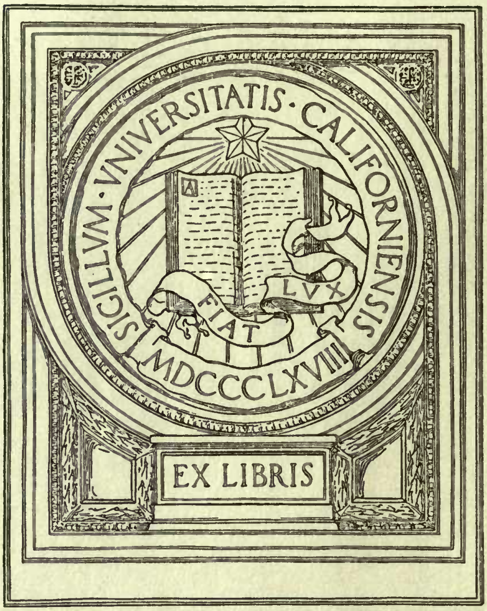


SIGILLVM · VNIVERSITATIS · CALIFORNIENSIS
FIAT LVX
MDCCCLXVIII
EX LIBRIS

STUDIES IN CHEMICAL DYNAMICS.

STUDIES

IN

CHEMICAL DYNAMICS

BY

J. H. VAN 'T HOFF

REVISED AND ENLARGED BY

DR. ERNST COHEN

Assistant in the Chemical Laboratory of the University of Amsterdam

TRANSLATED BY

THOMAS EWAN M. Sc., Ph. D.

Demonstrator of Chemistry in the Yorkshire College, Leeds

WITH A PREFACE BY PROFESSOR J. H. VAN 'T HOFF

AND

49 FIGURES IN THE TEXT

REESE LIBRARY OF THE UNIVERSITY OF CALIFORNIA

AMSTERDAM
FREDERIK MULLER & Co

LONDON
WILLIAMS & NORGATE

1896

QD501
H58

71504

Printed by the Amst. Boek- en Steendrukkerij v/h. Ellerman, Harms & Co.

PREFACE I.

The „Etudes de Dynamique Chimique" being out of print, the desirability of a new edition was suggested by the publisher.

This, however, gave rise to a difficult problem: the '*Etudes*' represented, at the time of their publication, a certain stage in my chemical thinking, beyond which, doubtless, everyone is now advanced. To introduce many changes would, however, take away from the original work its desired documentary character, while to change nothing would be to contribute nothing to making the contents acceptable to the public.

Dr. E. Cohen's proposal to revise the '*Etudes*' in the form of the old laboratory programme, in carrying out which he has very successfully assisted, came just at the right moment, and so, may this work serve as a suitable record of our little laboratory history.

Stühlingen, October 1895.

J. H. van 't HOFF.

PREFACE II.

The first edition of this work was published about twelve years ago under the title '*Etudes de Dynamique Chimique.*'

Since then many of the views put forward in it have proved to be uncommonly fruitful, on the one hand in explaining known facts, on the other, by suggesting new directions for investigation.

The object of the present German edition is not merely to reproduce the original book, but also to present the researches which have been engendered by it together with the parent memoir as a homogeneous whole; in doing this, much which has not hitherto been published has been included.

Amsterdam, October 1895.

ERNST COHEN.

NOTE BY THE TRANSLATOR.

The appearance of a revised edition of Professor VAN 'T HOFF'S classical '*Etudes de Dynamique Chimique*' seemed to provide a wished-for opportunity of introducing it to a wider circle of English readers by means of a translation; the paucity of works in our language dealing with the subject made this the more desirable.

The simplicity and originality of the treatment of chemical change and affinity make the book of the greatest value to the student seeking clear views on the fundamental problems of our science, whilst the fertility in ideas makes it uncommonly suggestive to the chemist already familiar with the outlines of the subject.

The nature of the contents is sufficiently indicated in the preceding prefaratory notes. The translation adheres closely to the sense of the original, occasional notes having been added for the sake of greater clearness.

I am greatly indebted to my friend A. C. WRIGHT M. A., B. Sc. for his kindness in reading the revised proofs.

May 1896.

THOS. EWAN.

REESE LIBRARY
OF THE
UNIVERSITY
OF CALIFORNIA

CONTENTS.

THE COURSE OF CHEMICAL CHANGE.

First Part. THE NORMAL CHEMICAL REACTION.

Page.
I. The monomolecular reaction. *Decomposition of arsenic hydride* 1
II. The bimolecular reaction. *Hydrolysis of esters* . . . 4
III. „ „ „ *Effect of molecular volume* . 15
IV. The polymolecular reaction. *Slow oxidation of phosphine, Simplicity of many reactions.* 25

Second Part. DISTURBING ACTIONS.

Chapter I. *Disturbing actions in liquids.*

I. Effect of the medium on the velocity of reaction. Action of contact 26
II. Influence of pressure on the velocity of reaction . . 30

Chapter II. *Disturbing actions in gaseous systems.*

I. The order of magnitude of the disturbing actions in gaseous systems 31
II. The nature of the disturbing actions in gaseous systems. Action of the walls of the vessel. Formation of cyamelide and of water; decomposition of phosphine . . 43
III. The nature of the disturbing actions in gaseous systems.
  a. *The rate of oxidation of phosphine* 50
  b. *The rate of oxidation of phosphorus, sulphur, and aldehyde.* 61

Page.

Chapter III. *Elimination of the disturbing actions*

I. Methods of eliminating the disturbing actions. Form and dimensions of the apparatus. Use of a solvent. Moistening the walls of the vessel 86

II. The first period of chemical change. Chemical induction 91

Third Part. APPLICATIONS.

I. Determination of the number of molecules which take part in a chemical reaction. A. Method in which the volume remains constant. 99

II. Determination of the number of molecules which take part in a chemical reaction. B. Method in which the volume varies 101

- 1. *Action of bromine on fumaric acid* 105
- 2. *Polymerisation of cyanic acid.* 107
- 3. *The action of stannous chloride on ferric chloride* . 110

III. Recognition of mixtures. Decomposition of dibromsuccinic, and iso-dibromsuccinic acids 113

IV. Comparison of the velocities of different reactions.

- a. *Hydrolysis of esters by bases* 115
- b. *Hydrolysis of esters by acids* 116

THE INFLUENCE OF TEMPERATURE ON CHEMICAL CHANGE.

