to *Q. spicata* SMITH, *Q. formosana* SKAN, and *Q. brevicaudata* SKAN: but is easily distinguished by the shape of the leaves. Mr. S. A. SKAN informs me that this new plant is the nearest to *Quercus spicata* SMITH, but sufficiently distinct in the long stalked leaves broad and rounded at the apex.

Quercus (*Pasania*) **Konishii** HAYATA, sp. nov. (Pl. XXXVII.). Ramuli juniores dense pubescentes angulati. Folia petiolata remotiuscula oblongo-elliptica 7–9 cm. longa 2–3 cm. lata apice cuspidato-acuminata basi angusta integra apicem versus serrata, serris obtusis, supra nitida, nervis et venis supra impressis subtus valde prominentibus, venis primariis lateralibus utrinque 7 sub angulo 45° egressis ad apices serrarum attingentibus, venulis tenuibus vix prominulis, petiolis sub-gracilibus 1–2 cm. longis dense pubescentibus. Amenta ad apicem ramuli 2–3-fasciculata erecta androgyna 5–8 cm. longa validiuscula erecta, floribus inferioribus fœmineis remotis solitariis, superioribus masculinis dense aggregatis. Fl. ♂: perianthium 6-lobatum, lobis obtusis incrassatis rotundatis, intus hirsutum extus tomentosum. Stamina 8-12, filamentis perianthio 3-plo-longioribus; antheræ globosæ glabræ; bracteis ovatis basi incrassatis concavis. Ovarii rudimentum dense albotomentosum. Fl. ♀: involucrum globosum tomentosum squamis incrassatis triangularibus obtusis multiseriatim suffultum; ovarium globoso-conicum, stylis trifidis incrassatis; bracteis subulatis incrassatis. Fructus secus pedunculum incrassatum foliis paullo breviorem dense dispositi. Cupula subpatelliformis medio depressa 8 mm. longa 3 cm. in diametro aequans intus pallida rubra leviter glauca pubescens extus griseo-pubescens, squamis latis basi 2-sulcatis minute cuspidatis arcte adpressis circ. 10-seriatis suffulta. Glans 2 cm. longa 3 cm. in diametro semiglobosa nitida brevissime apiculata, cicatrici margine depressa medio convexa.

HAB. Taitō: Tōkwasan, Shinshōshō, leg. N. KONISHI, 1906. Tōtōgyōho, ad 2500 ped. alt., Juli. 1906: Kōshun: Botansha, leg. G. NAKAHARA, Dec. 1906, (No. 747.): Nantō: Hinokiyama, leg. G. NAKAHARA, Feb. 1907.

Mr. S. A. SKAN informs me that this new plant appears to be a distinct new species and there is nothing at Kew near it among the Asiatic material.

Quercus serrata Thunb. Fl. Jap. p. 176; DC. Prodr. XVI.-2, p. 50; Franch. et Savat. Enum. Pl. Jap. I. p. 447; Hook. f. Fl. Brit. Ind. V. p. 601; Forbes et Hemsl. Ind. Fl. Sin. II. p. 520.

Hab. Taichū: Toshikaku, leg. Y. Tashiro, April. 1896.

Distrib. Japan, China, and Himalaya.

Quercus Junghuhnii Miq. (Fig. 2.); Fl. Ind. Bat. I.-1, p. 853; Ann. Bot. Gard. Calc. II. p. 78, t. 73.

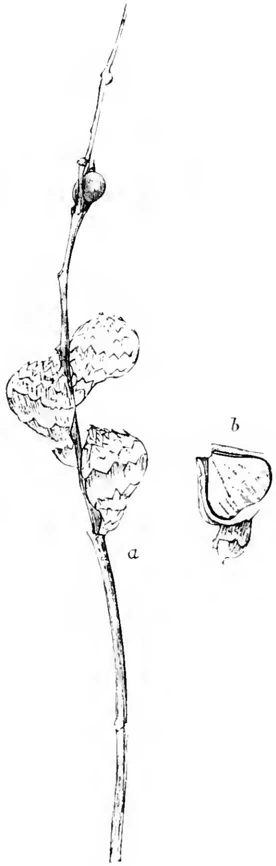

Fig. 2.

Quercus Junghuhnii Miq.

a— a branch of an inflorescence bearing fruits; *b*— a fruit, in vertical section, glans clearly seen.

Ramuli graciles griseo-fuscentes patentes. Folia petiolata patentia coriacea elliptico-ovata vel ovato-lanceolata 7 cm. longa 2 cm. lata margine integra extra medium grosse serrata apice longe cuspidata vel caudata leviter recurva basi rotundata æquilateralia rarius obliqua supra viridia costis impressis subtus ferrugineo-albicantia sub lente integumento tenuissimo lepidoto obtecta, costis prominentibus, venis primariis lateralibus utrinque circ. 10 apicem versus inconspicuis sub angulo 60 egressis, petiolis supra sulcatis semiteretibus 8 mm. longis. Fructus secus pedunculum gracilem erectum remote dispositi solitarii. Cupula turbinata valde obliqua 1 cm. in diametro sursum acuta deorsum abrupte attenuata in stipitem 7 mm. longum abeuns, glandem includens, extus squamis dentoideis in annulum dispositis 7—∞-seriatis sursum erectis deorsum adpressis, extus tenuiter cinero-tomentosa, intus sericea, crustaceo-fragilis. Glans subglobosa sursum attenuata acutiuscula glabra brunnea 8 mm. longa 9 mm. lata.

HAB. in monte Morrison, leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. Java.

I am informed by Mr. S. A. SKAN that this plant is certainly very near *Quercus cuspidata* THUNB., and still nearer *Q. Carlesii* HEMSL. in HOOK. Ic. Pl. t. 2591, from Foo-chow. But, in Mr. HEMSLEY'S species, the leaves are not so much rounded at the base, the fruit is not so distinctly stipitate, and it is broadest in the middle, not at the base. To my opinion, however, this Formosan plant is quit referable to the Javan species, although I have not yet seen the specimen of it.

Quercus variabilis BLUME, Mus. Bot. Lugd.-Bat. I. p. 297; DC. Prodr. XVI.-2, p. 50; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 447; MATSUM. et HAYATA, Enum. Pl. Formos. p. 394.

HAB. Taichū: Suiteiryō, leg. Y. TASHIRO, 1896, (No. 77); Biyōritsu: Banahōzan, leg. T. KAWAKAMI et U. MORI, Juli. 1906, (No. 1106).

DISTRIB. Japan.

Quercus sp.

HAB. Bunsanho (No. 3), et Heirinbi (No. 21), leg. N. KONISHI. Oct. 1899.

Very near *Q. glauca* THUNB.; but the leaves are much narrower and the veins are more elevated. The leaves of dried specimens are of a color of neutral tint.

Castanopsis SPACH.

Castanopsis indica A. DC. in SEEM. Journ. Bot. (1864) p. 182; DC.

Prodr. XVI.-2, p. 109; MIQ. in Ann. Mus. Bot. Lugd.-Bat. I. p. 119; HOOK. f. Fl. Brit. Ind. V. p. 620.

Castanea indica ROXB. Fl. Ind. ed.-CAREY, III. p. 643; BLUME, Mus. Bot. Lugd.-Bat. I. p. 284; WIGHT, Ic. Pl. Ind. or. t. 417.

Castanopsis tribuloides var. *formosana* HAYATA, in MATSUM. et HAYATA, Enum. Pl. Formos. p. 394.

HAB. Banchoryō: Rokurisha, leg. G. NAKAHARA, Oct. 1905, (No. 593).

DISTRIB. Tropical Himalaya.

Castanopsis taiwaniana HAYATA, sp. nov. (Fig. 3). Ramuli teretes dense ferrugineo-pubescentes. Folia breviter petiolata patentia oblongo-lanceolata 8–14 cm. longa 3½–5 cm. lata integerrima apice obtuse acuminata basi rotundata vel leviter attenuata coriacea rigida bicoloria supra glabra nitida pallido-viridia costis impressis venis inconspicuis, subtus ochraceo-lepidota costis prominentibus venis primariis lateralibus utrinque 10–13 sub angulo 60° egressis intra margines curvatis anastomosantibus, petiolis 1 cm. longis basi leviter incrassatis sulcatis semiteretibus; folia novella conduplicativa subtus dense ferrugineo-tomentosa, stipulis caducis lateralibus sub-obliquis obtusissimis integerrimis sub-coriaceis venis parallelis sericeis ab initio erectis dein revolutis. Amenta 10 cm. longa ex axillis foliorum superiorum solitaria simplicia erecta remotiflora. Fructus sessiles solitarii globosi magnitudine cum spinis 3 cm. æquantes. Cupula clausa intus spadiceo-sericea

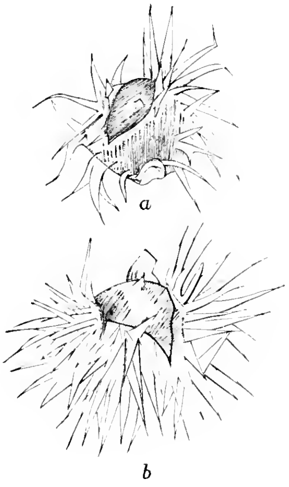

Fig. 3.
Castanopsis taiwaniana HAYATA.
a and *b*— fruits.

extus echinata, spinis confertis erectis subulatis rigidis rufescentibus sericeis. Glans solitaria globoso-trigona basi truncata leviter convexa ochraceo-rufescens pubescens vel subglabra.

HAB. Nantō, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 1185 et 1165); Shintiku: Goshizan, leg. T. KAWAKAMI, Dec. 1905, (No. 1294); Hokuho, leg. N. KONISHI, 1899, (No. 8).

This *Castanopsis* is very like *C. javanica* A. DC.; but differs from it in having subglabrous nuts and more strong spines on the involucres.

I am informed by Mr. S. A. SKAN that this new plant is very near to *C. Hystrix* A. DC., in which the leaves, though usually toothed, are sometimes quite intire, and that there is no specimen at kew of *C. Hystrix* with the spines of the involucre so stout and that is apparently the only difference.

Fagus LINN.

Fagus sylvatica LINN. Sp. Pl. ed.-2, p. 1416; DC. Prodr. XVI.-2. p. 118.

var. ?

HAB. Kushaku: Sōtenzan, ad 5600 ped. alt., leg. N. KONISHI, Feb. 1906, (spec. steril.).

Salicaceæ.

Salix LINN.

Salix sp.

HAB. in monte Morrison, ad 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 596).

It somewhat resembles the Japanese *S. Sieboldiana* BLUME. The specimens being all sterile are not yet determined.

Gymnospermeæ.

Coniferæ.

Libocedrus ENDL.

Libocedrus macrolepis BENTH. (Fig. 4). BENTH. in BENTH. et HOOK. Gen. Pl. III. p. 426; FORBES et HEMSL. Ind. Fl. Sin. II. p. 540; MASTERS, in Journ. Linn. Soc. XXXVII p. 411; MAYR, Fremdland. Wald-und Park-Bäume, p. 316. *Calocedrus macrolepis* KURZ, in Journ. Bot. (1873) p. 196.

HAB. Rinkōshō: leg. T. KAWAKAMI et U. MORI, Sept. 1906, (No. 1675).

As the descriptions of the male flowers and seeds were not sufficiently made previously, the following accounts may be properly added here.

Flores masculini ad ramulos brevissimos terminales oblongi, staminibus circ. 8, filamentis ad basin squamarum subpeltatis, squamis suborbicularibus vel subcordatis, loculis antheræ 2–3. Strobilus cylindraceo-oblongus. Semina samaroidea, alis cultriformibus.

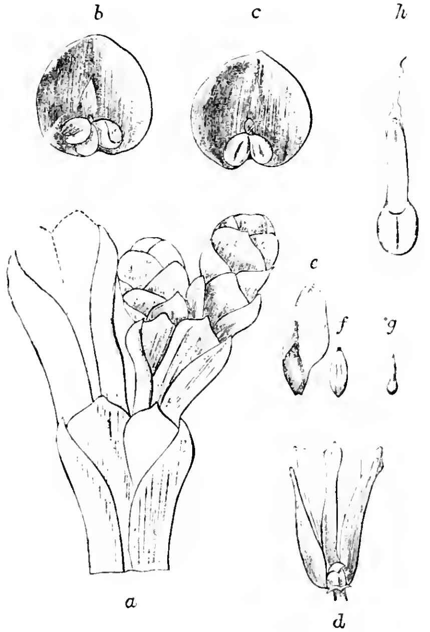

Fig. 4.

Libocedrus macrolepis BENTH. *a*— male flowers; *b* and *c*— stamens; *d*— a cone; *e*— a seed; *f*— an albumen; *g*— an embryo; *h*— the same, highly magnified.

Chamæcyparis SPACH.

Chamæcyparis formosensis MATSUM. in Tōkyō Bot. Mag. XV. p. 137; MATSUM. et HAYATA, Enum. Pl. Formos. p. 402.

HAB. in montibus Morrison, leg. R. TORII, 1900; Giyokusan, in montibus Morrison, ad 10634 ped. alt., (No. 554), et Seizan, in isdem montibus, ad 11579 ped. alt., (No. 584), leg. S. NAGASAWA, Nov. 1905; in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2103); Taitō: Bunshiseki, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2104).

DISTRIB. An allied species, *C. pisifera* S. et Z., occurs in Japan.

Chamæcyparis obtusa SIEB. et ZUCC. in "ENDL. Conif. p. 63"; PARL. in DC. Prodr. XVI.-2, p. 466; FRANCH. et SAVAT. Enum. Pl. Jap. I. p. 471; WARBURG, Monsunia, I. p. 190; BEISSN. Handb. Nadelh. p. 92.

Retinispora obtusa SIEB. et Zucc. Fl. Jap. II. p. 38; MIQ. Prol. Fl. Jap. p. 332.

Thuya obtusa MAST. Journ. Linn. Soc. XVIII. p. 491, Fig. 4.

forma **formosana**, (Fig. 5); HAYATA, in Gard. Chron. (1908) p. 194. Strobili ut typicæ multo minores 8 mm. in diametro æquantes, seminibus minoribus cum alis 2 mm. in diametro æquantibus.

Shinkō: Shirakku, leg. T. KAWAKAMI et U. MORI, Juni. 1906, (No. 1329); Arizan, in montibus Morrisson, leg. G. NAKAHARA, Nov. 1906.

DISTRIB. Japan.

This Formosan *Chamæcyparis* is in all respects the same as the Japanese species. But, the cone of the present plant is always much smaller than the Japanese one, and the seed is also smaller. Native botanists in the island suggest to me to separate it from the Japanese species as a new variety. For the present, however, it would be better to regard it as a form of the Japanese species.

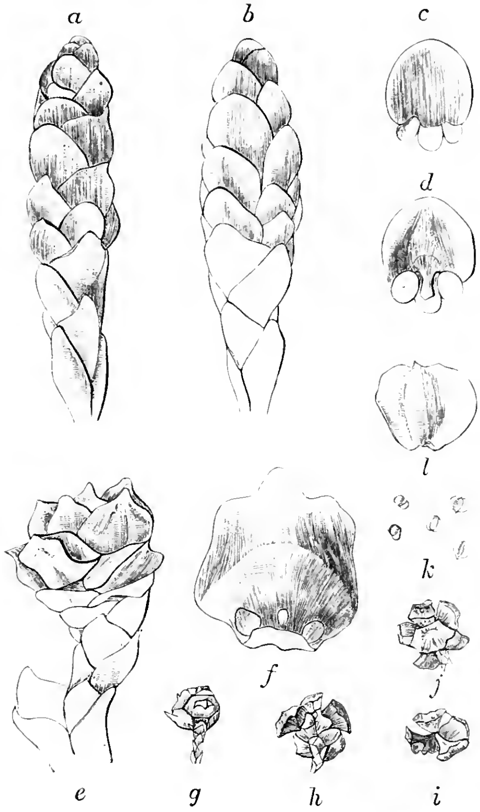

Fig. 5.

Chamæcyparis obtusa S. et Z. form. *formosana* *a*– a male flower; *b*– the same, seen from a different side; *c*– a stamen, seen from the outer side; *d*– the same, seen from the inner side; *e*– a female flower in an advanced stage; *f*– a scale; *g*– a cone; *h*– another cone, after opening; *i*– another form; *j*– another one; *k*– seeds; *l*– a seed, magnified.

Juniperus LINN.

Juniperus formosana HAYATA. (Pl. XXXVIII.) in Gard. Chron. (1908) p. 194.

Juniperus taxifolia HAYATA, in Tōkyō Bot. Mag. XX. p. 46; MATSUM. et HAYATA, Enum. Pl. Formos. p. 403.

Ramuli novelli triquetri in angulis prominentibus marginati glabri. Folia in totum lineari-angusta 14 mm. longa 2 mm. lata verticillato-ternata patentia integerrima acuminato-pungentia glabra supra concava glauca stomatifera subtus valde carinata prominentia convexa. Flores ignoti. Galbuli ad axillas foliorum inferiorum ramulorum novellorum solitarii, basi squamis ovato-acutis verticillatis 2-seriatim dispositis, globosi 7 mm. longi carnosi rufo-fuscentes supra medium vestigiis acutis bractearum intimarum notati. Semina 3, erecta trigono-elliptica apice mucronata, testa ossea, facie dorsali glandulis 3–4 resiniferis oblongis insculpta, facie ventrali pauce notata.

Hab. in monte Morrison, leg. R. Torii, 1900; Seizan, in montibus Morrison, ad 11579 ped, alt., leg. S. Nagasawa, Nov. 1905, (No. 752); in isdem montibus, ad 13000 ped. alt., (No. 2262), et ad 8000 ped. alt., (No. 2039), in montibus centralibus, (No. 2099), leg. T. Kawakami et U. Mori, Nov. 1906.

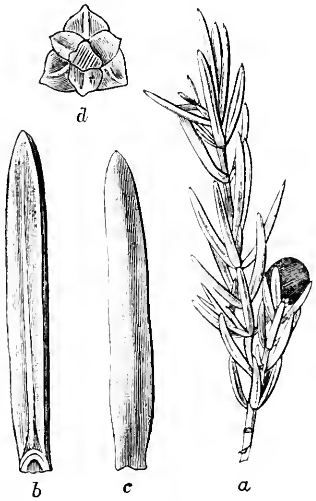

Fig. 6.

Juniperus taxifolia Hook. et Arn. from the Bonin islands.
a– a branch; *b*– a leaf, seen from within; *c*– the same, seen from without; *d*– bracts at the base of a fruit, seen from below.

Very like *J. communis* Linn.; but differs from it in having pointed vestiges on the fruits; also near *J. taxifolia* Hook. et Arn., but differs from it in having acute leaves; from *J. rigida* Sieb. et Zucc., in having less narrowed leaves and acute vestiges on the fruits.

The present plant has erroneously been regarded by myself and also by some other botanists as the same species as the Bonin *J. taxifolia*. On re-examining carefully the all specimens of the genus, *Juniperus*, from China, Formosa, Japan, the Bonin islands and Loo-choo archipelago, I have found that *J. taxifolia* is confined to the latter two archipelagos, but does not extend to either Formosa or China. The Formosan plant differs from the Bonin species in having pungent leaves. As to the *Juniperus* of China, I was so fortunate as to examine the same specimens which were studied by the late Dr. M. T. Masters, F. R. S., F. L. S. The Chinese plant collected by Mr. E. H. Wilson in West China, Changyang (Hupeh, No. 428), which is referred to *J. taxifolia* by that eminent authority[1]

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[1] M. T. Masters: Chinese Conifers collected by E. H. Wilson, in the Journal of Botany, Vol. XLI. p. 267, & On Chinese Conifers, in the Journal of the Linnean Society, XXXVII. p. 413.

is not to my opinion the same as the Bonin plant in which the leaves are altogether blunt, and the male flowers are much longer (see Fig. 6). Nor is the specimen[1] which was collected by M. A. HENRY (Hupeh, No. 2067, A!), referable to the juneper of the archipelago. The Chinese plant has pungent leaves and much shorter male flowers. Whether the *Juniperi* of Formosa and China are similar or not, demands further investigation. At present, I can only state that *J. taxifolia* does not extend to either Formosa or China, and that it is found in the Bonin, and Loo-choo islands, but nowhere else.

Juniperus morrisonicola HAYATA. (Fig. 7), in Gard. Chron. (1908) p. 194. Rami teretes, ramulis novellis viridibus trigonis. Folia omnia lanceolata apice acerosa patentiuscula 3–4 mm. longa 1 mm. lata verticillato-ternata supra cancava glaucescentia subtus leviter carinata. Flores masculini terminales ad ramulos brevissimos ovoidei 4 mm. longi 2 mm. lati, staminibus 8, filamentis in squamam peltatis, squamis suborbicularibus 1½ mm. in diametro æquantibus, loculis antheræ 3. Flores fœminei ad ramulos brevissimos terminales basi foliis squamiformibus bracteisque 6–9 ternato-verticillatis suffulti, squamis intimis 3 ovatis acutis verticillatis patentibus. Ovulum terminale solitarium squamis intimis circumdatum oblongum apice attenuatum. Galbuli solitarii globosi vel paullo longiores 6 mm. longi, sub maturitate nigricantes glabri medio vestigiis squamarum notati. Semina solitaria globoso-ovoidea 5 mm. long. 4 mm. lata, testa ossea sulcata. Embryo normalis; cotyledones 2.

HAB. ad summam montis Morrison, 13200 ped. alt., leg. SHIMOYAMA, 1899: ibidem, leg. R. TORII, 1900: ibidem, leg. S. NAGASAWA, 1905, (No. 585), et leg. T. KAWAKAMI, 1906, (No. 2142, fr.).

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[1] FORBES et HEMSL. Ind. Fl. Sin. II. p. 543.

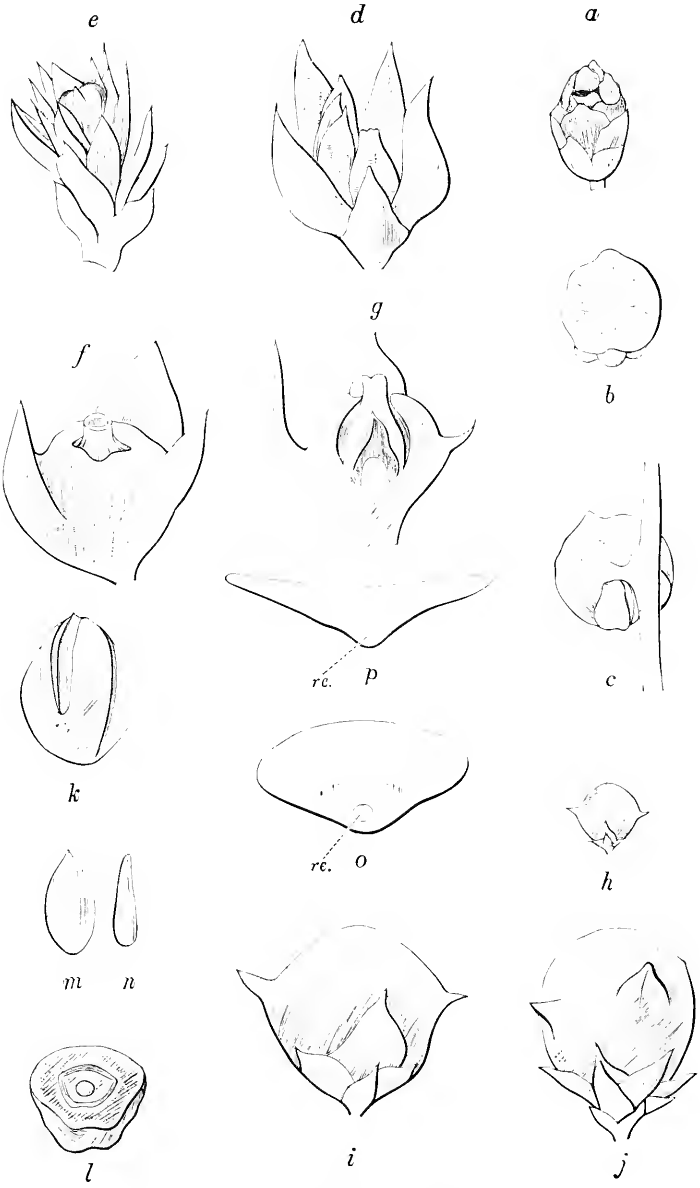

Fig. 7. *Juniperus morrisonicola* HAYATA.

a— a male flower ; *b*— a stamen ; *c*— the same, seen from the inner side ; *d*— a female flower ; *e*— the same, in a little advanced stage ; *f*— the same, in a more advanced stage ; *g*— the same, in vertical section, one side taken off, showing the hollow receptacle, ovule and nucellus (as the figure is drawn from a dry specimen, the nucellus is probably much more contracted than it really is) ; *h*— a fruit (natural size) ; *i*— the same, magnified ; *j*— the same, seen from a different side ; *k*— a seed ; *l*— the same, in section, the upper half taken away, showing the hard seed coat, albumen and embryo ; *m*— an albumen ; *n*— an embryo ; *o* and *p*— sections of different parts of a leaf, *re*=resin-canal.

The *Juniperus* described above was first found by Mr. SHIMOYAMA on the top of Mt. Morrison at an altitude of about 4000 m., in the year 1899. Although the same mountain was since botanized by several collectors, the specimens brought back to me were but fragments of a sterile branch. I could not get any more idea about this plant than that it is something like *Juniperus chinensis* LINN., until Mr. T. KAWAKAMI gave me a most perfect specimen of it. Examing the material, I have found that the plant is far different from *J. chinensis* LINN., in having a solitary ovule on a short branchlet, and in the shape of its cone. The leaves have a large single resin-canal near the phloëm. So far, the plant does not seem to have dimorphic leaves, all the specimens we have at present possessing but one kind of leaf.

Cunninghamia R. BR.

Cunninghamia, being a monotypic genus, implies only *C. sinensis* R. BR. It is, therefore, the most remarkable matter that we have here an addition of one more species belonging to this interesting genus. The new *Cunninghamia* was kindly sent to me by Mr. T. KAWAKAMI, Government Expert of Formosa. It was obtained by Mr. N. KONISHI on Mt. Randaisan at an altitude of about 2000 m. It is very rarely found in the coniferous forests, and attains a considerable height. It affords a good timber which bears some resemblance to *Chamæcyparis*.

Cunninghamia Konishii HAYATA, in Gard. Chron. (1908) p. 194. Arbor, ramis omnibus teretibus glabris foliorum spiraliter confertorum cicatricibus notatis. Gemmæ floriferæ nudæ depresso-globosæ, bracteis depresso-ovatis brevissime aristato-acutis.

Folia ramorum vetorum spiraliter conferta adnato-decurrentia anguste lineari-falcata incurvo-erecta acuta dorso leviter carinata, ramulorum juvenium longiora ascendento-patentia anguste lineari-lanceolata 15 mm. longa 2½ mm. lata ad basin oblique torta apice obtusiuscula margine sub lente serrulata rigida coriacea utraque pagine glaucescentia stomatibus multiseriatis instructis octavum in annum virentia demum exarida sensim soluta. Strobili sub maturitate ovato-globosi 20 mm. longi 15 mm. lati. Squamæ rotundatæ mucronatæ basi distincte unguiculatæ, unguibus brevibus, laminis dilatis, cordatis late depresso-ovatis margine integris lignescentibus sursum coriaceis et marginem versus subundulatis dorso apice leviter carinatis glabris. Bracteæ obsoletæ. Squamulæ 3 ad medio laminæ squamæ distinctæ fimbriatæ crenulatæ. Semina 3 ad medium squamularum affixa reversa libera ovato-elliptica. testis corioceis duriusculis, aiis angustis. Embryo ignotus.

HAB. Nantō: in monte Randaisan, ad 7000 ped. alt., leg. N. KONISHI, Mai. 1907.

Mr. T. KAWAKAMI informs me that the habit of this new plant is an intermediate between those of *Cunninghamia* and *Taiwania*. On examining the specimen carefully, I find that the cone of the plant has a secondary squama. Therefore, this should undoubtedly be referred to *Cunninghamia*. The leaf of this plant has stomata on both surfaces, while that of *C. sinensis* has no stoma on the upper surface, or a very few if at all. In the case of *Taiwania*, the stomata are found on both surfaces. The new *Cunninghamia* differs mainly from the other species in the arrangement and the shape of the leaves, and in having smaller cones and broader squamæ. The timber is like other Conifers, the bark is reddish brown and in all respects is very like that of *Chamæcyparis*, but it has an odour peculiar to itself. The leaf of the present plant is more persistent than that of the other: the former lasts for eight years, while the latter only lasting five years.

Taiwania HAYATA.

Taiwania cryptomerioides HAYATA, in Journ. Linn. Soc. XXXVII. p. 331, t. 16, et in Tōkyō Bot. Mag. XXI. p. 2, t. 1.

Cryptomeria japonica HAYATA, (non DON.) in Tōkyō Bot. Mag. XX. p. 46.

HAB. Arizan, in montibus Morrison, ad 7500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, et ibidem, leg. G. NAKAHARA; Taitō: Taironkōsha, ad 8000 ped. alt., leg. U. MORI, Nov. 1906.

DISTRIB. An endemic monotypic genus.

Cephalotaxus ZUCC.

Cephalotaxus sp.

HAB. in monte Morrison, leg. R. TORII, 1900; Ganzan, in montibus Morrison, ad 8012 ped. alt., leg. S. NAGASAWA, Nov. (1905), (No. 568); in monte Morrison, ad 8500 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2106); Taitō: Dakunsha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2105).

DISTRIB. The genus extends from Japan to China.

In the absence of cones, the species is indeterminable.

Taxus LINN.

Taxus sp.

HAB. Arizan, in montibus Morrison, leg. G. NAKAHARA, Oct. 1906: Taitō: Bunshisekisha, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2107).

In the absence of cones, it is impossible to determine it specifically.

Pinus LINN.

Pinus Armandi FRANCHET, Pl. David. I. p. 285, t. 12: MASTERS, in FORBES et HEMSL. Ind. Fl. Sin. II. p. 549.

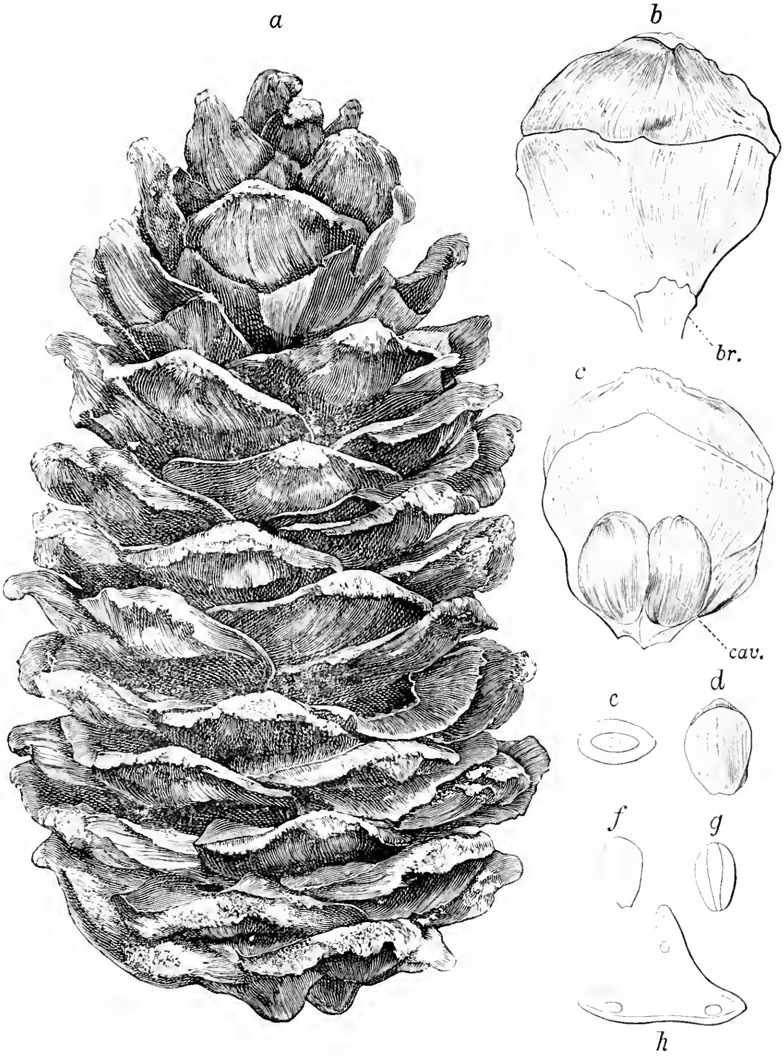

Fig. 8.

Pinus Armandi Franch. var. *Mastersiana* Hayata.

a—a cone, (slightly reduced); *b*—a scale detached from the middle part of the same cone, seen from the outer side; *c*—the same, seen from the inner side, seeds taken off, *cav.* = impression of the seeds; *d*—a seed; *e*—cross section of the same; *f*—an albumen; *g*—the same, in vertical section; *h*—cross section of a leaf.

var. **Mastersiana** HAYATA. (Fig. 8). in Gard. Chron. (1908) p. 194. Rami teretes fusci novelli glabri cicatricibus perularum et foliorum notati. Folia in fasciculo quinque acerosa filiformia tenuia acuta dorso plana triangularia in sectione margine et in carina remote serrulata 10 cm. longa. Strobili erecti ovato-cylindracei obtusi 14 cm. longi 7 cm. lati. Bracteæ minutissimæ. Squamæ numerosæ orbiculares v. subrhombeæ acutæ sursum reflexæ basi breviter cuneatæ lignescentes longitudinaliter rugosæ fuscæ dispermæ. Semina obovata 12 mm. longa 9 mm. lata apice leviter apiculata aptera compressiuscula, testa ossea crassa fusca glabra. Albumen crassum oleosum. Embryo cotyledonibus 5 verticillatis.

HAB. in monte Morrison, leg. R. TORII, 1900 : Hatsukwanzan, ad pedem montis Morrison, leg. YAMASHITA : Gyokusan, in montibus Morrison, ad 10634 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 582) ; in monte Morrison, ad 8000 ped. alt., (No. 2088), et in eodem monte, ad 9000 ped. alt., (No. 2095), leg. T. KAWAKAMI et U. MORI, Oct. 1906 ; in eodem monte, leg. G. NAKAHARA, Oct. 1905.

The present variety differs from the tipe in its reflexed squamæ and longer cones.

DISTRIB. Type : west central China.

Pinus formosana HAYATA. (Fig. 9).

Pinus morrisonicola HAYATA, in Gard. Chron. (1908) p. 194.

Ramuli teretes perularum rudimentis notati, novelli pubescentes. Gemmæ ovatæ perulatæ, perulis acutis membranaceis margine fractis. Folia in fasciculo quinque, fasciculis approximatis

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* The *Pinus* is for the first time printed under the name, *P. morrisonicola*, which is, however, an unfortunate name which is erroneously copied from my manuscript. The occurrence of the plant in the Mount Morrison is rather doubtful, for the *Pinus* is very local plant, being found only in some parts of the Taichū district.

acerosa rigidula 6–8 cm. longa arcuata sed non torta apice acuta dorso plana facie acute carinata triangularia in sectione margine et in carina remote serrulata. Strobili erecti ovato-elliptici obtusi, e squamis circ. 40 compositi 7–9 cm. longi 4–6 cm. lati, squamis ellipticis basi cuneatis sursum rotundatis leviter reflexis 3 cm. longis 1½ cm. latis coriaceo-crassis sublignescentibus concavis badio-fuscis dispermis semper abortu monospermis. Bracteæ brevissimæ. Semina ovata apice obtusa 10 mm. longa 6 mm. lata, testa coriacea pallide ferruginea glabra, ala membranacea tenui cultriformi 2 cm. longa 8 mm. lata.

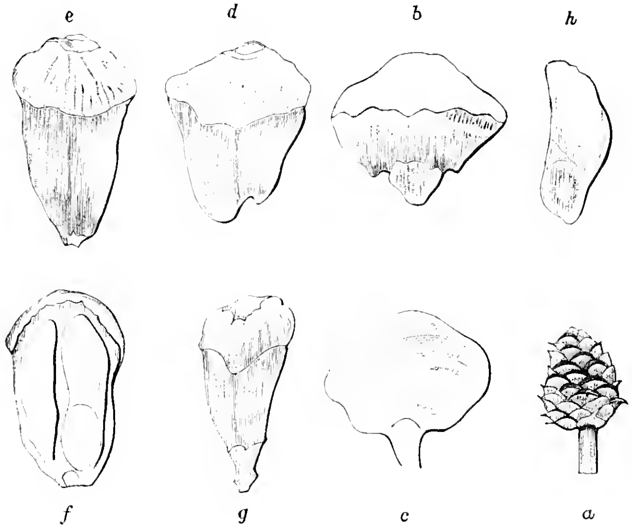

Fig. 9. *Pinus formosana* HAYATA.

a— a very young cone; *b*— a scale of the same cone, magnified; *c*— the same, seen from a different side; *d*— a scale detached from the basal portion of a mature cone; *e*— a scale detached from the middle portion of the same cone; *f*— the same, seen from the inner side; *g*— a scale detached from the apical portion of the same cone; *h*— a seed.

HAB. Shōhakulin, et inter Hokkōkei et Horisha, C. OWATARI, Jan. 1898; Taichū: Yagatayama, leg. G. NAKAHARA, Feb. 1907; ad summam montis Hanrizan, ad 8000 ped. alt., leg. MURATA, Sept. 1897; Taitō: Bunshiseki, leg. T. KAWAKAMI et U. MORI, Dec. 1906, (No. 2090).

DISTRIB. An allied species, *P. parviflora* S. et Z., occurs in Japan.

The present *Pinus* is very near *Pinus parviflora* S. et Z.; but differs from that in the shape of the cones. The scales of the cones of this new plant are usually reflexed and especially so in the scales of the basal part. The wings of the seeds are much larger than those of *P. parviflora* S. et Z.

According to Mr. G. NAKAHARA, the plant grows in the mountainous districts of the Taichū prefecture, at an altitude of 1500 m. Forming a forest along a valley, making lines parallel to the camphor forests, this pine gives a most remarkable feature to the vegetation of this spot. Attaining a height of about 15 m., and a diameter of a little less than 1 m., it describes an outline of a conical form, stretches out its branches quite loosely upwards from the middle of the trunk, and sends them down within the reach of one's arms. It grows mostly on a cliff of the clay slates, and faces itself to the valley below. The trunk presents a colour of grayish white and it is very straight like a fir, and the texture of the bark is very similar. The distribution of the pine is rather local, the habitat being limited to the western slope of the central mountain ranges in the middle part of the island.

Pinus sp. (aff. *P. Thunbergii* PARL.).

HAB. in monte Morrison, leg. R. TORII, 1900.

Pinus sp. (aff. *P. densiflora* S. et Z.)

HAB. in montibus centralibus, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906. (Nos. 2097 et 2094).

Picea LINK.

Picea morrisonicola HAYATA, sp. nov. (Fig. 10.).

Picea Glehni MATSUM. in Tōkyō Bot. Mag. XV. p. 141; MATSUM. et HAYATA, Enum. Pl. Formos. p. 401, (non FR. SCHM.).

Ramuli glabri, pulvinis oblongo-obovatis superne erectis in petiolum brevem ascendentem angustis, cicatricibus quadrangularibus. Gemmæ ovoideoconicæ, perulis scariosis ovatis obtusis. Folia linearia 6 mm–16 mm. longa $\frac{2}{3}$ mm. lata curvata quadangularia apice acuta utrinque stomatifera. Strobili oblongo-cylindracei 6 cm. longi deflexi? Bracteæ ovato-lanceolatæ obtusæ margine fractæ $\frac{1}{4}$ squamæ fructiferæ æquantibus. Squamæ planiusculæ obovato-orbiculares basi attenuatæ, apice truncatæ-rotundatæ subintegræ. Semina cum alis 1 cm. longa, alis subcultriformibus obovatis semen ipsum $1\frac{1}{2}$–2 plo superantibus.

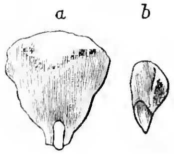

Fig. 10.

Picea morrisonicola HAYATA. *a*— a scale detached from the middle portion of a cone; *b*— a seed.

HAB. in monte Morrison, leg. R. TORII 1900: Hattsukwanzan, leg. YAMASHITA: in eodem monte ad 95000 ped. alt., leg. T. KAWAKAMI et U. MORI. Nov. 1906, (No. 2108).

Strobilus	(T. KAWAKAMI, No. 2108)	60 mm. longus	22 mm. latus.
,,	(R. TORII)	75 mm. ,,	30 ,,
,,	(,,)	65 mm. ,,	23 ,,

Near *P. Glehnii* MASTERS, but differs from it in having glabrous branchlets: also near *P. Watsoniana* MASTERS, but differs from it in having subtruncate squamæ of cones.

DISTRIB. An allied species, *P. Glehnii* MAST., occurs in Japan and Saghalien.

Keteleeria Carr.

Keteleeria Davidiana Beissn. var. **formosana** Hayata, (Fig. 11.). in Gard. Chron. (1908) p. 194. Ramuli dense puberuli. Folia laxe disposita plana lineari-lanceolata 30 mm. longa vel longiora 5 mm. lata, nervis utraque pagine prominentibus, margine parum deflexa vernicosa subtus vix pallidora apice obtusa (ramuli hornotini aristato-acuta) in pedem brevem compressum demum contortum attenuata, petiolis basi transverse insertis. Strobili erecti cylindracei obtusi 9 cm. longi 5 cm. lati. Squamæ coriaceæ ovato-rotundatæ v. cordatæ superne sensim attenuatæ apice subreflexæ basi breve unguiculatæ extus longitudinaliter striatæ puberulæ margine tenues irregulariter serrulatæ. Bracteæ squamis duplo breviores, spathulatæ membranaceæ dorso fuscæ apice cuspidatæ vel trifidæ irregulariter serrulatæ subpungentes supra medium contractæ. Semina pallida fulva basi acuta, ala concolore cultriformi, squamis æquilonga, cum alis 27 mm. in longitudine æquantia.