First Part. THE RELATION BETWEEN THE VELOCITY CONSTANT K AND THE TEMPERATURE.

a. *Application of thermodynamics* 122

b. *Experimental treatment of the subject* 127

1. Influence of the temperature on the rate of decomposition of dibromsuccinic acid. 127

Page.
2. Influence of the temperature on the rate of the reaction between sodiumchloracetate and caustic soda . . . 129
3. Influence of the temperature on the rate of change of chloracetic acid in aqueous solution 130
4. Influence of the temperature on the rate of hydrolysis of ethyl acetate by caustic soda 130
5. Influence of the temperature on the velocity of the reaction between potassium chlorate and ferrous sulphate in presence of sulphuric acid 132
6. Influence of the temperature on the rate of hydrolysis of ethyl acetate by caustic soda 133
7. Influence of the temperature on the inversion of cane sugar 133
8. Influence of the temperature on the action of sodium ethylate on methyl iodide 133
9. Influence of the temperature on the formation of nitriles from syn-aldoxime acetates and on the change of the latter into the anti-modifications. 133
10. Influence of the temperature on the rate of decomposition of the hydrides of arsenic and phosphorus. . . . 134

Second Part. THE TEMPERATURE OF IGNITION . . . 136

CHEMICAL EQUILIBRIUM.

First Part. THE THREE FORMS OF EQUILIBRIUM.

I. Homogeneous systems.
  a. *At constant temperature* 143
  b. *The temperature is variable* 148
    Application of thermodynamics 148
    Applications 150
II. Heterogeneous systems 155
  Cases investigated 156

REESE LIBRARY OF THE UNIVERSITY

Page.

III. 1. Condensed systems 163
2. Cases investigated. 167
   a. The transition temperature of polymorphous bodies 167
   b. The transition temperature of salts containing water of crystallisation 168
   c. The transition temperature in the formation and decomposition of double salts 169
   d. The transition temperature in cases of double decomposition 173
   e. The transition temperature of isomeric compounds 173
3. Solubility and vapour pressure at the transition temperature 174
4. Relation between the transition temperature of a hydrated salt and the vapour pressures of the salt and of solutions of it 179
5. Methods of determining the transition temperature 180
   a. The dilatometric method 181
   b. The thermometric method 184
   c. The crystallisation method. 186
   d. The identity methods 186
      α. Determination of solubility 186
      β. Determination of vapour pressure.
         1. Vapour pressures of solutions 187
         2. Pressure of dissociation 188
      γ. The solution pressure methods.
         1. Solutions 188
         2. Solution pressure of dissociation 192
      δ. Electrical methods.
         1. Electrical method with both stable and meta-stable phases 193
         2. Electrical method with stable and without meta-stable phases 198
   Further methods 203

Page.

Second part. THE THREE FORMS OF PHYSICAL EQUILIBRIUM.

I. Homogeneous systems 205
II. Heterogeneous systems 205
III. Condensed systems. 210

Third part. DIAGRAM OF THE INFLUENCE OF TEMPERATURE ON EQUILIBRIUM. DETERMINATION OF THE TRANSITION POINT OF SULPHUR 212

Fourth part. DISPLACEMENT OF EQUILIBRIUM WITH THE TEMPERATURE. PRINCIPLE OF MOBILE EQUILIBRIUM. 217

I. The principle of mobile equilibrium applied to heterogeneous systems.
  a. Physical equilibrium in heterogeneous systems. Evaporation and condensation. 217
  b. Chemical equilibrium in heterogeneous systems. 218

II. The principle of mobile equilibrium applied to condensed systems.
  a. Physical equilibrium in condensed systems. Fusion and solidification 219
  b. Chemical equilibrium in condensed systems. Incompatible systems 219

III. The principle of mobile equilibrium applied to homogeneous systems. 222

AFFINITY.

I. The comparison of chemical affinities 229
II. Measurement of affinity. The magnitude of the affinity which retains the water of crystallisation in salts. . 230
III. Determination of the work done by affinity 235

Page.
IV. Applications.
- 1. Work done by affinity at absolute zero. Diagram of the work done 241
- 2. Influence of pressure on the transition point. 242
- 3. Calculation of the transition point.
  - *a.* The allotropic modifications of sulphur . 248
  - *b.* The transformation of a mixture of sodium ammonium lævo- and dextro-tartrates into sodium and ammonium racemates . 250

V. The electrical work performed by a chemical change.
- 1. General considerations 251
- 2. Thermodynamics of the transition cell. . . . 254
- 3. Equilibrium-constant and electromotive force . 267

Appendix 274
Name index 276
Subject index 279

REESE LIBRARY
OF THE
UNIVERSITY
OF CALIFORNIA

THE COURSE OF CHEMICAL CHANGE.

FIRST PART.

THE NORMAL CHEMICAL REACTION.

I. THE MONOMOLECULAR REACTION.

Decomposition of Arsenic Hydride.

The most simple chemical change is that which can be accomplished within a single molecule, a change for the accomplishment of which the mutual action of several molecules is not requisite.

Whether it be a question of isomeric change, or of decomposition, the process is subject to the same law.

On these grounds we will call the chemical reaction of this kind *the monomolecular reaction.*

Experiment will show us that in this case there is proportionality between the quantity of substance still decomposable, and the quantity which undergoes decomposition in each instant, which may be represented by the following equation,

$$-\frac{dC}{dt} = kC,$$

where C is the concentration, (quantity in unit volume),

t, the time, and k a constant[1], which we will call the *velocity constant.*

---

[1] It is of course assumed here that the reaction takes place at constant temperature, and consequently the heat evolved or absorbed by it may be neglected.

The decomposition which was studied in order to test this equation is the following; —

$$AsH_3 = As + 3H.$$

If we assume that the arsenic hydride decomposes in accordance with the simple equation just given[1], it will be easy, by determining the pressure of the decomposing gas (at constant volume), to calculate the undecomposed part of it in unit volume.

Let C_o and P_o be the concentration of the arsenic hydride, and the total pressure at the beginning,

and C_t and P_t the values after a partial decomposition.

Then[2]

$$P_t = P_o + \frac{1}{2} P_o \frac{(C_o - C_t)}{C_o},$$

or

$$C_t = C_o \left(3 - \frac{2 P_t}{P_o}\right) \ldots\ldots\ldots (1)$$

The apparatus for making the determinations of the pressure will be fully described later. (p. 41).

The results obtained are given in the following table.