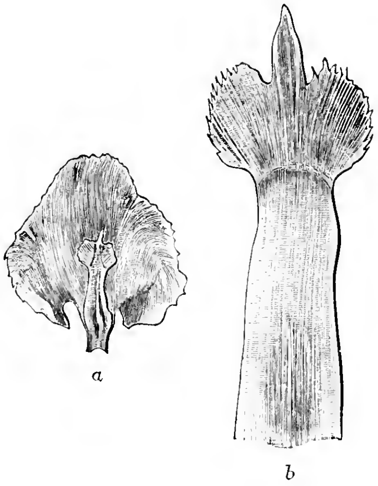

Fig. 11.
Keteleeria Davidiana Franch. var. *formosana* Hayata. *a*— a scale of a cone; *b*— the bract of the same scale, magnified.

Hab. Shinjuki, Shinkōchō, leg. N. Konishi, Nov. 1902; Bunsanho, leg. T. Tashiro, Juni. 1899.

Distrib. Type: west central China.

This new variety differs from the type in having spathulate bracts which are contracted a little above the middle portion. The cone is shorter and the wing of the seed is narrower. The leaf is acute or obtuse, but not truncate or emarginate as is the case with the type.

Tsuga CARR.

Tsuga formosana HAYATA, (Fig. 12). in Gard. Chron. (1908) p. 194. Ramuli novelli tenues glabri pallido-fuscentes. Gemmæ perulatæ, perulis obtusis integris. Folia approximata distincte petiolata, petiolis brevibus semiteretibus parum incurvis, linearia 8 mm.–16 mm. longa 1½mm.– 2 mm. lata apice obtusa vel emarginata integerrima glabra coriacea. Strobili ovoidei 2–2.3 cm. longi 1.3 cm. lati, squamis circ. 20. Squamæ imbricatæ coriaceæ basi truncatæ sursum suborbiculares integræ 1½ cm. longæ 1 cm. latæ substriatæ pallidæ fuscescentes. Bracteæ brevissimæ rhomboideæ apice brevissime 2–lobatæ irregulariter dentatæ. Semina parva obovata, 4 mm. longa vel longiora, alis membranaceis tenuibus cultriformibus pallido-ferrugineis 7 mm. longis.

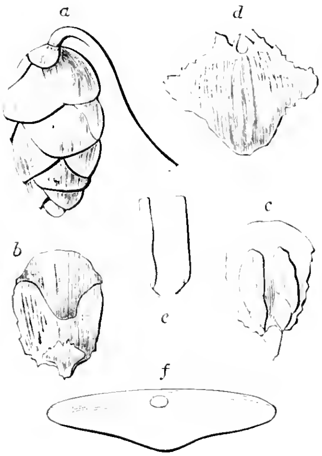

Fig. 12.

Tsuga formosana HAYATA. *a*— a cone; *b*— a scale, seen from the outer side; *c*— the same, seen from the inner side; *d*— the bract of the same scale, magnified; *e*— leaves, seen from different sides; *f*— cross section of a leaf.

HAB. in monte Morrison, leg. R. TORII, 1900; Giyokusan, in montibus Morrison, ad 10634 ped. alt., leg. S. NAGASAWA, Nov. 1905, (Nos. 553 et 552); in monte Morrison, ad 8000 ped. alt., (No. 2364), et eodem monte, ad 9000 ped. alt., (No. 2110), leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. An allied species, *T. diversifolia* MAXIM., occurs in Japan.

This *Tsuga* very much resembles *T. diversifolia* in the shape of cones and bracts, but differs from it in the seeds having longer wings and in the glabrous branchlets. It also bears some resemblance to *T. Sieboldi* CARR., in the shape of the cones and seeds, but is easily distinguished from the latter by the shape of the bracts, and by the shorter leaves. This new plant is, I think, just an intermediate form of *T. Sieboldi* and *T. diversifolia*.

Pseudotsuga CARR.

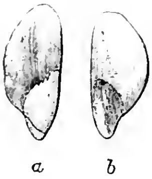

Fig. 13.

Pseudotsuga japonica SHIRASAWA. *a*— a seed; *b*— the same, seen from a different side.

Pseudotsuga japonica SHIRASAWA, (Fig. 13). in Tōkyō Bot. Mag. IX. p. 84; HAYATA, in Tōkyō Bot. Mag. XX. p. 45; MATSUM. et HAYATA, Enum. Pl. Formos. p. 400; M. T. MASTERS, in Journ. Linn. Soc. XXXVII. p. 424.

HAB. in monte Morrison, leg. T. KAWAKAMI et U. MORI, Oct. 1906.

DISTRIB. Japan.

Abies JUSS.

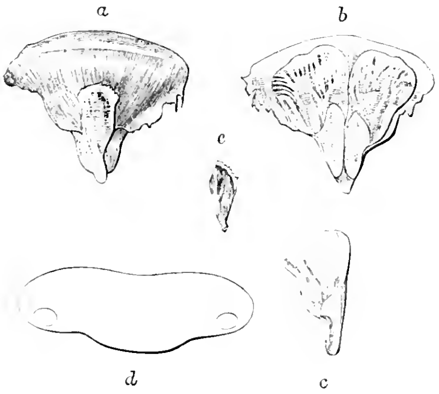

Fig. 14.

Abies Mariesii MAST. var. *Kawakamii* HAYATA. *a*— a scale; *b*— the same, seen from the inner side; *c*— a seed; *d*— section of a leaf; *e*— a seed, wing taken off.

Abies Mariesii MAST. var. **Kawakamii** HAYATA, n. v. (Fig. 14).

Abies Mariesii HAYATA, in MATSUM. et HAYATA, Enum. Pl. Formos. p. 400, (non MASTERS).

Ramuli ferruginei pilosissimi, pulvinis obovatis pauce prominentibus, cicatricibus depressis ovato-oblongis. Folia approximata late linearia a basi angustiora ad apicem sinsim dilata apice rotundato-obtusa et emarginata supra impressa subtus carinata inter carinam marginemque argentea stomatifera. Strobili laterali erecti ovato-cylindracei apice retusi 7½ cm. longi 4 cm. lati. Bracteæ ⅔ plo squamam in longitudine æquantes obovatæ angustæ supra medium leviter constrictæ et transverse coloratæ apice dilato-rotundatæ mucronatæ fractæ ecostatæ. Squamæ late rotundato-cuneatæ 2 cm. longæ 2½ cm. latæ basi vix auriculatæ abrupte stipitatæ margine sursum integerrimæ deorsum fractæ. Semina cum alis 18 mm. longa, alis truncatis, seminibus alisque nigricantibus.

HAB. in monte Morrison, ad 11220 ped. alt., leg. R. TORII, 1900; ibidem, leg. HONDA, 1896, (No. 98.); Seizan, in montibus Morrison, ad 11579 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 583.); in monte Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 2369 et 2372).

DISTRIB. An ally, *A. Mariesii* MAST., occurs in Japan.

This differs from the type in having longer cylindrical cones, black coloured wings and seeds; from *A brachyphylla* MAXIM., this differs in having shorter cones and in the position of the resin-canal lying close to the epiderm.

Monocotyledones.

Orchideæ.

The species belonging to this family are about twenty in number, and must be very interesting ones. Owing to the lack of literature, I am at present obliged to put off the study of this family. The work of these orchids will be specially treated in the near future.

Hæmodoraceæ.

Peliosanthes ANDR.

Pelicsanthes courtallensis WIGHT, Ic. Pl. Ind. or. t. 2051; BAKER, in Journ. Linn. Soc. XVII. p. 504; HOOK. f. Fl. Brit. Ind. VI. p. 266.

HAB. Arizan, in montibus Morrison, ad 8000 ped. alt., leg. G. NAKAHARA, 1906; in monte Morrison, ad 6500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2327).

DISTRIB. Travancore.

Liliaceæ.

Smilacina DESF.

Smilacina japonica A. GRAY, Bot. Jap. p. 414; MIQ. Prol. Fl. Jap. p. 313; FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 53; MAXIM. Mél. Biol. XI. p. 857.

Smilacina hirta MAXIM. Prim. Fl. Amur. p. 276.

Smilacina japonica var. *mandschurica* MAXIM. Mél. Biol. p. XI. p. 857.

Tovaria japonica BAKER, in Journ. Linn. Soc. XIV. p. 570; WRIGHT, in FORBES et HEMSL. Ind. Fl. Sin. III. p. 110.

HAB. in monte Morrison, leg. G. NAKAHARA, Oct. 1905; in eodem monte, ad 13000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1900, (No. 2384).

DISTRIB. China and Japan.

Tricyrtis WALL.

Tricyrtis lasiocarpa MATSUM. in Tōkyō Bot. Mag. XI. p. 79; MATSUM. et HAYATA, Enum. Pl. Formos. p. 448.

HAB. Suizan, in montibus Morrison, ad 7703 ped. alt., (No. 730), et Ganzan, in isdem montibus, ad 9141 ped. alt., (Nos. 645 et 695), leg. S. NAGASAWA, Oct. 1905; in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2321).

Tricyrtis stolonifera MATSUM. in Tōkyō Bot. Mag. XI. p. 78; MATSUM. et HAYATA, Enum. Pl. Formos. p. 442.

HAB. in monte Morrison, ad 9000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2319).

Metanarthecium MAXIM.

Metanarthecium foliatum MAXIM. "Decas Pl. Nov. (1882) p. 10."

HAB. in monte Morrison, ad 9000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2328); ibidem, leg. G. NAKAHARA.

DISTRIB. Japan.

Disporum SALISB.

Disporum sp. nov.? Rhizoma repens crassum, caulibus simplicibus sursum foliatis. Folia alterna petiolata oblonga apice abrupte in acumen longum attenuata crassiuscula. Baccæ (ut videntur) ad axillas solitariæ longe pedunculatæ. Flores ignoti.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2329).

Polygonatum ADANS.

Polygonatum officinale ALL. var. **Maximowiczii** FRANCH. et SAVAT.

MAXIM. in Mél. Biol. XI. p. 851; PALIBIN, Conspect. Fl. Koreæ, III. p. 10; FORBES et HEMSL. Ind. Fl. Sin. III. p. 108; MATSUM. et HAYATA, Enum. Pl. Formos. p. 436.

Polygonatum Maximowiczii FR. SCHMIDT, Reis. Amur. p. 185, n. 449.

Polygonatum officinale ALL. *γ. pluriflorum* MIQ. Prol. Fl. Jap. p. 312.

HAB. in herbidis Taiton, ad 4000 ped. alt., leg. U. FAURIE, 1903, (No. 544).

DISTRIB. Type: extends from western Europe through Russia, Siberia and Mongolia to northern China and Japan. Variety: through Japan to Saghalien Manchuria and northern China.

Paris LINN.

Paris lancifolia HAYATA, (Pl. XXXIX.). in Tōkyō Bot. Mag. XX. p. 52. Rhizoma repens multinodosum. Caulis simplex circ. 20–50 cm. longus glaberrimus. Folia ad apicem caulis 7–8 verticillata sessilia lanceolata vel lanceolato-angusta acuminata circ. 12 cm. longa 1 cm. lata 1–nervia, nervis superne impressis subtus prominentibus. Flores ad apicem caulis inter folia verticillata solitarii longe pedunculati exserti, pedunculis 7 cm. longis erectis. Segmenta perianthii distincta 5–mera 2–seriata, exteriora patentissima herbacea lanceolata acuminata 5–6 cm. longa 7–8 mm. lata supra basin leviter contracta, interiora filiformia 2½–3 cm. longa. Stamina 8–10, filamentis ovarium vix superantibus. Ovarium depresso-globosum apice truncatum concavum marginibus prominentibus ad apices carpellorum paullo cornutum, 1–loculare 5–placentiferum, stylo 5-fido, ramis recurvis. Baccæ depresso-globosæ 12 mm. longæ 15 mm. in diametro oligospermæ.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 693); in monte Morrison, ad 9000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1953).

Commelinaceæ.

Aneilema R. Br.

Aneilema divergens Clarke, in Commel. et Cyrt. Beng. t. 16, et in DC. Monogr. Phanerog. III. p. 203; Hook. f. Fl. Brit. Ind. VI. p. 376; Forbes et Hemsl. Ind. Fl. Sin. III. p. 151; Matsum. et Hayata, Enum. Pl. Formos. p. 446.

Aneilema herbaceum Kunth, var. *divergens* Clarke, in Journ. Linn. Soc. XI. p. 448.

Hab. in monte Morrison, ad 6000 ped. alt., leg. T. Kawakami et U. Mori, Oct. 1906, (No. 2326).

Distrib. India and South China.

Cyanotis Don.

Cyanotis arachnoidea Clarke, in DC. Monogr. Phanerog. III. p. 250; Hook. f. Fl. Brit. Ind. VI. p. 386; Henry, List Pl. Formos. p. 99; Forbes et Hemsl. Ind. Fl. Sin. III. p. 157; Matsum. et Hayata, Enum. Pl. Formos. p. 449.

Cyanotis pilosa Wight, Ic. Pl. Ind. or. t. 2083.

Hab. in monte Morrison, ad 3000 ped. alt., leg. T. Kawakami et U. Mori, Oct. 1906, (No. 2325).

Distrib. India and Malay.

Juncaceæ.

Luzula DC.

Luzula effusa Buch. in Engl. Bot. Jarhb. VI. p. 196, et XII. p. 106; Hook. f. Fl. Brit. Ind. VI. p. 401; Diels, Fl. Centr. Chin. p. 237, et Fl. Tin ling shan, in Engl. Bot. Jahrb. XXXIV. Beibl. p. 17; Forbes et Hemsl. Ind. Fl. Sin. III. p. 161.

Hab. in monte Morrison, leg. G. Nakahara, Oct. 1905; eodem monte, ad 12500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2381).

DISTRIB. Central China and Himalaya.

Luzula spicata DC.; HOOK. f. Fl. Brit. Ind. VI. p. 401; BUCH. in ENGL. Bot. Jahrb. XII. p. 128; SOWERBY, Engl. Bot. X. p. 1553.

HAB. in montibus Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2300); ad summam ejusdem montis, ad 13094 ped. alt., leg. S. NAGASAWA, Nov. 1905, (No. 599).

DISTRIB. Widely spread in the alpine regions of Europe, and also in Himalaya and North America; generally in the arctic Zone.

Juncus LINN.

Juncus effusus LINN. Sp. Pl. ed.-2. p. 464; KUNTH, Enum. Pl. III. p. 320; BUCH. in ENGL. Bot. Jahrb. XII. p. 228; " FRANCHET. Pl. David. II. p. 137 "; HOOK. f. Fl. Brit. Ind. VI. p. 392; DIELS, Fl. Centr. Chin. p. 238; FORBES et HEMSL. Ind. Fl. Sin. III. p. 163.

HAB. in montibus Morrison, ad 9000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1821); Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, Oct. 1906, (No. 677).

DISTRIB. Asia, America, Africa, Australia and Europe.

Juncus Maximowiczi BUCH. in ENGL. Bot. Jahrb. XII. p. 394.

HAB. in montibus Morrison, leg. G. NAKAHARA, Oct. 1905.

DISTRIB. Japan.

Aroideæ.

Arisæma sp. (*A. consanguineum* SCHOTT ?)

HAB. in montibus Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2330).

Alocasia (*macrorrhiza* Schott ?)

Hab. in Kagi: Burokusha, leg. T. Kawakami et U. Mori, Oct. 1906, (No. 1752).

Cyperaceæ.

Bulbostylis Kunth.

Bulbostylis capillaris Kunth var. **trifida** Clarke (Fig. 15), in Hook. f. Fl. Brit. Ind. VI. p. 652; Forbes et Hemsl. Ind. Fl. Sin. III. p. 248; Makino, in Tōkyō Bot. Mag. IX p. 390.

Bulbostylis trifida Kunth, Enum. Pl. II. p. 213.

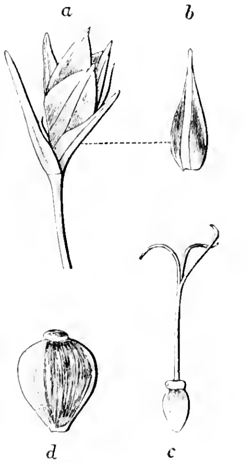

Fig. 15.
Bulbostylis capillaris Kunth var. *trifida* Clarke. *a*— a spikelet; *b*— a glume; *c*— an ovary; *d*— a seed.

Scirpus trifidus Hance, in Journ. Bot. (1878) p. 112.

Hab. in monte Morrison, ad 8000 ped. alt., leg. T. Kawakami et U. Mori, Oct. 1906, (No. 1840).

Distrib. In tropical warm countries; very common in central and southern China and also in southern parts of Japan.

In the present specimens, the spikelets are very small, glumes boat-shaped, lanceolate, ovate, maculate a little above the middle portion, carinate and bearing a small bristle at the apex. Nuts truncate, obovate, longitudinally maculate. (Fig. 15.)

Scirpus Linn.

Scirpus morrisonensis Hayata, sp. nov. (Fig. 16). Culmi plus minus fasciculati gracillimi rigiduli erecti 40–50 cm. alti basi 1 mm. in sectione striati teretes, vaginis inferioribus scariosis ovatis brevibus brunneis superioribus elongatis membranaceis transverse truncatis in laminam brevem productis, laminis lanceolatis minute serrulatis. Spicula quasiterminalis oblongo-elongata leviter arcuata pallido-fusca obtusa parum compressa circ. 10–flora circ. 1 cm. longa 0.7 mm. lata, squamis arcte imbricatis omnibus fertilibus membranaceis obtusis obscure carinatis superioribus ovatis basi breve decurrentibus inferioribus late ovatis basi truncatis, nervo mediano infra apicem evanido, versus apicem fusco-castaneis marginibus pallidis, binis inferioribus latioribus brevibus. Achænium obovatum v. obovato-ellipsoidale trigonum 1½ mm. longum glabrum læve fusco-rubrum, stylo persistenti exserto apice 2–3 fido, setis 6 capillaribus achænio brevioribus.

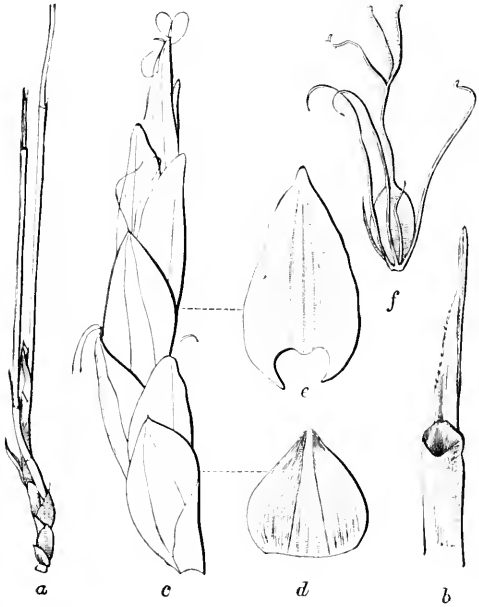

Fig. 16.

Scirpus morrisonensis HAYATA.

a— the basal portion of caules; *b*— a sheath; *c*— a spikelet; *d*— a scale detached from the basal portion of the same spikelet; *e*— a scale detached from the middle portion of the same; *f*— a flower.

HAB. in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1843).

Carex LINN.

The following five species were kindly examined by the Rev. KUEKENTHAL. Owing to the imperfectness of the specimens, as he wrote me, the identification is not easy one. Nevertheless, the descriptions of the plants here given may be of some interest.

Carex sp. (aff. *C. breviculmi* R. BR. subsp. *Royleana* (NEES) KUEK.). Culmi 5–8 cm. longi firmi scabridi apice 2–3 spicas gerentes. Folia 5–7 cm. longa 2 mm. lata culmo breviora firma subtus carinata glaucescentia apice sæpe circinnato-curvata basi vaginata, vaginis 15 mm. longis. Spicæ 2–3; terminalis masculina teres 7 mm. longa 1 mm. lata sæpe basi attenuata, squamis ovatis basi truncatis apice acutis 6 mm. longis 2–3 mm. latis subtrinerviis, nervis castaneis; reliquiæ fœmineæ subsessiles pauciflcræ 8–9 mm. longæ, squamis late ovatis acuminatis late 1–nerviis, nervo producto castaneo, partibus marginibus hyalinis. Utriculus 2–costatus ad costas minute denticulatus ovatus rostratus ore obscure bidentatus glaber. Achænium apice contractum triquetrum 3–costatum. Styli basi conico-crassati. Stigma 3–fidum.

HAB. in monte Morrison, ad 13000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2383).

This *Carex* is very small in its habit and a floriferous culm has a very few spikes on its top. Short branches are sometimes seen at the basal portion of culms.

Carex sp. nov.?

HAB. in monte Morrison, ad 12000 ped. leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2385).

The Rev. KUEKENTHAL informs me that this plant may be a species not yet described; but the specimen is too imperfect to draw a description of it.