Time in hours t	Pressure in mm. P	$k = \frac{1}{t} \log \frac{P_o}{3 P_o - 2 P_t}$
0	784.84	—
3	878.50	0.09076
4	904.05	0.09051
5	928.02	0.09079
6	949.28	0.09051
7	969.08	0.09056
8	987.19	0.09060

To control the accuracy of the differential equation

$$-\frac{dC}{dt} = kC,$$

it must be integrated.

---

[1] That this is really the case will be shown later.

[2] See appendix, note 1.

We find

$$-\log C = kt + \text{constant}.$$

Eliminating the integration constant by means of equation (1), we get: —

$$k = \frac{1}{t} \log \frac{C_o}{C_t} = \frac{1}{t} \log \frac{P_o}{3 P_o - 2 P_t}.$$

These values of k have been calculated, and are set down in the third column of the table; their constancy shows that the requirements of the differential equation are satisfied.

A further example of a monomolecular reaction is the decomposition of phosphine, which will be considered later.

From the preceding we may draw the following general conclusion, which however contains nothing unexpected in the case of a monomolecular reaction.

The quantity decomposed in unit time is independent of the volume of the decomposing substance.

This proposition may also be proved in the following way:

Suppose that two equal quantities Q occupy at the beginning of two experiments two different volumes V_1 and V_2, it is easy to see that the corresponding quantities X_1 and X_2, which remain undecomposed at the end of the same interval of time t, will be the same in both cases.

Applying the equation

$$kt = \log \frac{C_o}{C_t}$$

we obtain

$$kt = \log \frac{\frac{Q}{V_1}}{\frac{X_1}{V_1}} = \log \frac{Q}{X_1} = \log \frac{\frac{Q}{V_2}}{\frac{X_2}{V_2}} = \log \frac{Q}{X_2}$$

$$\text{from which } \frac{Q}{X_1} = \frac{Q}{X_2}, \text{ or } X_1 = X_2.$$

II. THE BIMOLECULAR REACTION.

Hydrolysis of Esters.

We will call a change in which the interaction of several molecules is required, *polymolecular.*

The most simple case of this sort is the reaction between two molecules, or the *bimolecular reaction.*

If we call the concentrations of the two reacting substances C_1 and C_2, the decrease of concentration which the substances undergo in each instant, will be proportional to the concentrations of both of them, that is

$$-\frac{d\,C_1}{dt} = k_1\,C_1\,C_2 \text{ and } -\frac{d\,C_2}{dt} = k_2\,C_1\,C_2$$

where t is the time, and k_1 and k_2 are constants.

As the unit of concentration of a body we will choose the molecular weight of it, in kilograms in a cubic metre. If we are considering, for example, the hydrolysis of ethyl acetate by caustic soda, the concentration is unity when 40 kgrms of caustic soda and 88 kgrms of the ester are present in a cubic metre.

As will be seen in what follows, the accuracy of the equations has been confirmed by experiment; the experiments on this point were carried ont by L. T. Reicher.[1]

The hydrolysis of ethyl acetate by caustic soda, represented by the equation

$$NaOH + C_2H_5OOC_2H_3 = CH_3COONa + C_2H_5OH,$$

was studied.

Warder[2] had already found that this reaction takes place at the ordinary temperature with a velocity which allows of its course being followed.

It is thus a question in this case of verifying the equation

$$-\frac{d\,C_1}{dt} = k\,C_1\,C_2.$$

---

[1] Lieb. Ann. 228, 257, 1885.

[2] Berichte. 14, 1361, 1881.

where C_1 is the concentration of the caustic soda, C_2 that of the ester, t the time, and k some constant.

Consider now an aqueous solution of base and ester, which are acting on each other at a given temperature; then at any moment during the reaction the concentration of the base, C_1, can be determined by titration with an acid; from this the concentration of the ester, C_2, may be calculated if the base be used in excess and its concentratration, C_∞, be determined after the reaction is complete. We have then,

$$C_2 = C_1 - C_\infty$$

Substituting this value in the original equation, we obtain

$$-\frac{d\ C_1}{dt} = k\ C_1\ (C_1 - C_\infty),$$

from which by integration

$$\frac{1}{C_\infty} \log \frac{C_1}{C_1 - C_\infty} = kt + \text{constant}.$$

If we make two determinations, say C_1 and C_t, and if the time intervening between them is t, we find, eliminating the constant of integration;

$$k = \frac{1}{C_\infty\ t} \log \frac{C_t\ (C_1 - C_\infty)}{C_1\ (C_t - C_\infty)},$$

or introducing common logarithms in place of the Naperian,

$$k = \frac{2.3025}{C_\infty\ t} \operatorname{Log} \frac{C_t\ (C_1 - C_\infty)}{C_1\ (C_t - C_\infty)}.$$

As the apparatus used will be referred to again, it is fully described here. (Fig. 1).

In order to obtain a constant temperature the essential part of the apparatus, A, is placed within two glass cylinders F and G; into the first of these water at a high pressure from the water supply is conducted by two fine jets from the tubes L und L,; by means of the currents produced in this way a uniform temperature is maintained.

This temperature is determined by means of a thermometer N which allows $^1/_{10}$ of a degree to be read.

The second vessel G, contains ice water, or warm water, according as the temperature of the water supply is too high or too low.

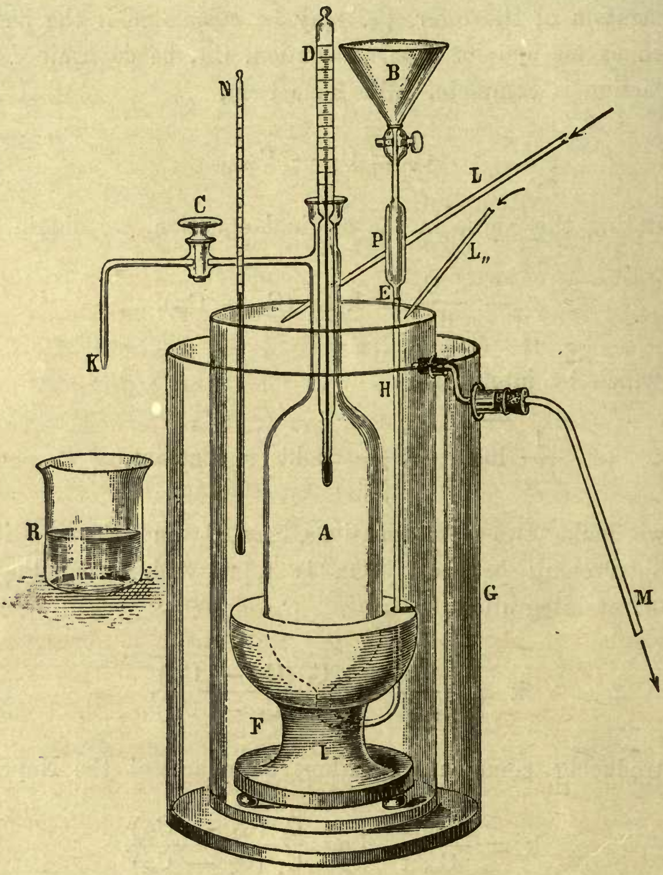


Fig. 1.