Carex sp. (aff. *C. Makinoensi* FRANCH.). Rhizoma? Folia fasciculorum 20–30 cm. longa 2 mm. lata culmo florigero paullo breviora basi vaginata, vaginis 2–3 cm. longis, oribus truncatis, supra et margine scabrida. Culmi florigeri graciles 30 cm. longi

3–4 foliati, foliis superioribus basi vaginatis laminis spica æquilongis. Spicæ 3–4, remote dispositæ; terminalis masculina elongata pedunculata 3 cm. longa 2 mm. lata, squamis obovatis vel late cuneatis marginatis, marginibus badio-fuscis; reliquiæ fœmineæ elongatæ, 2 cm. longæ spica masculina latiores breve pedunculatæ erectæ, floribus remotis, squamis ovatis marginatis acutis basi truncatis. Utriculus 2–carinatus multinervius pubescens, compressus apice rostratus distincte 2-dentatus. Stigma 3–fidum. Achænium trigonum 3–costatum glabrum apice leviter in collum brevissimum coronatum.

HAB. in monte Morrison, ad 9000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2380).

I am informed by the Rev. KUEKENTHAL that this *Carex* have same resemblance to *C. Makinœnsis* FRANCH.

Carex sp. (aff. *C. tristachya* THUNB.). Rhizoma tenue repens, culmos florigeros graciles et fasciculas steriles ad apicem rhizomatis emittens. Folia fasciculorum culmis paullo longiora 17 cm. longa 3–4 mm. lata utraque pagine et margine scabrida. Culmi florigeri graciles circ. 15 cm. longi foliis brevibus instructi; foliis superioribus longe vaginatis in laminam longam vel brevem desinentibus. Spicæ 3–4; terminalis masculina tenuissima breve pedunculata 15 mm. longa 0.5 mm. lata, squamis obovatis basi truncatis marginibus membranaceis subtrinerviis apice tenuiter ciliatis et brevissime mucronatis; reliquiæ fœmineæ pedunculatæ lineares laxifloræ 1–2 cm. longæ, squamis pallidis late ovatis utriculo paullo brevioribus, marginibus hyalinis subtrinerviis, nervo medio ultra apicem in mucronem breviter producto. Utriculus pubescens sub maturitate 3 mm. longus tenuiter membranaceus obovatus breve stipitatus 2–costatus, multinervatus distincte rostratus, rostro bifido, ore scabro. Stigma trifidum. Achænium pallidum glabrum trigonum 3-costatum stipitatum apice abrupte contractum in collum brevissimum coronatum, disco coriaceo albido styli basi conica emarcida superato.

HAB. in monte Morrison, ad 7000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1907, (No. 1846).

This *Carex* somewhat resembles *C. pseudo-conica* FRANCH. et SAVAT., but differs from it in the contracted apex of the achænium possessing collar-like body at the base of the style. The Rev. KUEKENTHAL informs me that the plant is like *C. tristachya* THUNB.

Carex sp. nov. (aff. *C. japonica* THUNB.).

HAB. in monte Morrison, ad 10000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2998).

The Rev. KUEKENTHAL informs me that this *Carex* may be a species not yet described. It is not, however, advisable to draw a description from such an imperfect specimen.

Gramineæ.

Isachne R. BR.

Isachne Clarkei HOOK. f. Fl. Brit Ind. VII. p. 24.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1839).

DISTRIB. Himalaya.

Panicum LINN.

Panicum montanum ROXB. Fl. Ind. ed.-CAREY, I. p. 313; KUNTH, Enum. Pl. I. p. 126; BENTH. Fl. Hongk. p. 412; HOOK. f. Fl. Brit. Ind. VII. p. 53; FORBES et HEMSL. Ind. Fl. Sin. III. p. 331; MERRILL, in Philipp. Journ. Scie. I. Supp. Bot. p. 27.

HAB. in monte Morrison, ad 6500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1848).

DISTRIB. South China, the Malay archipelago, and from Ceylon northward to the mountains of India.

Oplismenus BEAUV.

Oplismenus undulatifolius BEAUV. var. **imbecillis** HACK.; MERRILL, in Philipp. Journ. Scie. I. Suppl. Bot. pp. 28, et 364; HAYATA, in Tōkyō Bot. Mag. XXI. p. 50.

HAB. in monte Morrison, ad 5000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1845).

DISTRIB. Type: Japan. China and the Himalayas. Variety: the Malay archipelago.

Arundinella RADDI.

Arundinella setosa TRIN.; BENTH. Fl. Hongk. p. 416; HOOK. f. Fl. Brit. Ind. VII. p. 70; HACK. in Bull. Herb. Boiss. VII. (1899) p. 723; FORBES et HEMSL. Ind. Fl. Sin. III. p. 342; MATSUM. et HAYATA, Enum. Pl. Formos. p. 515.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1847).

DISTRIB. South China, the Philippine islands, India and Ceylon.

Miscanthus ANDERSS.

Miscanthus sinensis ANDERSS. var. **formosanus** HACK. in Bull. Herb. Boiss. Sér. 2, IV. (1904) p. 526; MATSUM. et HAYATA, Enum. Pl. Formos. p. 518.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1826): in montibus centralibus, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2366).

DISTRIB. Type: Japan. China and the Malay archipelago.

Saccharum LINN.

Saccharum Narenga HAM.; HACK. Monogr. Androp. p. 119; HOOK. f. Fl. Brit. Ind. VII. p. 120; DIELS, Fl. Centr. Chin. p. 222; FORBES et HEMSL. Ind. Fl. Sin. III. p. 349; MATSUM. et HAYATA, Enum. Pl. Formos. p. 519.

Saccharum porphyrocomum HACK. Monogr. Androp. p. 120.

Eriochrysis Narenga NEES, ex STEUD. Syn. Gram. p. 411.

HAB. Nantō: Horisha, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2379).

DISTRIB. India, Burma, and South China.

Spodiopogon TRIN.

Spodiopogon Kawakamii HAYATA, in Tōkyō Bot. Mag. XXI. p. 54.

HAB. Kagi: Tappansha, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1837).

Spodiopogon tainanensis HAYATA, in Tōkyō Bot. Mag. XXI. p. 53.

HAB. Kagi: Kishirei, leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1855).

Pollinia TRIN.

Pollinia ciliata TRIN.; STEUD. Syn. Gram. p. 410; HACK. Monogr. Androp. p. 176, et in Bull. Herb. Boiss. VII. (1899) p. 723; HOOK. f. Fl. Brit. Ind. VII. p. 116; FORBES et HEMSL. Ind. Fl. Sin. III. p. 354.

var. **Wallichiana** HACK. Monogr. Androp. p. 177, et in Bull. Herb. Boiss. VII. (1899) p. 723; MATSUM. et HAYATA, Enum. Pl. Formos. p. 521.

HAB. in monte Morrison, ad 6500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1848).

DISTRIB. South China, India, and Malay.

Cymbopogon SPRENG.

Cymbopogon Nardus RENDLE subsp. **marginatus** var. **Gœringii**

RENDLE, in FORBES et HEMSL. Ind. Fl. Sin. III. p. 376; MATSUM. et HAYATA, Enum. Pl. Formos. p. 531.

Andropogon Nardus LINN. var. *Gœringii* HACK. Monogr. Androp. p. 607, et in Bull. Herb. Boiss. VII. (1899) p. 642, et Sér. 2, III. (1903) p. 501; PALIBIN, Conspect. Fl. Koreæ, III. p. 30.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 1841).

DISTRIB. The Philippine islands, South China, and Japan.

Agrostis LINN.

Agrostis Clarkei HOOK. f. Fl. Brit. Ind. VII. p. 257; HAYATA, in Tōkyō Bot. Mag. XXI. p. 52.

HAB. in monte Morrison, ad 12500 ped. alt., Oct. 1906, (No. 2374); in montibus centralibus, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2365).

DISTRIB. The Himalayas.

Calamagrostis ADANS.

Calamagrostis arundinacea ROTH; HANCE, Journ. Bot. (1878) p. 234; HACK, in Bull. Herb. Bioss. VII. (1899) p. 652, et Sér. 2, III. (1903) p. 502.

Deyeuxia sylvatica KUNTH, Enum. Pl. I. p. 243; HOOK. f. Fl. Brit. Ind. VII. p. 266; FORBES et HEMSL. Ind. Fl. Sin. III. p. 395.

HAB. in monte Morrison, ad 8000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (Nos. 1838 et 1820).

DISTRIB. Japan, the Himalayas, Temperate Asia, and Europe.

var. **nipponica** HACK. in Bull. Herb. Boiss. VII. (1899) p. 652, et Sér. 2, IV. (1904) p. 523.

Calamagrostis nipponica FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 168 et 599.

HAB. ad monte Morrison, 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2373).

DISTRIB. Japan and the Philippine islands?

Deschampsia BEAUV.

Deschampsia cæspitosa BEAUV.; HACK. in Bull. Herb. Boiss. VII. (1899) p. 702; MAXIM. Prim. Fl. Amur. p. 323; HOOK. f. Fl. Brit. Ind. VII. p. 273; FORBES et HEMSL. Ind. Fl. Sin. III. p. 399.

Aira cæspitosa LINN.; STEUD. Syn. Gram. p. 219.

HAB. in monte Morrison, ad 12500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2375).

DISTRIB. Central China, Japan, Himalaya; generally in the temperate and cold regions of the northern and southern hemispheres; and also in the alpine regions in the Tropics.

Deschampsia flexuosa TRIN.; LEDEB. Fl. Ross. IV. p. 420; HACK. in Bull. Herb. Boiss. VII. (1899) p. 702.

Aira flexuosa LINN. var. *montana* FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 172.

HAB. in monte Morrison, ad 13000 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906; in montibus centralibus, leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2364).

DISTRIB. Japan; the arctic regions of Asia and Europe.

Trisetum PERS.

Trisetum subspicatum BEAUV.; STEUD. Syn. Gram. p. 225; HACK. in Bull. Herb. Boiss. VII. (1899) p. 703; FORBES et HEMSL. Ind. Fl. Sin. III. p. 400; BENTH. Fl. Austral. VII. p. 588; MAKINO, in Tōkyō Bot. Mag. XX. p. 44.

Avena subspicata CLAIRV.; HOOK. f. Fl. Brit. Ind. VII p. 278; THOMÉ, Fl. Deut. Öst. Sch. I. p. 145.

HAB. in monte Morrison, ad 12500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2378).

DISTRIB. The Himalayas, central China and the Kurile islands; generally in the alpine and frigid regions.

Arundo Linn.

Arundo formosana Hack. in Bull. Herb. Boiss. VII. p. (1899), p. 724; Forbes et Hemsl. Ind. Fl. Sin. III. p. 408; Matsum. et Hayata, Enum. Pl. Formos. p. 540.

Hab. Taitō: Taiwnkōsha, leg. T. Kawakami et U. Mori, Nov. 1906, (No. 2305).

Distrib. An endemic plant.

Brachypodium Beauv.

Brachypodium Kawakamii Hayata, (Pl. XL.) in Tōkyō Bot. Mag. XXI. p. 51. Perennis ascendens subcæspitosa circ. 20 cm. alta. Folia convoluto-teretia, laminis 5–6 cm. longis 6–7–nerviis, extus glaberrimis intus scabris pauce hirsutis, vaginis 2 cm. longis, ligulis latioribus brevibus leviter ciliolatis. Spiculæ paucæ sæpe ad unam terminalem reductæ longe pendunculatæ sæpe cernuæ, pedunculis filiformibus, 6–7–floræ compressæ 2 cm. langæ 3 mm. latæ, rhachillis inter flores articulatis hirsutissimis; floribus hermaphroditis sæpe superioribus imperfectis. Glumæ 2 inferiores vacuæ 7–nerviæ florentibus minores et breviores muticæ subglabræ; gl. [I.] 7–mm. longa; gl. [II.] longior. Gluma florens rigidula angusta dorso rotundata 7–9–nervia integra in aristam rectam 4 mm. longam desinens; palea gluma vix brevior 7 mm. longa latiuscula 2–carinata, carinis ciliatis, apice truncata et emarginata. Stamina 3. Lodiculæ 2 oblongæ obtusæ basi oblique stipitatæ margine ciliolatæ, lateribus interioribus basi callosis. Ovarium obovatum apice appendicula brevi villosa coronatum. Styli longiusculi, stigmatibus laxe plumosis. Achænia angusta oblonga a dorso compressa antice late sulcata palea adherentia.

Hab. in monte Morrison, ad 12500 ped. alt., leg. T. Kawakami et U. Mori, Oct. 1906, (No. 2377).

As a complete description of the present species was not previously made, I have taken this occasion to give a full account of the plant. It is perhaps the smallest species of *Brachypodium*, which species is very remarkable for its terete leaves and its simplest form of an inflorescence reduced into one spicule. The leaves are very slender and they measure but 1 mm. in diameter, and 3 mm. in circumference.

Brachypodium sylvaticum BEAUV.; MIQ. Prol. Fl. Jap. p. 174; FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 185; HACK. in Bull. Herb. Boiss. XII. (1899), p. 714; HOOK. f. Fl. Brit. Ind. VII. p. 363; LEDEB. Fl. Ross. IV. p. 346; FORBES et HEMSL. Ind. Fl. Sin. III. p. 431.

HAB. in monte Morrison, ad 12000 ped. alt., leg. T. KAWAKAMI et U. MORI, Nov. 1906, (No. 2302).

DISTRIB. North Asia, and the mountains of India and Europe.

Festuca LINN.

Festuca ovina LINN.; MIQ. Prol. Fl. Jap. p. 170; FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 181; THOMÉ, Fl. Deut. Öst. Sch. I. p. 114, t. 53; WAGNER, Deut. Fl. ed-3, p. 82; FORBES et HEMSL. Ind. Fl. Sin. III. p. 429; var. **vulgaris** KOCH; HACK. in Bull. Herb. Boiss. VII. (1899) p. 713, et Sér. 2, III. (1903), p. 506; HAYATA, in Tōkyō Bot. Mag. XXI. p. 51.

HAB. in monte Morrison, ad 12500 ped. alt., leg. T. KAWAKAMI et U. MORI, Oct. 1906, (No. 2376).

DISTRIB. North Asia; Japan and China.

Arundinaria MICH.

Arundinaria niitakayamensis HAYATA, in Tōkyō Bot. Mag. XXI p. 49.

HAB. in monte Morrison, ad 9000 ped. alt., (No. 1842), et ad 8500 ped. alt., (No. 1849), leg. T. KAWAKAMI et U. MORI, Oct. 1906.

Cryptogamiæ.

Lycopodiaceæ.

Lycopodium LINN.

Lycopodium clavatum LINN. Sp. Pl. ed.-2, p. 1564; HOOK. Brit. Fern. t. 49: BAKER, Fern All. p. 26; THUNB. Fl. Jap. p. 341; MIQ. Prol. Fl. Jap. p. 348; MAXIM. in Mél. Biol. VII. p. 341; FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 197; LUERSS. in ENGL. Bot. Jahrb. IV. p. 366; DIELS, Fl. Centr. Chin. p. 210; WARB. Mons. I. p. 97; HAYATA, in Tōkyō Bot. Mag. XX. p. 20.

HAB. in monte Morrison, leg. S. NAGASAWA, T. KAWAKAMI et G. NAKAHARA, Nov. 1905.

DISTRIB. West and East China and Japan; arctic and alpine zones of both hemispheres; also mountains of Tropical Asia, Africa and America.

Lycopodium complanatum LINN. Sp. Pl. ed.-2, p. 1567; BAKER, Fern All. p. 28; DIELS, Fl. Centr. Chin. p. 210.

var. **Chamæcyparissus** A. BR. "in DŒLL, Rhein Flora p. 36"; BAKER, Fern All. p. 29; MAXIM. in Mél. Biol. VII. p. 341; FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 198; HAYATA, in Tōkyō Bot. Mag. XX. p. 21.

HAB. in monte Morrison, leg. S. NAGASAWA, T. KAWAKAMI et G. NAKAHARA, Nov. 1905.

DISTRIB. Japan and central and southern China; generally in the temperate zone of both hemispheres; also in some tropical regions of Asia and America; subcosmopolitan.

Lycopodium obscurum LINN. Sp. Pl. ed-2, p. 1566; BAKER, Fern

All. p. 24; HAYATA, in Tōkyō Bot. Mag. XX. p. 21; KOMAROV, Fl. Manshur. I. p. 159.

Lycopodium japonicum THUNB. Fl. Jap. p. 341; MAXIM. in Mél. Biol. VII. p. 341; FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 197.

Lycopodium dendroideum MICHX.; MIQ. Prol. Fl. Jap. pp. 348 et 390; HOOK. Exot. Fern. t. 7.

HAB. in monte Morrison, leg. T. KAWAKAMI, S. NAGASAWA et G. NAKAHARA, Nov. 1905.

DISTRIB. Japan, Kamtchatka, Siberia, Manchuria, and North America. Not yet known from central and southern China.

Lycopodium serratum THUNB. Fl. Jap. p. 341; A. GRAY, Bot. Jap. pp. 422 et 436; MIQ. Prol. Fl. Jap. pp. 348 et 390; BAKER, Fern All. p. 12; MAXIM. in Mél. Biol. VII. p. 341; DIELS, Fl. Centr. Chin. p. 210; WARB. Mons. I. p. 96; HAYATA, in Tōkyō Bot. Mag. XX. p. 20.

HAB. in monte Morrison, ad 13094 ped. alt., leg. S. NAGASAWA, (No. 735); ibidem, leg. T. KAWAKAMI et G. NAKAHARA, Nov. 1905.

DISTRIB. In the tropical or subtropical regions, and in some temperate countries as Japan and China.

This Morrison plant is of a form having much broader leaves than the Japanese species.

Polypodiaceæ.

Polystichum ROTH.

Polystichum amabile SM.; DIELS, in Nat. Pfl.-fam. I-4, p. 193; MATSUM. et HAYATA, Enum Pl. Formos. p. 582.

Aspidium amabile BLUME; METT. in Ann. Mus. Bot. Lugd.-Bat. I. p. 227; MIQ. Prol. Fl. Jap. pp. 340 et 389: HOOK. Sp. Fil. IV. p. 25, t. 225; HOOK et BAKER, Syn. Fl. p. 254; FRANCH. et SAVAT. Enum. Pl. Jap. II. p. 232.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, Oct. 1905, (No. 659).

DISTRIB. Japan and central and eastern China and the Malay archipelago.

Polystichum niitakayamense HAYATA, (Pl. XLI.) in Tōkyō Bot. Mag. XXI. p. 14.

Stipites 10–12 cm. longi fusco-pallidi paleacei leviter canaliculati basin teretes, paleis oblongis vel linearibus. Frondes 25–30 cm. longæ 2 cm. latæ erectæ circumscriptione lineares pinnatæ, pinnis 7–8 mm. longis 5 mm. latis approximatis horizontaliter patentibus oblongis vel oblongo-quadrangularibus angulo inferiore affixis, basi superiore transverse truncatis auriculatis, basi superiore et apice aristatis, margine obscure crenulatis. Indusium 0. Sporangium fuscum longe pedicellatum. Sporæ oblongæ tuberculatæ.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, 1905, (No. 698).

Asplenium LINN.

Asplenium laciniatum DON. "Prodr. Fl. Nep. p. 8"; HOOK. Sp. Fil. III. p. 164, t. 200, A; HOOK. et BAKER, Syn. Fil. p. 211; CLARKE, Rev. Fern. North Ind. p. 481; BEDD. Fern. South Ind. p. 49, t. 145; HAYATA, in Tōkyō Bot. Mag. XXI. p. 12.

HAB. Suizan, in montibus Morrison, ad 7702 ped. alt., leg. S. NAGASAWA, 1905, (No. 656).

DISTRIB. The temperate regions of the Himalayas and Japan. Not yet found in the Philippines or China.

Asplenium Trichomanes LINN.; HOOK. Sp. Fil. III. p. 136, et Brit. Fern. t. 29; METT. in Ann. Mus. Bot. Lugd.-Bat. II. p. 234; MIQ. Prol. Fl. Jap. p. 337; HOOK. et BAKER, Syn. Fil. p. 196; CHRIST, Farn. Erd. p. 192; BEDD. Fern. South Ind. p. 49, t. 147; HAYATA, in Tōkyō Bot. Mag. XXI. p. 14; DIELS, Fl. Centr. Chin. p. 198.

Asplenium anceps SOL.; HOOK. et GREV. Ic. Fil. t. 195.

HAB. in monte Morrison, leg. G. NAKAHARA, 1906.

DISTRIB. Subcosmopolitan in the temperate and cold regions of both hemispheres.

Coniogramme FÉE.

Coniogramme fraxinea (DON.) FÉE; DIELS, in Nat. Pfl.-fam. I.-4. p. 262; COPELAND, Polyp. Philipp. p. 66; HAYATA, in Tōkyō Bot. Mag. XXI. p. 15.

Gymnogramme javanica BLUME, Fl. Jav. II. p. 95, t. 41; HOOK. et BAKER, Syn. Fil. p. 381; MIQ. Prol. Fl. Jap. p. 335; FRANCH. et SAVAT, Enum. Pl. Jap. II. p. 248; HENRY, List Pl. Formos. p. 116.

HAB. Sanchōkei, leg. S. NAGASAWA, 1905, (No. 721).

DISTRIB. Tropics in the old world.

Plagiogyria KUNZE.

Plagiogyria glauca (BLUME) METT. Plagiog. p. 273; Bedd. Fern. Brit. Ind. t. 90.

Lomaria glauca BLUME, "Enum. Fl. Java. Fil. p. 204"; CLARKE, Rev. Fern. North Ind. p. 472; HOOK. Sp. Fil. III. p. 22; HOOK et BAKER, Syn. Fil. p. 182.

var. **philippinensis** CHRIST, in Bull. Herb. Boiss. VI. (1898) p. 151; COPELAND, Polyp. Philipp. p. 98; HAYATA, in Tōkyō Bot. Mag. XX. p. 22.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, 1905.

DISTRIB. The Philippine islands.

Plagiogyria Matsumureana MAKINO, in Tōkyō Bot. Mag. VIII. p. 335; HAYATA, in Tōkyō Bot. Mag. XXI. p. 14.

Lomaria Matsumureana MAKINO, in Tōkyō Bot. Mag. VIII. p. 90.

HAB. Rakurakusha, leg. G. NAKAHARA, 1905, (No. 458).

DISTRIB. Japan.

Pteridium GLED.

Pteridium aquilinum KUHN. var. **lanuginosum** BORY; COPELAND, Polyp. Philipp. p. 104; HAYATA, in Tōkyō Bot. Mag. XXI. p. 12.

HAB. Ganzan, in montibus Morrison, ad 9141 ped. alt., leg. S. NAGASAWA, 1905, (No. 676).

DISTRIB. Tropics.

Polypodium LINN.

Polypodium lineare THUNB. var. ? HAYATA, in Tōkyō Bot. Mag. XXI. p. 13.

HAB. in monte Morrison, leg. G. NAKAHARA, 1905.

DISTRIB. Type: Tropics of the old world; Japan and China.

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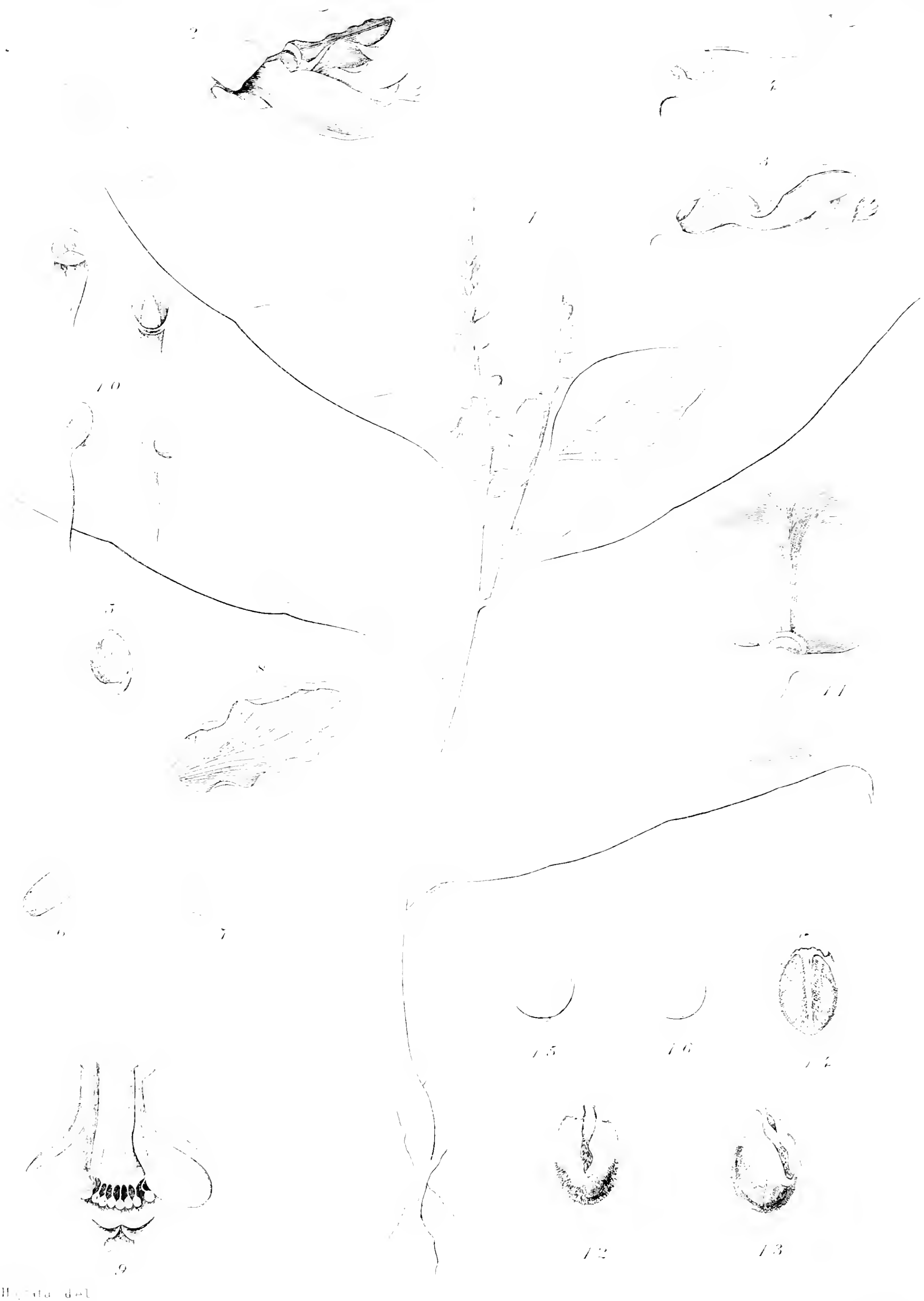
PLATE I.

Polygala arcuata HAYATA.

Fig. 1. The plant.
2. A flower.
3. The same, sepals taken off, showing petals.
4. A pistil.
5. The superior sepal of the exterior series.
6 and 7. The inferior sepals of the exterior series.
8. A sepal of the interior series.
9. Petals and stamens seen from above, petals a little expanded.
10. Stamens, seen from various sides.
11. A capsule
12. A seed, seen from the dorsal side.
13. The same, seen from the lateral side.
14. The same, seen from the ventral side.
15. An albumen.
16. An embryo.



B. Hayata del.

PLATE II.

PLATE II.

Stellaria stellato-pilosa HAYATA.

Fig. 1. A branch.

2. A leaf detached from an upper portion of a stem.
3. Transverse section of a leaf, showing stellate hairs on both sides of the leaf.
4. A stellate hair on the upper surface of a leaf.
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6. A flower.
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8. A capsule with persistent sepals and petals.
9. A capsule after dehiscence.
10. A placenta in a capsule
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12. An embryo.

B. Hayata del.

T. Fujiwara lith.

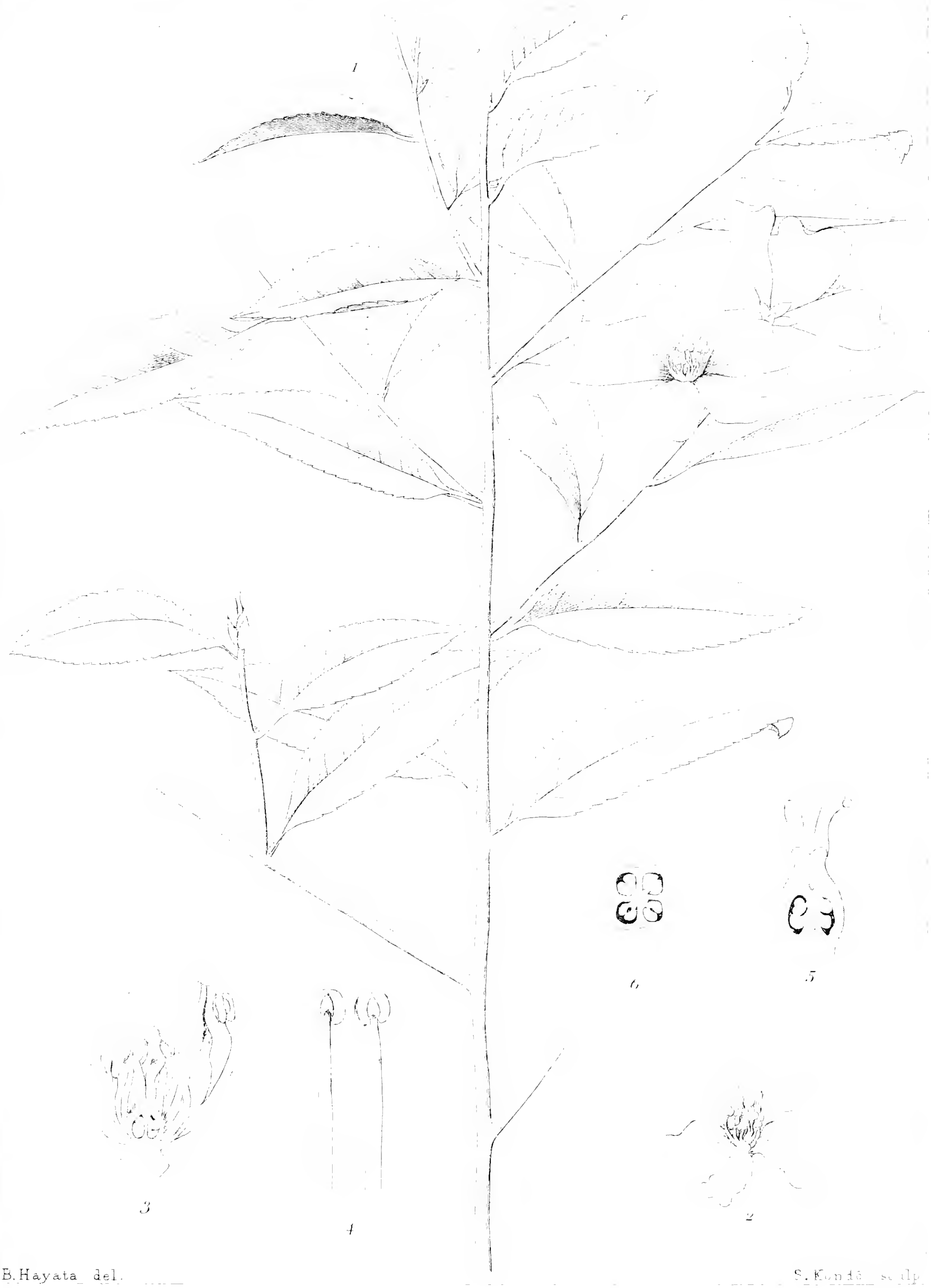
B. HAYATA.
FLORA MONTANA FORMOSÆ.

PLATE III.

PLATE III.

Thea brevistyla HAYATA.

Fig. 1. A branch.
2. A flower.
3. Vertical section of a flower, upper parts of the petals taken off.
4. Stamens, one seen from the ventral side, and the other, from the dorsal side.
5. Vertical section of an ovary.
6. Cross section of the same ovary.



B.Hayata del.

S.Kondō sculp.

B. HAYATA.
FLORA MONTANA FORMOSÆ.

PLATE IV.

PLATE IV.

Rubus elegans HAYATA.

Fig. 1. The plant.
2. A leaf, detached from the basal portion of a stem.
3. A flower seen from the under side.
4. A petal.
5. Fruits.
6. Vertical section of the same.
7. A stamen, seen from the inner side.
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9. A fruit.
10. Another one, highly magnified.

B. Hayata del.

PLATE V.

PLATE V.

Potentilla leuconota DON. var. *morrisonicola* HAYATA.

Fig. 1. The plant.
2. A radical leaf.
3. A flower, seen from the upper side.
4. Another one, seen from the under side.
5. Stamens, one seen from the ventral side, and the other, from the dorsal side.
6. A pistil.
7. Fruits on a receptacle.
8. A fruit.
9. The same, in vertical section.
10. An embryo.

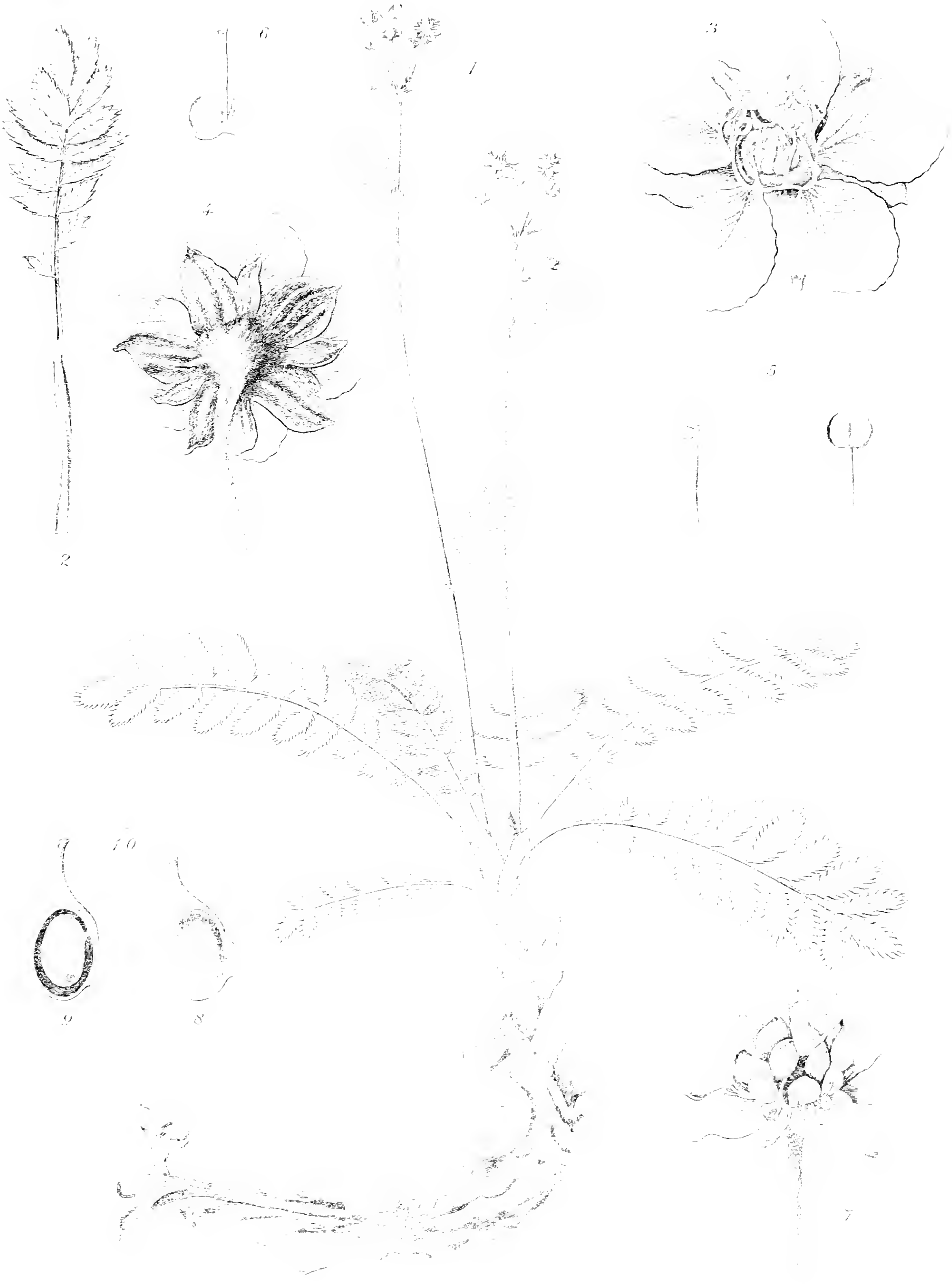
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PLATE VI.

PLATE VI.

Hydrangea glabra HAYATA.

Fig. 1. The plant.
2. A fruit.
3. The same, in cross section.
4. A seed.
5. An embryo.

B.Hayata del.

PLATE VII.

PLATE VII.

Hydrangea integra HAYATA.

Fig. 1. The plant.
2. A fruit.
3. The same, in vertical section.
4. A seed.
5. An embryo.

B Hayata det.

B. HAYATA.

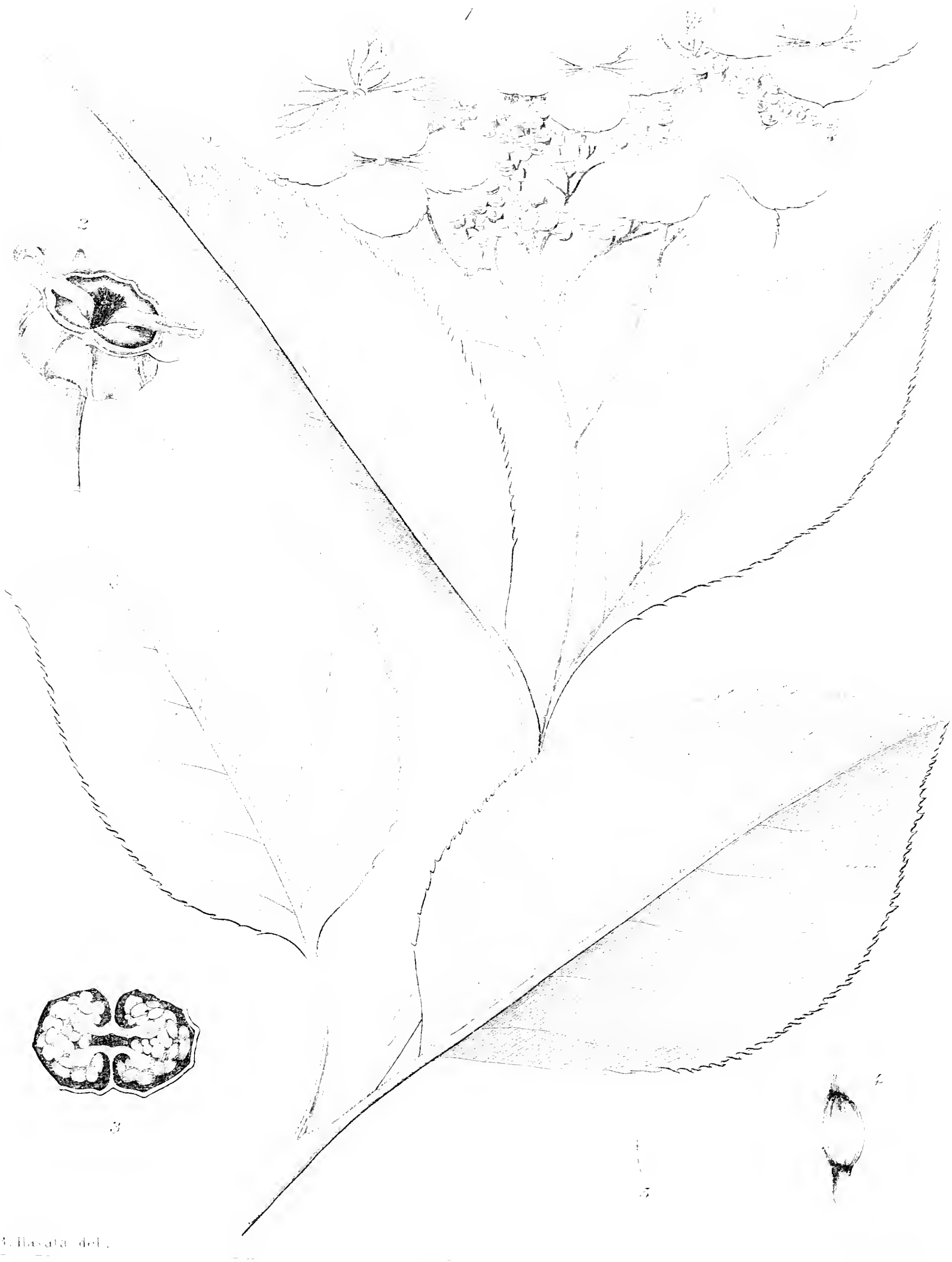
FLORA MONTANA FORMOSÆ.

PLATE VIII.

PLATE VIII.

Hydrangea Kawakamii HAYATA.

Fig. 1. The plant.
2. A fruit.
3. The same, in cross section.
4. A seed.
5. An embryo.



B. Hayata del.

PLATE IX.

PLATE IX.

Ribes formosanum HAYATA.

Fig. 1. A branch.
2. Calyx and petals, laid open.
3. Styles.
4. A fruit.
5. Seeds.
6. A seed (highly magnified)
7. An embryo.

B. Hayata del.

B. HAYATA.

FLORA MONTANA FORMOSÆ.

PLATE X.

PLATE X.

Barthea formosana HAYATA.

Fig. 1. A branch.
2. A flower-bud.
3. A flower.
4. A petal.
5. A portion of the upper margin of a petal
6. A longer stamen, (dorsal view.)
7. The same, (lateral view.)
8. A shorter stamen, (lateral view.)
9. An ovary, in vertical section.
10. The same, in cross section, stamens are seen in the holes of the wall of the calyx tube.
11. A capsule, a part of the calyx taken off.
12. Seeds, seen from different sides.
13. An embryo.

B.Hayata del.

B. HAYATA.

FLORA MONTANA FORMOSÆ.

PLATE XI.

PLATE XI.

Thladiantha formosana HAYATA.

Fig. 1. A branch.
2. A flower, seen from above.
3. The same, seen from below.
4. A flower-bud.
5. Stamens and glands at the base of filaments.

B. Hayata del.

[illegible]

B. HAYATA.

FLORA MONTANA FORMOSÆ.