To prevent evaporation of the ester during the reaction the liquid is placed in the glass vessel A, which may be closed by the glass tap C, and which it completely fills; liquid may be removed from A for the titrations, by displacing it through C by means of mercury, which is allowed to run in from the funnel B.

The manipulation of the experiments requires the cooperation of two observers, and consists of three operations; filling, mixing, and drawing off samples.

A quantity of the aqueous solution of the ester is first placed in the apparatus, such that when the latter is subsequently wholly filled by the addition of the alkaline solution, a small excess of alkali shall be present. It is therefore necessary to know to begin with, the concentrations of the solutions of ester and soda, and also the capacity of A.

The apparatus is then filled with the solution of ester, placed in position as shown in the figure, and the solution of the base, (protected from the carbon dioxide of the air), introduced gradually through H in such a way that the solutions of ester and alkali form separate layers over each other. During the time which is needed for the filling, the temperature in F is regulated in the way described, so that when the apparatus is quite full the temperature of the liquid in it is about 0°.4 below that desired; this will be indicated by the thermometer D.

In order to mix the liquids thus introduced, some mercury is allowed to flow through B into A, the tap C closed, the apparatus removed from the cylinder, and shaken uniformly several times so that the mercury effects the mixture of the liquids; if necessary the temperature is then raised to the desired point by warming with the hand. The apparatus is now placed in its original position and the real experiment may be begun as soon as the temperature of the water in the cylinder F has reached the desired point.

Before drawing of a sample, a volume of mercury corresponding to the part of the apparatus which projects above the water in F, is poured in through the funnel B, on opening the tap C this displaces the liquid in that part of the apparatus which possibly does not possess the correct temperature. When the mercury has fallen to the mark E, the tap is closed again, and 100 cc. of mercury poured into B. The one observer then brings a measured quantity, R, of sulphuric acid of known strength under the opening K, and quickly opens the tap C completely; the time is noted by the second observer on a chronometer indicating seconds, and also the moment at which the mercury has fallen very nearly to the mark E. By partially closing C the last small quantity flows out slowly until E is reached, when the tap is closed completely. This manipulation is repeated each time a sample is drawn off, and since the sulphuric acid employed is amply sufficient to neutralise the alkali present, the hydrolysis taking place in 100 cc. of the liquid is stopped at a given time, in the space of a few seconds (about 9).

If time allows, the excess of sulphuric acid is at once titrated with baryta water of known strength using phenol-phthaleïn as indicator (or rosolic acid in experiments with ammonia).

Samples are drawn off at intervals of some minutes until only about 100 cc. of the mixture are left in the apparatus, which serve for the determination of the final titre after the reaction may be regarded as complete (viz. after at least 24 hours). It is obvious that after the last sample has been taken the temperature need no longer be regulated.

The results obtained are contained in the following table:[1]

Time in minutes.	Titre of base in the mixture. T.	k.
0	61.95	—
4.89	50.59	2.31
11.36	42.40	2.33
29.18	29.35	2.28
∞	14.92	—

In calculating the values of k it is to be noticed that in the expression given on page 5,

$$k = \frac{2.3025}{C_\infty \ t} \text{ Log } \frac{C_t \ (C_1 - C_\infty)}{C_1 \ (C_t - C_\infty)}$$

---

[1] The temperature was 9°.4.

the quotient, the logarithm of which occurs, may be written thus

$$\frac{T_t\ (T_1 - T_\infty)}{T_1\ (T_t - T_\infty)},$$

since the values of C (the concentrations, in kgrm. mols. per cubic metre, of the free caustic soda) are proportional to those of T (the quantities of free caustic soda expressed in cc. of the baryta solution employed).

C_∞ is the final concentration (in kgrm. mols. per cubic metre) of the caustic soda in the mixture in which the reaction has taken place, the concentration being unity when 40 kgrms NaOH are present in each cubic metre.

If the baryta solution is N times normal we have

$$C_\infty = T_\infty \frac{N}{100}.$$

The value of k becomes therefore

$$k = \frac{2.3025 \times 100}{T_\infty\ Nt} \operatorname{Log} \frac{T_t\ (T_1 - T_\infty)}{T_1\ (T_t - T_\infty)}.$$

These values of k are entered in the third column of the table[1], their practical identity shows that the requirements of the original differential equation are satisfied.

The equation

$$- \frac{dC_1}{dt} = k\ C_1\ C_2$$

leads us to the conclusion, that each of the bodies taking part in the reaction has an equal influence on its velocity.

L. Th. Reicher[2] has confirmed this experimentally, and has shown that the same value of the constant k is obtained, whether excess of caustic soda, or of the ester, be employed.

In this case also, the hydrolysis of ethyl acetate by caustic soda was studied.

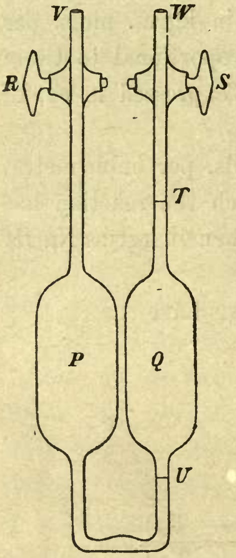
---

[1] $N = \frac{1}{22.797}$.

[2] Lieb. Ann. 238, 276, 1887.

The apparatus used is shown in fig. 2.

The most important condition to be fulfilled in these experiments, is that the free soda contained in the mixture, must not be exposed to the air either during its introduction, or afterwards within the apparatus itself.



Fig, 2.

The apparatus consists of two fairly strong vessels, P and Q, which communicate by a thick-walled tube, and which may be closed above by taps R and S. At U and T there are two marks. The volume from R to the mark U was 125.7 cc., from U to T 100.2 cc.

In order to find the final titre, the apparatus, after being carefully cleaned and dried, is exactly filled from R to U with the alkaline solution of known strength through the tube V; the piece of tube V R is then cleaned and filled with mercury, and finally, through S, so much more of this metal introduced that in all 10 cc. of it have been employed. The exit tube K of the apparatus A (fig. 1) which has already been described, is now united to V by a short india rubber tube, and with the help of mercury which is poured into the funnel B, the mixture of caustic soda and ester is allowed to flow into P so slowly that it remains as a separate layer over the solution of soda; this can be plainly seen by the sharp boundary between the two layers.

The apparatus being filled in this way to the mark T, the taps are closed, and the liquids mixed by transferring the mercury alternately from one vessel to the other 100 times, shaking vigorously meanwhile. The contents are then allowed to stand for at least 24 hours, after which the titration is proceeded with.

This is done by first pouring in some mercury above S, and attaching a tube for drawing off the liquid at V; W is then connected to a gas holder containing air and the liquid driven out to the mark T, after which (from T to U) 100.2 cc. of the mixture are allowed to flow into a measured quantity of sulphuric acid which must be in excess. This is then titrated back.

A second 100.2 cc. of liquid is now driven out of the apparatus after running mercury into Q through S up to the mark T, in the way just described.

The results obtained with this apparatus are contained in the following table: —

(Temperature 15°.8).

a. Experiments with excess of caustic soda.[1]

Time in minutes. t	Titre of the base in the mixture. (T)	k
0	62.09	—
3.74	54.33	3.47
6.28	50.60	3.48
10.48	46.28	3.43
13.59	43.87	3.44
∞	33.06	—

b. Experiments with excess of ester.[2]

Time in minutes. t	Titre of the base in the mixture. (T)	k
0	38.94	—
2.52	31.32	3.47
5.04	25.92	3.43
8.34	20.74	3.41
10.71	17.85	3.42
∞	23.65	—

In both cases the values of the constants agree together very well; k, in the last column of table *a*, is calculated in the way described on page 9. In the second table, *b*, where excess of ester was used, the sign of T_∞ must be changed in the formula for k (page 9) so that in table *b*

---

[1] $N = \frac{1}{24.07}$.

[2] $N = \frac{1}{23.485}$.

$$k = \frac{2.3025 \times 100}{T_\infty \, Nt} \, \mathrm{Log} \, \frac{T_1 \, (T_t + T_\infty)}{T_t \, (T_1 + T_\infty)}.$$

At the present time a considerable number of researches on this subject are in existence; as further examples of bimolecular changes the action of acids on acetamide (OSTWALD)[1], and that of bases on lactones studied by P. HENRY[2], are to be mentioned.

A simplification which may be introduced by using the reacting substances in equivalent quantities will now be pointed out.

In this special case, the ratio of the concentrations of the substances does not change during the reaction; by choosing the units in a suitable way, only one single concentration need be taken into account.

This concentration, which refers to both bodies, will be called the *concentration of the system.*

In place of the equations

$$-\frac{d\,C_1}{dt} = k_1 \, C_1 \, C_2 \text{ and } -\frac{d\,C_2}{dt} = k_2 \, C_1 \, C_2$$

we may write the following,

$$-\frac{d\,C}{dt} = k\,C^2$$

C being the concentration of the system.

Integrating we obtain

$$\frac{1}{C} = kt + \text{constant} \ldots\ldots \; (1)$$

Considering for example the hydrolysis of an ester by caustic soda, (in equivalent quantities), the concentration of the system is proportional to the titre of the alkali in the solution, therefore

$$C_t = C_1 \frac{T_t}{T_1}$$

where C_1 and T_1 are the original values of the concentration and titre, C_t and T_t their values after a partial decomposition.

---

[1] Journ. prakt. Chem. (2), 27, 1, 1883.

[2] Zeit. phys. Chem. 10, 96, 1892.

Eliminating by means of this equation the constant of integration in equation (1), we get

$$k = \frac{1}{t}\left(\frac{1}{C_t} - \frac{1}{C_1}\right) = \frac{1}{t\,C_1}\,\frac{T_1 - T_t}{T_t}.$$

On comparing this expression with that which was obtained for the monomolecular reaction, (page 3),

$$k = \frac{1}{t} \log \frac{T_1}{3\,T_1 - 2\,T_t},$$

a great difference is apparent.[1]

While in the case of a monomolecular reaction the value of k depends exclusively on the choice of the unit of time (t), in the case of the bimolecular reaction its value is also a function of the unit of concentration (C).

The following statement indicates the difference in the courses of the mono- and bi-molecular reactions: —

In a bimolecular reaction the quantity decomposed depends on the volume of the decomposing system.

This proposition is obvious, when one remembers that the bimolecular reaction differs from the monomolecular, in the fact that in the former, the encounter of the reacting molecules must occur.

A further simplification takes place if in a bimolecular reaction one of the reacting bodies is present in great excess. For since its concentration, C_2, is then not perceptibly changed during the reaction, C_2 in the equation

$$-\frac{d\,C_1}{dt} = k_1\,C_1\,C_2$$

is to be considered as a constant, so that

$$-\frac{d\,C_1}{dt} = k\,C_1,$$

that is the process takes place in the same way as a monomolecular reaction.

Processes of this kind have been examined in great number.[2]

---

[1] This expression corresponds in every way to that obtained on page 3, —

$$k = \frac{1}{t} \log \frac{P_o}{3\,P_o - 2\,P_t}.$$

[2] Wilhelmi, Ostwald's Klassiker der exacten Wissenschaften, No. 29. — Wittwer, Pogg. Ann. 94, 598 (1855). — Harcourt and Esson, Phil. Trans. (1866) 193; (1867) 117. — Ostwald, Journ. prakt. Chem. 28, 449 (1883); 29. 385; 31. 307.

Buchanan[1] has studied the action of a large excess of water on monochloracetic acid at 100°, and found that it takes place according to the following equation: —

$$C_2H_3ClO_2 + H_2O = C_2H_4O_3 + HCl.$$

As may be foreseen, the reaction in this case goes forward as if it were monomolecular, because the concentration of the water may be regarded as constant.

In order to confirm this, a solution containing 4 grams of chloracetic acid per litre was heated for a definite time in sealed tubes, (of 15 cc. capacity), which were suspended in boiling water. The reaction was then stopped by sudden cooling, and the titre of the acid in the solution determined by means of $N/_{10}$ ammonia.