PLATE XII.

PLATE XII.

Sanicula petagnioides HAYATA.

Fig. 1. The plant.
2. An umbel.
3. A male flower, seen from side.
4. The same, seen from below.
5. The same, seen from above.
6. A stamen, seen from within.
7. The same, seen from without.
8. A perfect flower.
9. A fruit.
10. The same, in cross section.

8

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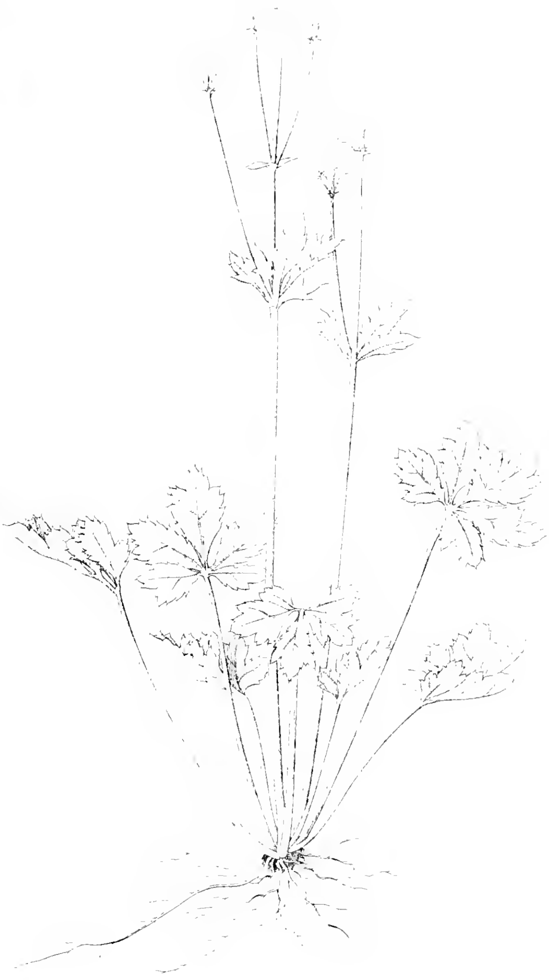

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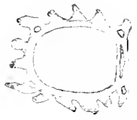

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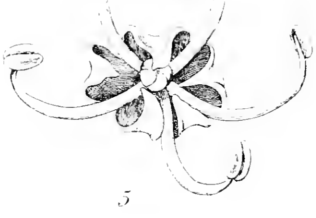

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4

B. Hayata del

S. Kondō sculp.

PLATE XIII.

PLATE XIII.

Fatsia polycarpa HAYATA.

Fig. 1. The plant.
2. An umbel, not yet unfolded.
3. The same, seen from a different side.
4. An outer larger bract.
5. Two inner smaller bract.
6. A flower-bud.
7. The same, in vertical section.
8. An ovary, in cross section.
9. Stamens, seen from different sides.
10. A flower.
11. The apex of a style.
12. A petal.

B. Hayata del.

PLATE XIV.

PLATE XIV.

Oreopanax formosana HAYATA.

Fig. 1. A branch.
2. A head.
3. The same, in vertical section.
4. A flower, in vertical section.
5. An ovary, in cross section.
6. An ovary, in a more advanced stage.
7. Stamens, seen from different sides.
8. A head of fruits.
9. A ruminate albumen.
10. The same, in vertical section, the embryo is seen.
11. The same embryo, more enlarged.
12. Section of a fruit; a seed is ripe, while the other is abortive.
13. A seed (lateral view).
14. The same (dorsal view).
15. An inferior bract.
16. A lateral bract.
17. Hairs covering all over the plant.
18. A stellate hair dotting the surface of a leaf and inflorescence.

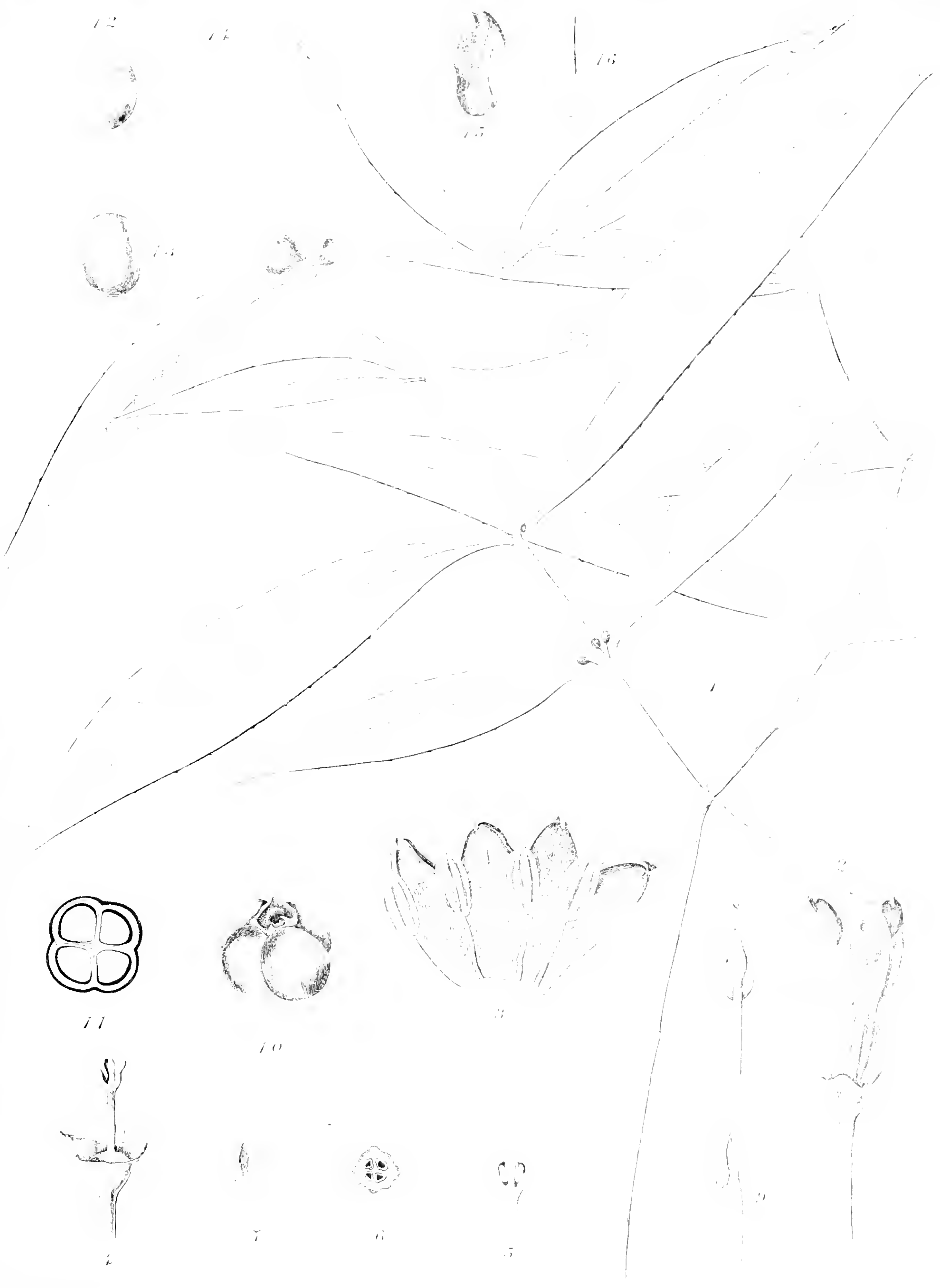
B. Hayata del.

PLATE XV.

PLATE XV.

Damnacanthus angustifolius HAYATA.

Fig. 1. A branch.
2. A flower.
3. Corolla and stamens, laid open.
4. A flower showing the ovary, corolla and stamens taken off.
5. An ovary, in vertical section.
6. The same, in cross section.
7. An ovule.
8. A stamen (dorsal view).
9. The same (lateral view).
10. A fruit.
11. The same, in cross section.
12. A seed (ventral view).
13. The same (dorsal view).
14. An albumen, in section, the embryo seen.
15 and 16. An embryo, seen from different sides.



B. Hayata del.

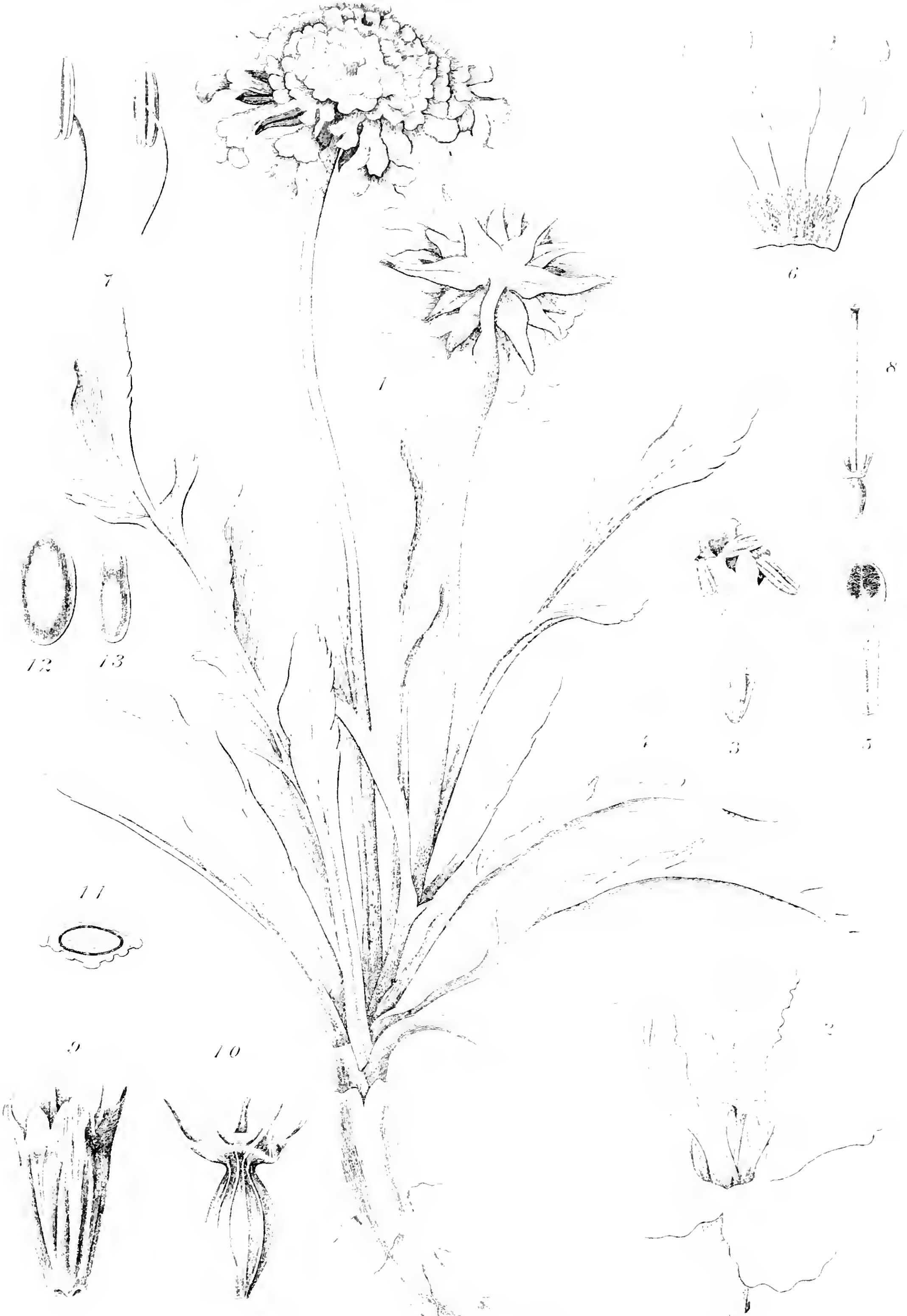
B. HAYATA.
FLORA MONTANA FORMOSÆ.

PLATE XVI.

PLATE XVI.

Scabiosa lacerifolia HAYATA.

Fig. 1. The plant.
2. A marginal flower.
3. A disc-flower.
4. Cross section of an involucel.
5. A bract of a flower.
6. Corolla and stamens, laid open.
7. Stamens, seen from different sides.
8. An inferior ovary.
9. A fruit in the involucel.
10. The same, the involucel taken off.
11. Cross section of the same.
12. An albumen.
13. An embryo.



B. Hayata del.

B. HAYATA.

FLORA MONTANA FORMOSÆ.

PLATE XVII.

PLATE XVII.

Leontopodium microphyllum HAYATA.

Fig. 1. The plant.
2. A cyme of heads.
3. A head.
4. A bract of an involucre.
5. A female and fertile flower.
6. A perfect and sterile flower.
7. A female fertile flower, pappus taken off, corolla seen.
8. Stamens of a perfect and sterile flower.
9. A style of the same flower.
10. A stamen, more magnified.
11. An apical portion of a style.
12. Setæ of a pappus.

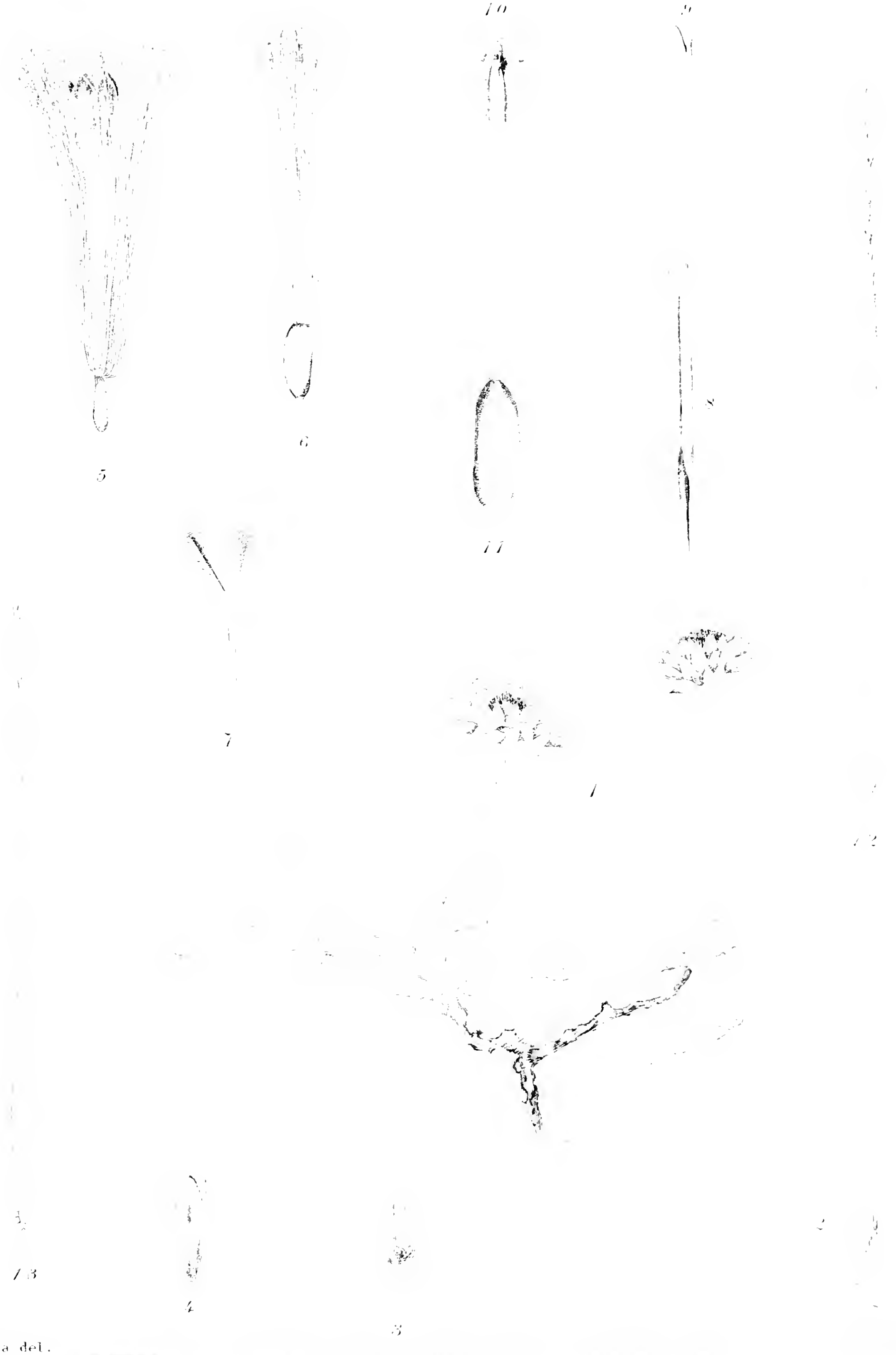
B. Hayata del.
S. Kondō sculp.

PLATE XVIII.

PLATE XVIII.

Anaphalis Nagasawai HAYATA.

Fig. 1. The plant.
2. An inner bract.
3. An outer-most bract.
4. An inner-most bract.
5. A perfect and sterile flower.
6. A female and fertile flower.
7. The apical portion of the style of a perfect flower.
8. A stamen of a perfect flower.
9. The apical portion of the style of a female flower.
10. The apical portion of the corolla of a femal flower.
11. An achene.
12. A bristle of the pappus of a perfect flower.
13. A bristle of the pappus of a female flower.



B. Hayata del.

PLATE XIX.

PLATE XIX.

Gnaphalium lineare HAYATA.

Fig. 1. The plant.
2. A head.
3. A female flower.
4. A perfect flower.
5. A stamen of the same flower.
6. The apical portion of the style.
7. The apical portion of the corolla of a female flower.
8. An achene.
9. A bristle of a pappus.
10. An outer-most bract.
11. An inner-most bract.

B. Hayata del.

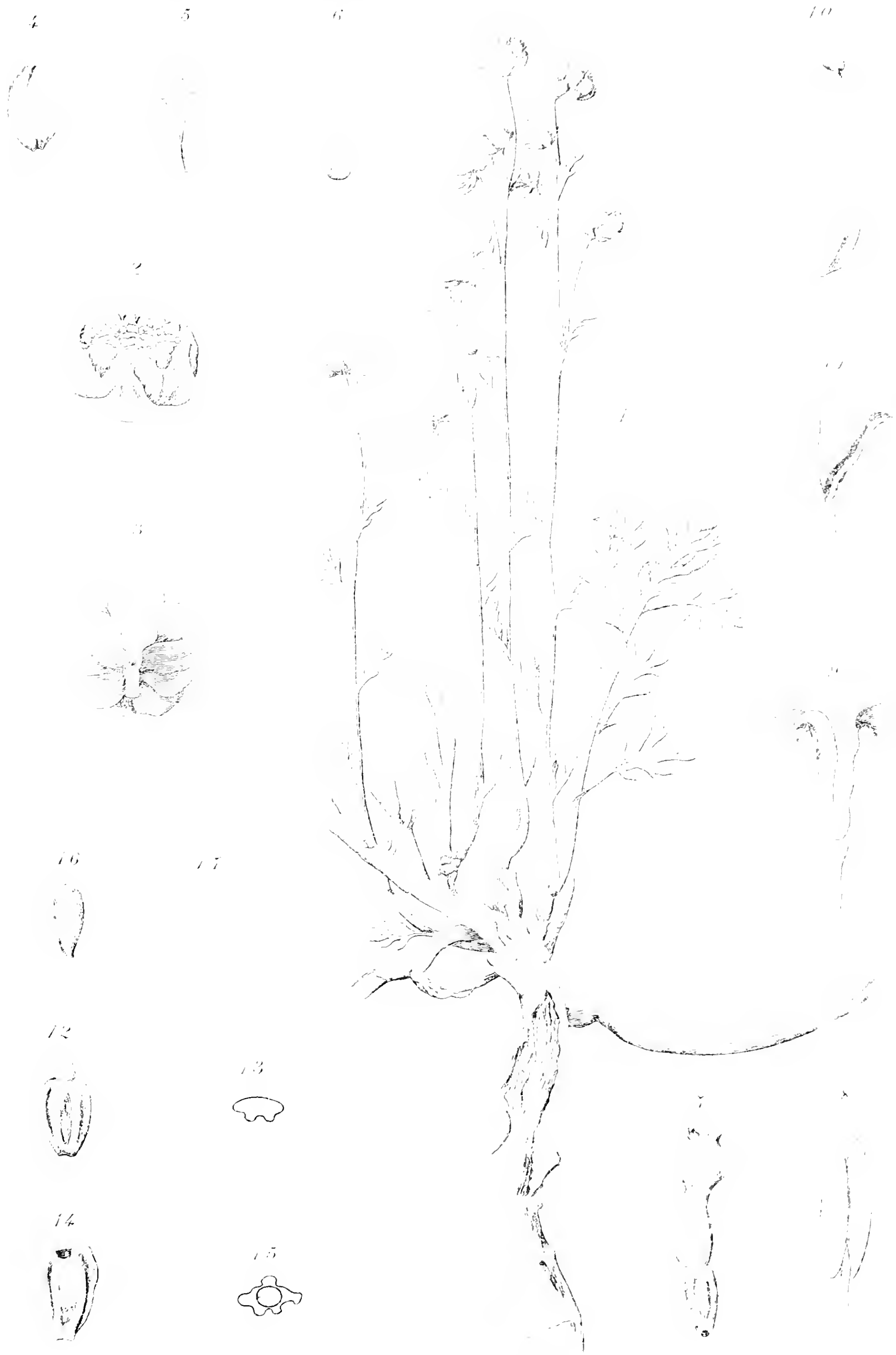
T. Fujiwara sc.