C_1 and T_1 being the concentration and titre respectively at the beginning, and C_t and T_t the same quantities after partial decomposition, we have the relationship

$$C_t = C_1 \frac{2T_1 - T_t}{T_1}$$

The following table contains the experimental results.

Time in hours. $\frac{t}{60}$	Titre of the solution. T	$k=\frac{1}{t}\log\frac{C_1}{C_t}=\frac{1}{t}\log\frac{T_1}{2T_1-T_t}$
0	12.90	—
2	13.45	0.000158
3	13.90	0.000195
4	14.20	0.000192
6	14.60	0.000170
10	15.80	0.000184
13	16.40	0.000176
19	17.60	0.000173
25	18.50	0.000165
34.5	20.50	0.000187
43	20.65	0.000155
48	21.30	0.000159

Obviously the reaction takes place as if it were monomolecular.

---

[1] Berichte, 4, 340, 1871.

III. THE BIMOLECULAR REACTION.

Effect of molecular volume.

In order to determine this, Schwab investigated the following process which is analogous to a hydrolysis,

$$C_2\,H_2\,Cl\,O_2\,Na + NaOH = C_2\,H_3\,O_3\,Na + NaCl.$$[1]

Assuming that the change takes place in accordance with the above chemical equation, the quantity of the undecomposed compound in unit volume, may be determined by means of the titre of the alkali in the solution which is undergoing the change.

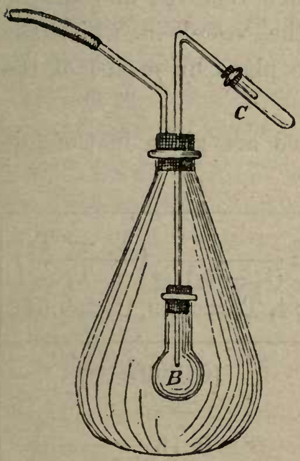


Fig. 3.

If the sodium chloracetate and the caustic soda be used in molecular proportions, the simplification before mentioned may be employed.

We have then only to take into consideration the concentration of the system, which refers both to the sodium chloracetate, and to the caustic soda.

The experiments were made with the apparatus shown in fig. 3.

The large flask contained initially 553.9 cc. of a caustic soda solution (containing 1.9935 grams NaOH)[2] at a temperature of 100°; the small flask B in which there were 2.3542 grams of chloracetic acid[3] could be shattered at a given moment.

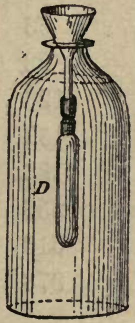


Fig. 4.

Since the molecular ratio between the quantity of the acid and of the soda was 1 : 2, a mixture of sodium chloracetate and caustic soda in the desired proportions is produced by bringing the two liquids together.

---

[1] See also Buchanan, Berichte. 4. 863, 1871.

[2] Prepared from sodium amalgam.

[3] 1.3879 grams of this acid required 18.18 cc. of 0.8077 N caustic soda solution for saturation, the calculated quantity being 18.2 cc.

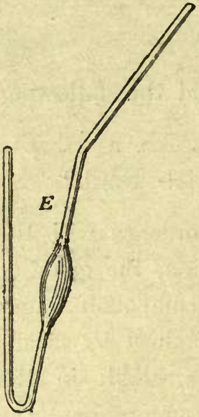


Fig. 5.

After a suitable interval the titre of 17.75 cc. of the liquid was determined in the following way: — The liquid was expelled at C by blowing, and poured through a funnel into the tube D, which was surrounded by ice in order to stop the reaction.

The funnel was then removed and the liquid transferred to the vessel in which the titration was to take place by means of the pipette E. (fig. 5).

The results obtained are given in the following table.[1]

Time in minutes. t	Titre of 17.75 cc. in terms of N/20 sulphuric acid = T	$k = \frac{1}{(t_t - t_2) C_2} \left(\frac{T_2 - T_t}{T_t} \right)$ $t_2 = 4, T_2 = 14.9, C_2 = 0.042$
0	15.97 (calculated)	(0.399)
4	14.9	—
13	14.1	0.15
23	13.3	0.15
33	12.75	0.138
63	11.15	0.136
93	10.0	0.131
123	8.95	0.133
153	8	0.138
183	7.3	0.138
258	5.95	0.141
318	5.15	0.144
378	4.55	0.145

---

[1] In calculating the value of k the initial concentration has not been used, that observed after 4 minutes had elapsed being taken (viz. $C_2 = 0.042$); in this way we eliminate an irregularity in the course of the reaction which exists in the first period and which is due partly to the incomplete mixture of the substances and partly to the heat evolved by the neutralisation. The change is accelerated by these causes to such an extent, that the value of k is trebled (0.399).

UNIVERSITY OF C

It is obvious that the course of the reaction here investigated is not normal. The values of k obtained at the beginning of the reaction, refer in fact to an aqueous solution, whilst those which were obtained later are affected by the action of the sodium chloride formed during the reaction.

Schwab[1] has avoided this difficulty by studying the decomposition in very dilute aqueous solution; with this object he used solutions of different initial concentrations.

Chloracetic acid was mixed with caustic soda in dilute solution in the ratio $C_2 H_3 Cl O_2 : 2 Na OH$; the formation of sodium glycolate being prevented by cooling.

From this solution five others were prepared which contained respectively 32, 16, 8, 4, and 2 grams of chloracetic acid per litre. These solutions were brought into glass tubes which were then sealed. Six tubes of each series were kept for a certain time in boiling water, after which the titre of their contents was determined by means of $N/_{20}$ sulphuric acid. From this the quantity undecomposed was calculated.

The following mean values of k were found in this way.

Value of k.	Concentration.
0.18	0.2
0.163	0.099
0.14	0.059
0.128	0.038
0.131	0.015

A deviation comes to light in these numbers which was concealed in the experiments described on p. 16, and which is nevertheless of a fundamental character. *The value of k decreases with decreasing concentration to a certain limit (0.13), after which it remains constant.*

We see accordingly, that here the equation for the bimolecular reaction,

$$\frac{1}{C} = kt + \text{const},$$

is only true for small concentrations.

---

[1] Inaugural Dissertation, Amsterdam 1883.

The agreement between the requirements of the formula and the numbers found experimentally is sufficiently good for concentrations smaller than 0.038.

This concentration may be called the *gaseous concentration*, because it is not very far removed from that which the mixture of sodium chloracetate and caustic soda would have at normal temperature and pressure in the gaseous condition viz: — 0.023.

This experimental result was the origin of a series of experiments on the course of the decomposition in a very weak solution (initial concentration = 0.04984); they were carried out with great care in sealed tubes.

The following are the results.

Time in minutes. t	Titre of 30 cc. in terms of $N/_{20}$ H_2SO_4 = T.	$k = \frac{1}{t\,C_1}\left(\frac{T_1 - T_t}{T_t}\right)$
0	25.25	—
45	19.55	0.1300
90	16	0.1289
180	11.7	0.1291

The constancy of k leaves nothing to be desired.

Owing to the fundamental nature of the deviation just described, it is of interest to trace its origin.

We assumed, in deducing the equation for the bimolecular reaction, that the quantity of the two bodies decomposed in unit time was proportional to the quantities of each of them in unit volume; this assumption includes another which is not fulfilled in the experiments, namely, the volume of the reacting substances themselves must be zero.

The non-fulfilment of this condition appears to be the cause of the irregularity observed. On the one hand the irregularity disappears when the concentration becomes small, that is, when the space occupied by the reacting bodies vanishes in comparison with the whole volume, on the other hand the deviation changes in the way which might be expected, k increasing with the concentration.

IV. THE POLYMOLECULAR REACTION.

We may now go a step further and write down the differential equations for more complicated cases. If we consider a reaction which may be ascribed to the mutual action of n molecules, we have

$$-\frac{d\,C_1}{dt} = k_1\,C_1\,C_2\ldots.C_n;\ \text{etc.};\ -\frac{d\,C_n}{dt} = k_n\,C_1\,C_2\ldots.C_n;$$

where C_1, $C_2\ldots.C_n$, are the concentrations of the substances reacting on each other, $k_1\ldots.k_n$ are constants, and t is the time.

When the reacting bodies are present in the proportions in which they take part in the reaction, the equations may be simplified to one single expression,

$$-\frac{d\,C}{dt} = k\,C^n,$$

where C is the concentration of the system.

Integrating this, we find[1]

$$\frac{1}{C^{n-1}} = k\,t + \text{constant},$$

in which the value of k is (n—1) times that which it had in the differential equation.

It would be interesting if it were possible to realise the different cases which follow from this equation, that is if it were possible to study the course of a tri- ($n = 3$), or quadri- ($n = 4$), molecular reaction.

It is not difficult to find chemical equations which represent three, four, or more molecules as interacting; as for example

---

[1] V is supposed to be constant.

$$4\ PH_3 = P_4 + 6\ H_2$$

or the case investigated by Hood[1],

$$KClO_3 + 6\ FeO = KCl + 3\ Fe_2O_3.$$

Researches on this subject have, however, shown that the greater number of such equations give an entirely false idea of the mechanism of the reactions, only expressing the quantitative aspect of them.

This mechanism is generally very simple, in almost all cases it is mono- or bimolecular, rarely trimolecular.

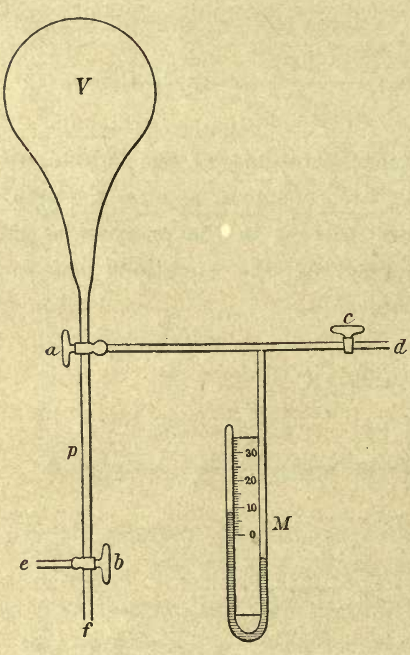


Fig. 6.

So for example the decomposition of phosphorus (or arsenic) hydride takes place as if it were monomolecular, that is according to the equation,

$$PH_3 = P + H_3$$

whilst Hood's reaction appears to be bimolecular.

According to the researches of J. van de Stadt[2], which will be described below, the slow oxidation of phosphine may, under certain circumstances, follow a very simple course, namely that of a bimolecular reaction.

He found that the following are the principal changes which may occur during this slow oxidation: —

$$(1)\quad 2\ PH_3 + 4\ O_2 = P_2O_5 + 3\ H_2O$$
$$(2)\quad 2\ PH_3 + 3\ O_2 = 2\ H_3PO_3$$
$$(3)\quad PH_3 + O_2 = HPO_2 + H_2$$

---

[1] Phil. Mag, (5). 20, 323, 1885.

[2] Zeit. phys. Chem. 12, 322. 1893. Inaugural Dissertation. Amsterdam, 1893.

Equation (1) represents the change which occurs in the ordinary combustion of phosphine.

By means of the apparatus shown in figure 6, changes (2) or (3) could be brought about at will, and so could be separately studied; metaphosphorous acid which was previously unknown was prepared in the course of this investigation.

Oxidation to phosphorous acid.

The principal condition which must be fulfilled if reaction (1) is to be excluded, is that the gases must be brought together in a suitably dilute condition and as dry as possible; instantaneous oxidation can be insured, and excess of one or other avoided; only in this way.

The flask V is evacuated at d by means of the air pump, and c closed; e is connected to the phosphine, f to the oxygen gasholder, while p acts as a gas pipette the contents of which may be transferred to V by turning a. The tap a is so arranged that V may be placed in communication with the manometer M or with the pipette p; the tap b allows the apparatus to be placed in communication with e or with f, or to be closed entirely.

In the dark room the gas required is admitted, one pipette full at a time, into the flask until its admission fails to produce any further luminosity, showing it to be present in excess. The following results were obtained, the + sign indicates that luminosity was observed after admission of the gas;

$$\begin{array}{rll} & \quad PH_3 & \qquad O_2 \\ 13 \times & \left\{ \begin{array}{l} 1 + 1 - \\ 1 + 1 - \\ \cdots\cdots\cdots \\ 1 + 1 - \end{array} \right. & \qquad \begin{array}{l} 1 + 1 + 1 - \\ 1 + 1 + 1 - \\ \cdots\cdots\cdots\cdots \\ 1 + 1 + 1 - \end{array} \\ \hline & \quad 26 & \qquad 39 \end{array}$$

The manometer remained stationary during these 65 admissions of gas, although one pipette full alone produced a pressure of 0.7 mm. in the flask.