PLATE XX.

PLATE XX.

Artemisia niitakayamensis HAYATA.

Fig. 1. The plant.
2. A head.
3. The same, seen from a little below.
4. An outer-most bract.
5. An inner bract.
6. An inner-most bract.
7. A perfect flower.
8. A stamen of the same flower.
9. The apical portion of the style.
10. A female flower.
11. The apical portion of the style of the same flower.
12. An achene.
13. The same, in cross section.
14. Another achene.
15. The same, in cross section.
16. A seed.
17. An embryo



B.Hayata del.

B. HAYATA.

FLORA MONTANA FORMOSÆ.

PLATE XXI.

PLATE XXI.

Artemisia oligocarpa HAYATA.

Fig. 1. The plant.
2. A head.
3. A female flower.
4. A perfect and sterile flower.
5. The stamens of the same flower.
6. The upper portion of the style of the same flower.
7. The same, more magnified.
8. A stamen of the same flower.
9. The upper portion of the corolla.
10. An Achene.
11. An embryo.

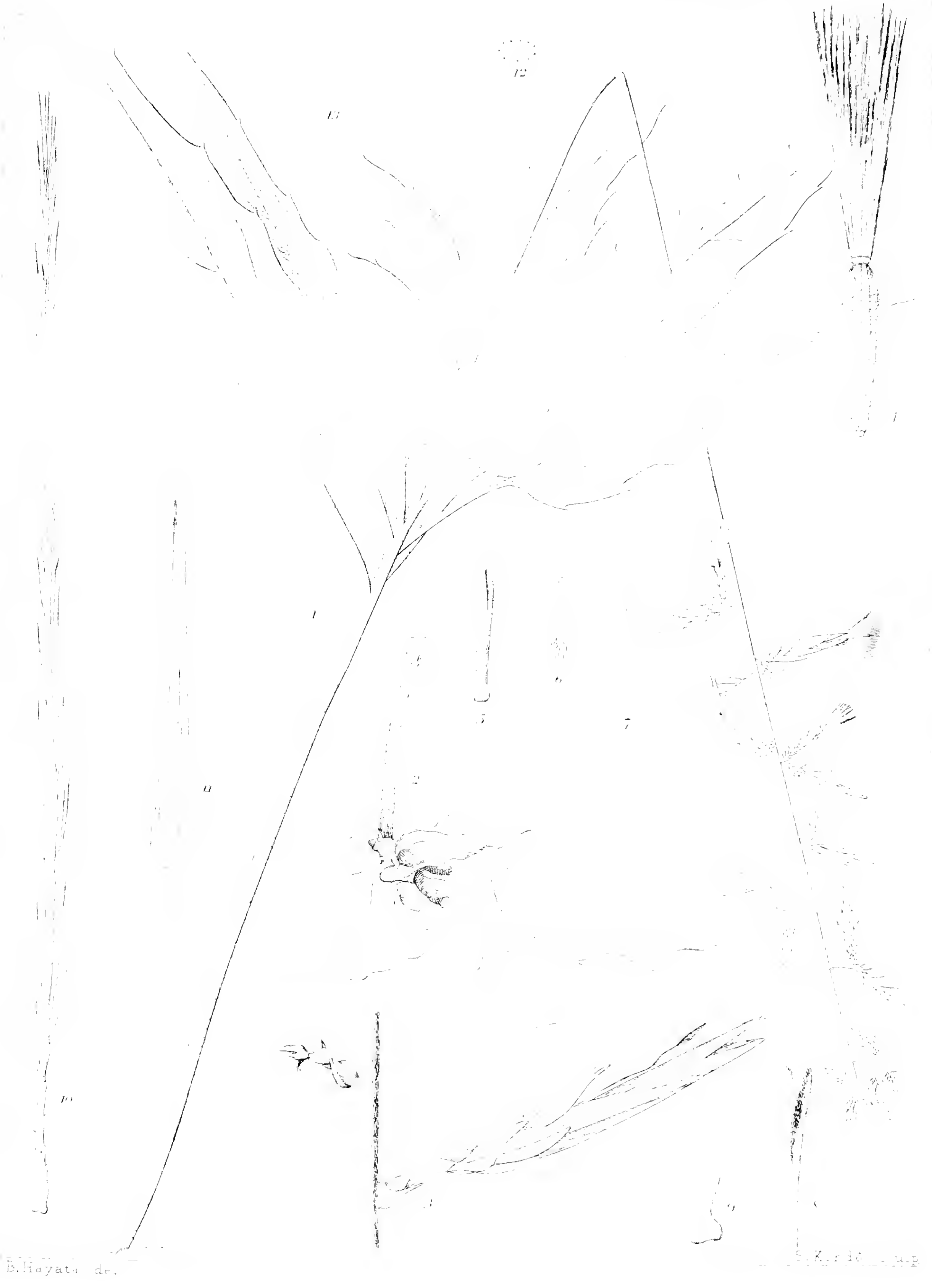
B.Hayata del.

PLATE XXII.

PLATE XXII.

Ainsliaea macroclinidioides HAYATA.

Fig. 1. The plant.
2. Roots.
3. A part of an inflorescence.
4. A cleistogamous flower.
5. The corolla of the same flower.
6. The stamens of the same flower.
7. The style of the same flower.
8. The upper portion of the same style.
9. The basal portion of the same style.
10. A bristle of a pappus.
11. A stamen, much more magnified.
12. Cross section of an achene.
13. An embryo.



B. Hayata del.

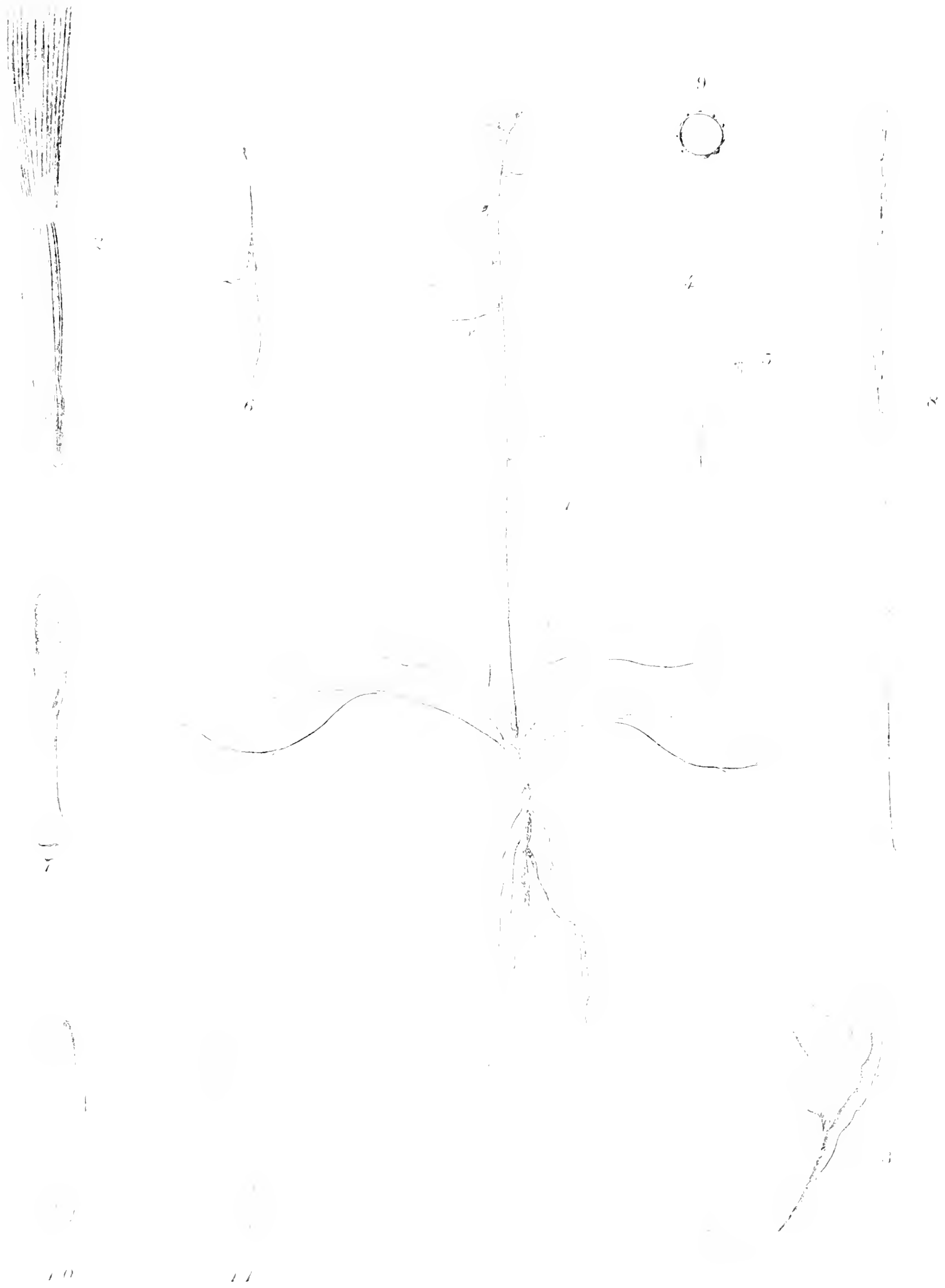
S. Kondō imp.

PLATE XXIII.

PLATE XXIII.

Ainsliæa morrisonicola HAYATA.

Fig. 1. The plant.
2. A cleistogamous flower.
3. A radical leaf.
4. Corolla.
5. Stamens.
6. A stamen, much more magnified.
7. A style.
8. A bristle of a pappus.
9. Cross section of an achene.
10. A seed.
11. An embryo.



B. Hayata del.

PLATE XXIV.

PLATE XXIV.

Vaccinium Merrillianum HAYATA.

Fig. 1. A branch.
2. Seeds (natural size)
3. A seed, highly magnified.
4. An albumen.
5. An embryo.

B.Hayata del.

B. HAYATA.
FLORA MONTANA FORMOSÆ.

PLATE XXV.

PLATE XXV.

Gaultheria Itoana HAYATA.

Fig. 1. The plant.
2. A flower-bud.
3. A flower.
4. A stamen (ventral view).
5. The same (dorsal view).
6. The same (lateral view).
7. An ovary.
8. The same, in cross section.
9. A fruit.
10. The same, in vertical section.
11. Seeds.
12 and 13. The same, seen from different sides, highly magnified.
14. An albumen.
15. An embryo, in the same proportion.
16. The same, much more magnified.

B.Hayata del.

PLATE XXVI.

PLATE XXVI.

Rhododendron pseudo-chrysanthum HAYATA.

Fig. 1. A branch.
2. An inflorescence.
3. An inner-most bract.
4, 5, 6, 7, 8, 9 and 10. Bracts of different series.
11. An outer-most bract.
12. A corolla, laid open.
13. Stamens.
14 and 15. The same, seen from different sides.
16. An ovary.
17. The same, much more magnified.
18. The upper portion of a style.
19. Cross section of an ovary.
20. A capsule, in vertical section.
21. Cross section of a capsule.
22. Seeds (natural size).
23. A seed highly magnified.
24. An embryo.

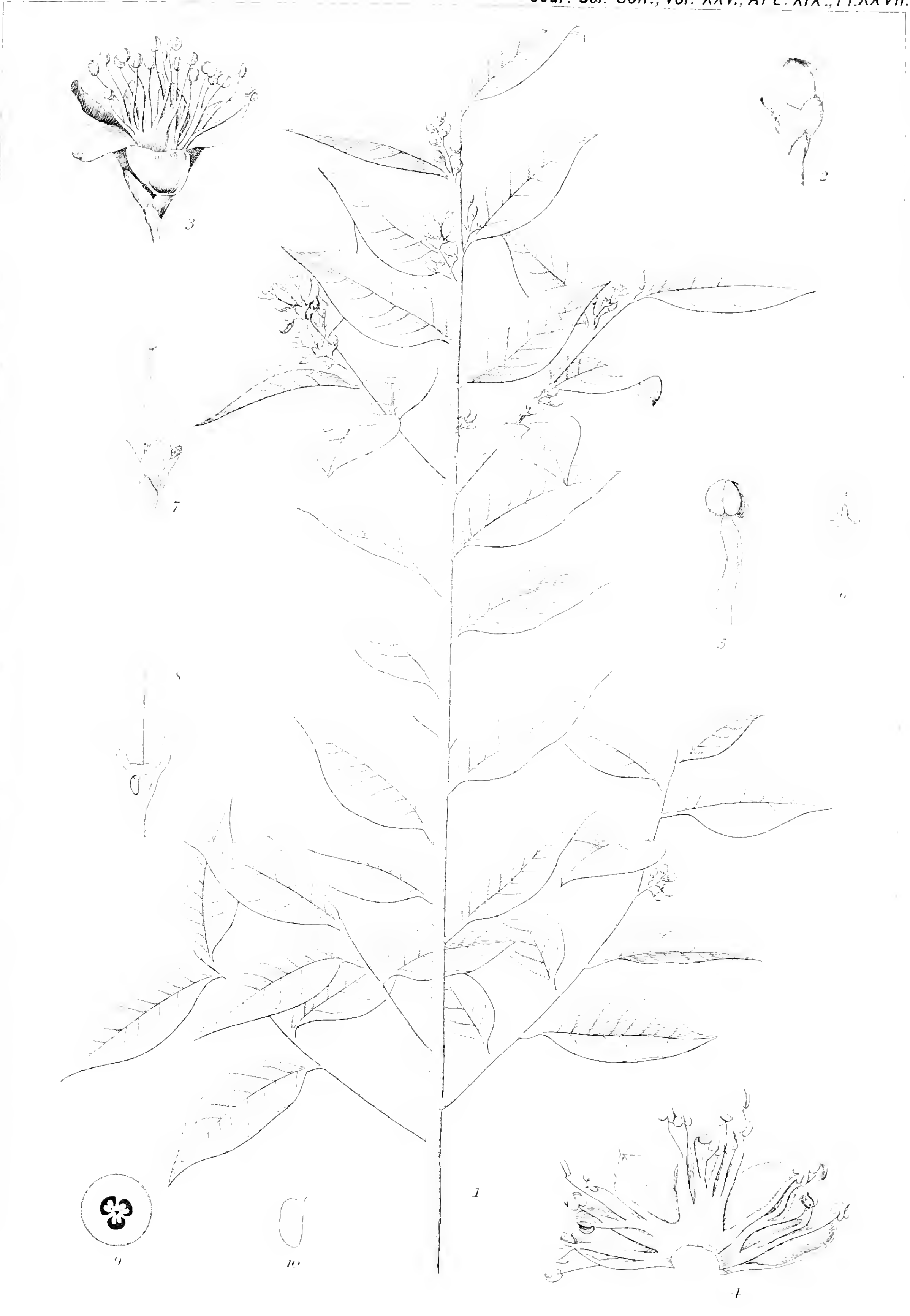
B. Hayata del.

PLATE XXVII.

PLATE XXVII.

Symplocos morrisonicola HAYATA.

Fig. 1. A branch.
2. A flower-bud.
3. A flower.
4. Corolla and stamens laid open.
5. A stamen, seen from without.
6. The same, seen from within.
7. A calyx.
8. The same, in vertical section.
9. Cross section of an ovary.
10. An ovule.



B.Hayata del.

S. Kondō sculp.

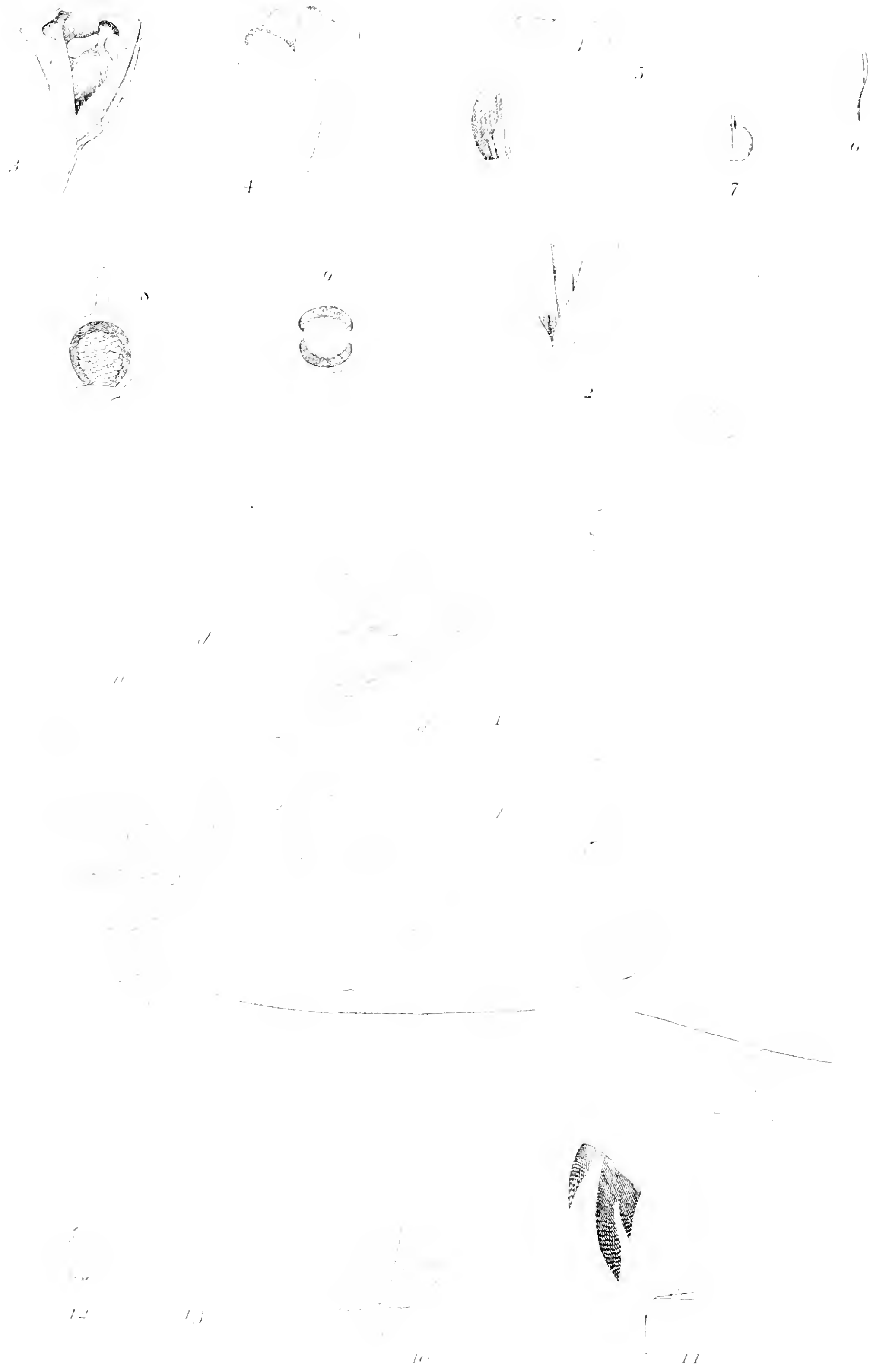
PLATE XXVIII.

PLATE XXVIII.

Lagunia dentata (ELMER) HAYATA.

Fig. 1. The plant.

2. A deformed flower.
3. A flower.
4. The same, a part of the calyx taken off, the corolla seen.
5. The same corolla, laid open.
6. A stamen, seen from without.
7. An ovary.
8. The same, in vertical section,much more magnified.
9. The same, in cross section.
10. A capsule.
11. The same, after opening.
12. A seed.
13. An embryo.



B. Hayata del.

K. Nakazawa sculp.

B. HAYATA.

FLORA MONTANA FORMOSÆ.

PLATE XXIX.

PLATE XXIX.

Veronica morrisonicola HAYATA.

Fig. 1. The plant.
2. A flower, seen from side.
3. The same, seen from above.
4. A corolla, laid open.
5. An ovary.
6. A branch bearing fruits.
7. A fruit.
8. The same, in vertical section.
9. The seeds (natural size).
10. A seed, magnified.
11. An embryo.

B. Hayata del.

PLATE XXX.

PLATE XXX.

Polygonum minutum HAYATA.

Fig. 1. The plant.
2. A sheath.
3. A flower on a branchlet.
4. A flower.
5. A perianth, laid open.
6. An ovary.
7. Stamens, seen from different sides.
8. An ovary.
9. A fruit.
10. The same, in vertical section, showing the embryo in it.
11. The embryo.

B.Hayata del.

PLATE XXXI.

PLATE XXXI.

Polygonum morrisonense HAYATA.

Fig. 1. The plant.
2. A branch, showing sheaths.
3. A head.
4. Bracts, seen from different sides.
5. A flower.
6. A perianth, laid open.
7. An ovary.
8. A stamen with a gland at the base of the filament.
9. A fruit.
10. A seed.
11. An embryo.

B. Hayata del.

[illegible]

PLATE XXXII.

PLATE XXXII.

Peperomia Nakaharai HAYATA.

Fig. 1. The plant.
2. A spike.
3. A female flower, seen from the dorsal side.
4. The same, seen from lateral side.
5. The same, in a more advanced stage.
6. A fruit.

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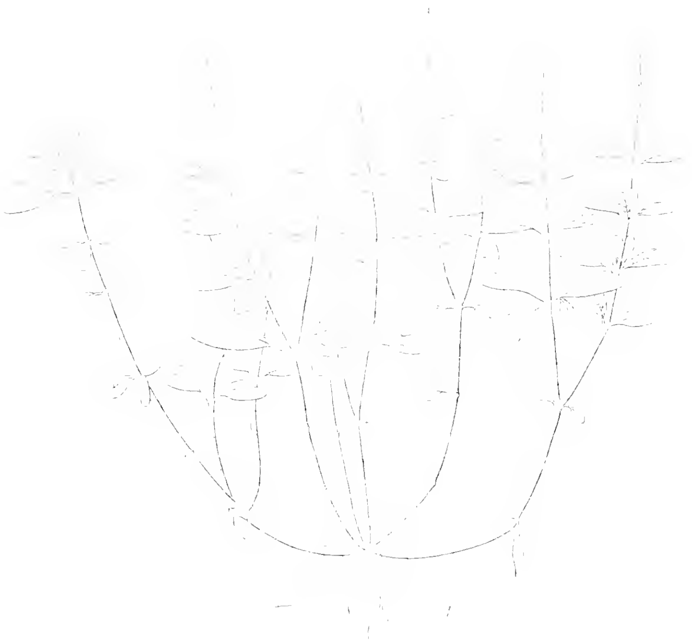

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B. Hayata

B. HAYATA.

FLORA MONTANA FORMOSÆ.

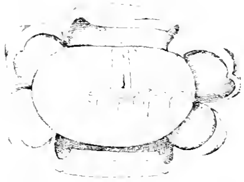
PLATE XXXIII.

PLATE XXXIII.

Balanophora spicata HAYATA.

Fig. 1. A male plant.
2. A female plant.
3. A male flower.
4. A stipe with female flowers.
5. A female flower.

3



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B. Hayata del.

K. Nō [illegible]

PLATE XXXIV.

PLATE XXXIV.

Balanophora parvior HAYATA.

Fig. 1. A male plant.
2. A female plant.
3. A male flower.
4. A stipe with female flowers.
5. A female flower.

PLATE XXXV.

PLATE XXXV.

Ficus vaccinioides HEMSL. et KING.

Fig. 1. The plant.
2. A dwarf.
3. A leaf with stipules.
4. An axil, showing stipules.
5. A leaf.
6. A receptacle.
7. The same, seen from below.
8. Another form of a receptacle.
9. A receptacle, in vertical section.
10. Bracts at the mouth of the same receptacle.
11. A male flower.
12. A stamen.
13, 14, 15 and 16. Various forms of female flowers and gall flowers.
17 and 18. Ovaries, seen from different sides.

B. Hayata del.

PLATE XXXVI.

PLATE XXXVI.

Elatostema minutum HAYATA.

Fig. 1. The plant.
2. A receptacle in an axil.
3. The same, detached from the axil.
4. A fruit.

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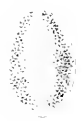

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B. Hayata del.

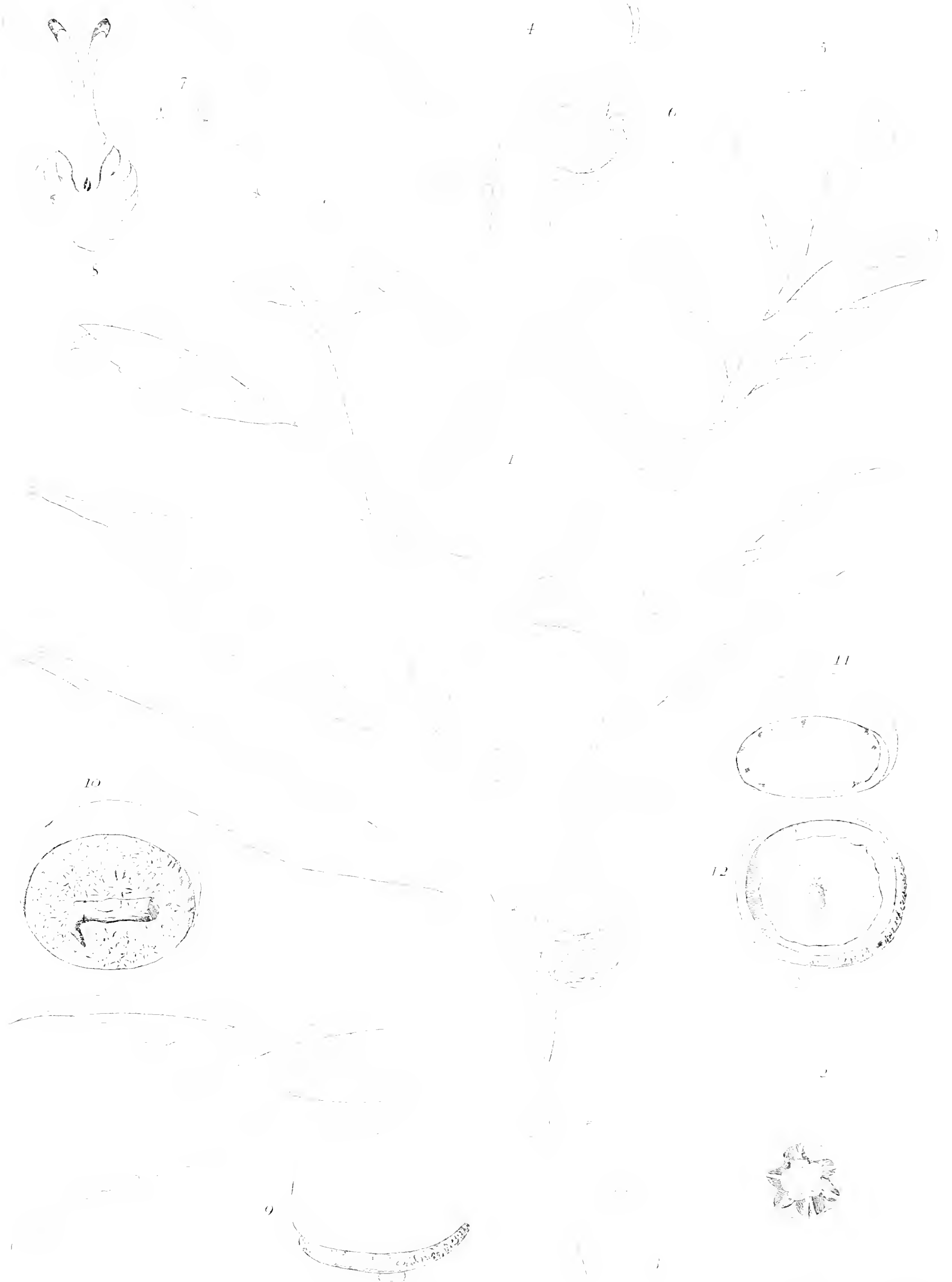
K. Nakazawa sculp.

PLATE XXXVII.

PLATE XXXVII.

Quercus (Pasania) Konishii HAYATA.

Fig. 1. A branch.
2. A male flower.
3. Stamens, seen from different sides.
4. Female flower.
5. A bract at the base of a flower.
6. A rudimental stamen in a scale of a flower.
7. Rudimental stamens, seen from different sides, more magnified.
8. A female flower, in vertical section.
9. A fruit, seen from a little above.
10. The same, seen from a little below.
11. The same, cup taken off, seen from below.
12. The same, showing the under side of the glans.



B.Hayata del.

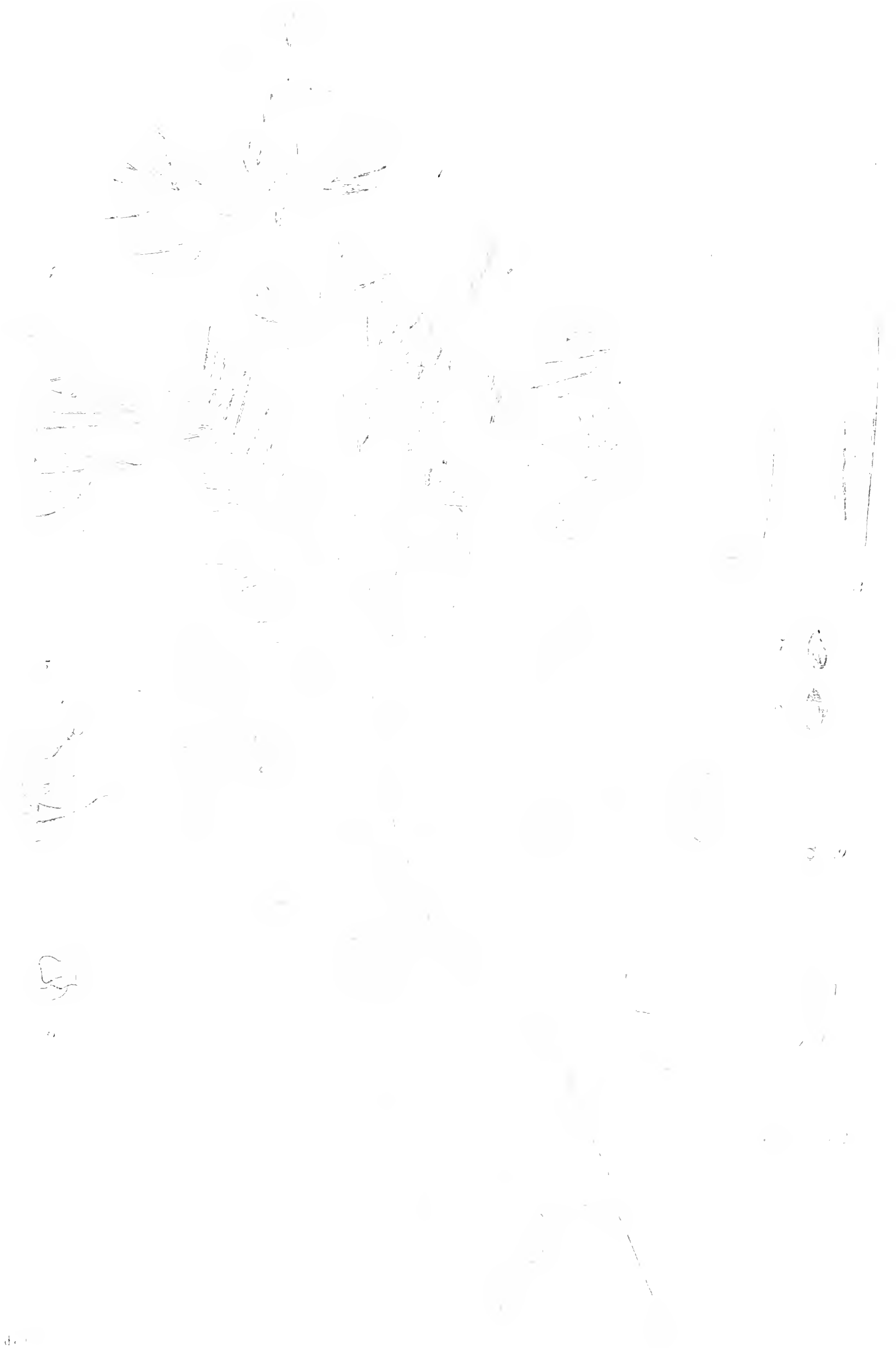
K.Nakazawa sculp.

PLATE XXXVIII.

PLATE XXXVIII.

Juniperus formosana HAYATA.

Fig. 1. A branch.
2. A leaf, seen from the inner side.
3. The same, seen from the outer side.
4. A fragment of a branch.
5. A fruit.
6. Bracts at the base of a fruit, magnified.
7. A seed (lateral view).
8. The same (dorsal view).
9. The same, in cross section.
10. A fruit showing vestiges upon it.
11. An albumen.
12. An embryo.



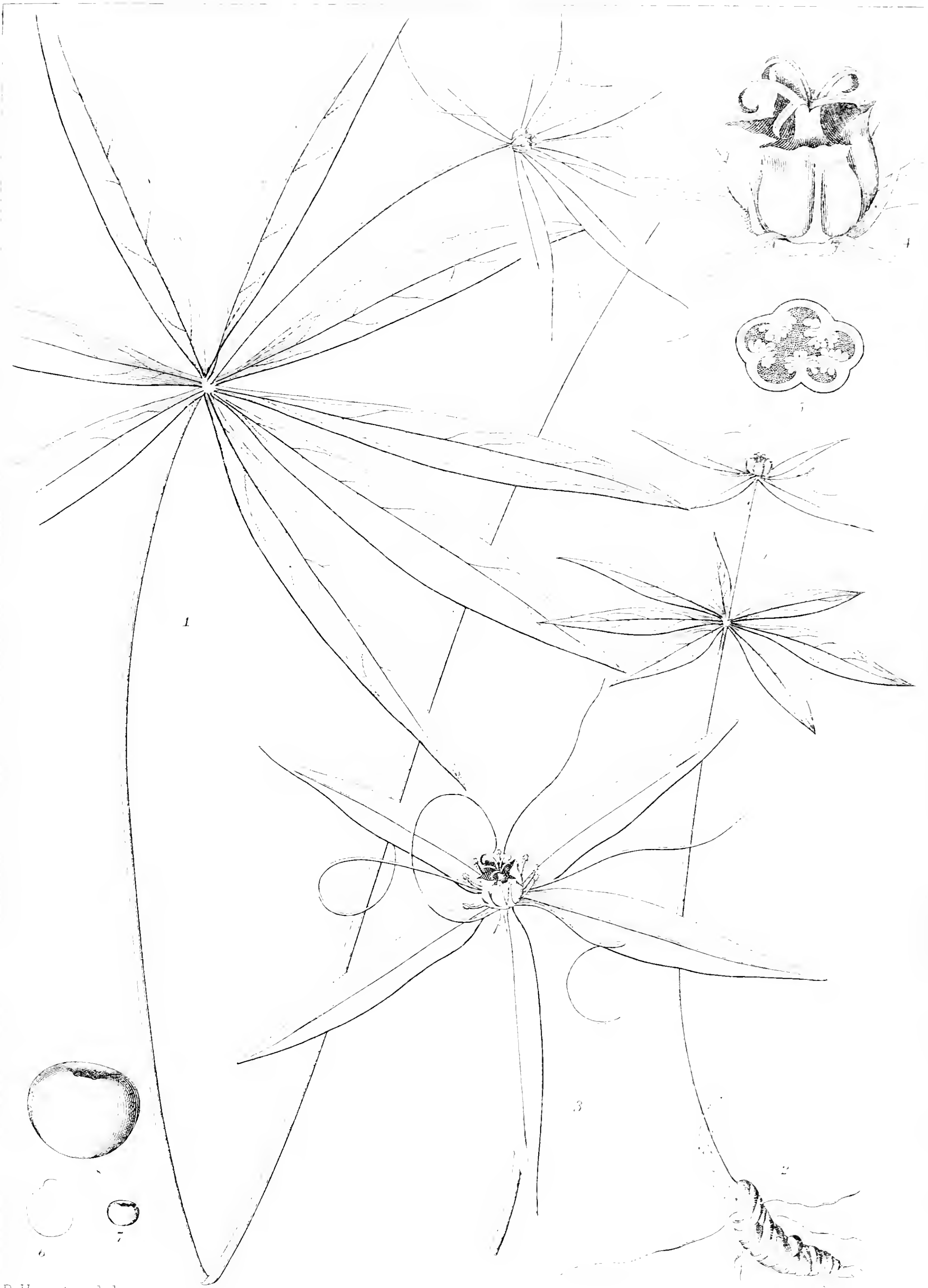
B. Hayata del.

PLATE XXXIX.

PLATE XXXIX.

Paris lancifolia HAYATA.

Fig. 1. A full grown plant.
2. A small form.
3. A flower, a little magnified.
4. An ovary.
5. Cross section of an ovary.
6. An embryo (magnified).
7. An albumen (natural size).
8. The same albumen, in the same proportion as the embryo shown in Fig. 6.



B. Hayata del.

S. Kondō sculp.

PLATE XL.

PLATE XL.

Brachypodium Kawakamii HAYATA.

Fig. 1. The plant.
2. A flowering glume.
3. The same, the palea and rhachilla are taken off.
4. A palea, its section is figured near it.
5. An ovary with its lodicules.
6. The same ovary, more magnified.
7. The same, seen from a different side.
8. Two lodicules belonging to an ovary.
9. A stamen.
10. An achene, seen from different sides.
11. Cross section of the same.
12. The basal portion of the same achene.
13. The basal portion of a culm.
14. A part of a leaf, showing its ligule.

B. Hayata del.

K. Nakazawa sculp.

B. HAYATA.

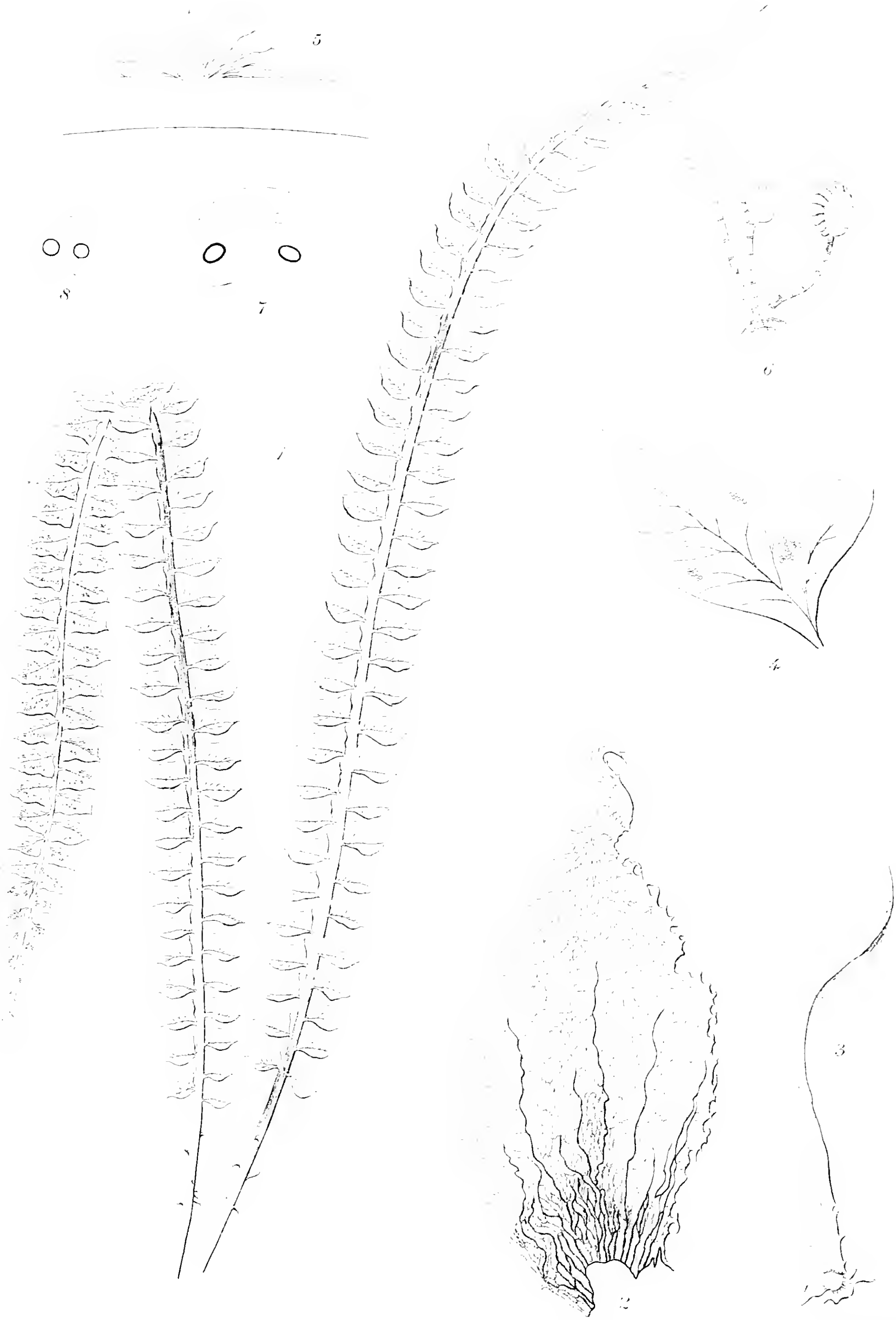
FLORA MONTANA FORMOSÆ.

PLATE XLI.

PLATE XLI.

Polystichum niitakayamense HAYATA.

Fig. 1. Fronds of the plant.
2. A chaff, detached from the basal portion of a frond.
3. Another one, detached from the middle portion of a frond.
4. A pinna.
5. Section of a sorus.
6. Sporangia.
7. Section of the basal portion of a frond.
8. Section of the middle portion of a frond.



B. Hayata del.