The flask was covered with a coating which became solid and crystalline on standing over night, and then melted at 63° and gave the reactions of phosphorous acid, (melting point 70°). Everything points therefore to the change having taken place entirely according to equation (2).

Oxidation accompanied by liberation of hydrogen.

If in the experiment just described the admission of the gas to V be brought about slowly by opening the tap a gradually, a greenish blue flame, which is frequently intermittent and which in daylight only betrays its existence by the formation of a cloud, is seen instead of the phosphorous acid flame which in the dark is almost blinding and often accompanied by a slight explosion.

The reaction accompanying it is quite different from the former one; a quantitative experiment carried out in the apparatus already described (fig. 6) gave the following result;

PH_3	O_2
1 + 1 + 1 —	1 + 1 + 1 —
1 + 1 + 1 —	1 + 1 + 1 —
1 + 1 + 1 —	1 + 1 + 1 —

The manometer now indicates an evolution of gas, corresponding to an increase of pressure of $5^{3}/_{4}$ mm., that is, since one pipette full gave 0.7 mm., nearly 9 pipettes full. Therefore the gases react together in equal volumes, and leave behind a third gaseous substance equal in volume to either of them. A very accurate confirmation of this may be obtained by adding oxygen carefully to phosphine in excess; the addition of 17 consecutive pipettes full of oxygen, each of which produced a blue flame on entering the flask, left the level of the manometer unchanged at $28^{1}/_{4}$ mm.

Formation of metaphosphorous acid.

Although the gas produced in the last experiments was found to be hydrogen, and the equation for the change was therefore probably $PH_3 + O_2 = H_2 + HPO_2$, the compound HPO_2, the formation of which is assumed, could not be isolated with the experimental arrangements described.

In place of it a yellow or brown deposit was formed, which was partly moist and soluble in water, and in short was evidently a non-homogeneous product of secondary reactions.

A good result was however at once obtained when the two gases were mixed by diffusion instead of by allowing them to flow into each other. They must also be very dilute; at a pressure of 50 mm., even when the gases diffuse into each other the action is too violent, and no pressures greater than about $25^1/_2$ mm. are suitable. To obtain the necessary quantity under these circumstances, the flask V was allowed to remain in connexion with the air pump, and filled with phosphine at a pressure of $25^1/_2$ mm.; the air pump was filled with oxygen at $25^1/_2$ mm., and the tap a opened.

The manometer indicated the gradual combination by a decrease of pressure.

This was,

after	2	hours	$3^1/_2$	mm.
,,	5	,,	$5^1/_2$	,,
,,	21	,,	$9^1/_2$	,,
,,	24	,,	$9^1/_2$	,,

This decrease corresponds to the desired change, for as the volumes of the flask and of the air pump were in the ratio 0.69 : 1, a decrease in pressure of about $10^1/_2$ mm. would be anticipated.

The flask had in the meantime become covered with glittering, feathery crystals which were at once seen to differ from phosphorous acid; they did not melt at 80°. (H_3PO_3 melts at 70°, H_3PO_2 at 17°).

In addition, their behaviour with aqueous vapour was very characteristic; on admitting a very little water through a, the coating of crystals first liquefied, and then after a few minutes solidified entirely, forming long needles, which plainly consisted of phosphorous acid,

$$HPO_2 + H_2O = H_3PO_3$$

subsequently these again liquefied, and the aqueous solution now formed showed the well known reaction of phosphorous acid with silver nitrate.

The change which occurs during slow oxidation.

The question as to which of the above changes occurs during the slow oxidation of phosphorus hydride, and to what extent it occurs, still remained to be answered.

11.89 cc. of phosphine and 6.69 cc. of oxygen were mixed together in a eudiometer and heated in a water bath to 50° until the pressure no longer decreased.

The volume of gas remaining, 10.3 cc., was free from oxygen, and contained 6.2 cc. phosphine and 4.1 cc. hydrogen.

11.89 — 6.2 = 5.69 cc. PH_3 and 6.69 cc. O_2 had thus disappeared forming 4.1 cc. H_2. Assuming that the latter had been formed in the same way as before, that is from 4.1 cc. PH_3 and 4.1 cc. O_2, we have 5.69 — 4.1 = 1.59 cc. PH_3 and 6.69 — 4.1 = 2.59 cc. O_2 which have reacted together in some other way, probably to form phosphorous acid as their volumes are approximately in the ratio 2 : 3.

In the slow oxidation, therefore, we are dealing with the two processes

$$2\,PH_3 + 3\,O_2 = 2H_3PO_3 \quad . \; . \; . \; . \; (a)$$

$$\text{and } PH_3 + O_2 = HPO_2 + H_2 \quad . \; . \; . \; . \; (b)$$

That the latter does not occur alone is doubtless due to the very considerable concentration (the pressure was approximately one atmosphere) at which this slow oxidation took place.

The following observations, made by VAN 'T HOFF, confirm this result. Oxygen and phosphine in the ratio of 361 : 177 were allowed to react partly at the ordinary temperature, but for the greater part at 50°. A residue of 196 mm. O_2 and 42 mm. PH_3 was left unchanged, 70 mm. H_2 being produced at the same time. [1]

Therefore,

$$177 - 42 = 135\ PH_3, \text{ and } 361 - 196 = 165\ O_2$$

had undergone change.

---

[1] The volume of the gases being constant, the quantity is measured by the pressure.

According to equation (*b*), 70 mm. of hydrogen are formed from equal amounts of phosphine and oxygen, so that after subtracting 70 from each of the above quantities in order to allow for the formation of the 70 mm. of hydrogen, we obtain 65 mm. PH_3 and 95 mm. O_2, quantities which are nearly in the ratio 2 : 3.

This result agrees very well with the hypothesis that the oxidation takes place partly according to equation (a), partly according to (b); only in this case, owing to the greater quantity of oxygen, rather more of the phosphine (just half of it) is changed into phosphorous acid than in the first experiment.

The slow oxidation therefore takes place approximately according to the equation

$$4\ PH_3 + 5\ O_2 = 2\ HPO_2 + 2\ H_3PO_3 + 2\ H_2,$$

in which the phosphorous acid might occur as the pyro-acid $H_4P_2O_5$.

As bearing on the simplicity of many reactions the results of Smithells and Dent[1] are interesting; they found that the combustion of cyanogen takes place in two phases, viz:—

$$C_2N_2 + O_2 = 2\ CO + N_2,$$

whilst in the second phase the carbon monoxide is oxidised to carbon dioxide.

We are dealing therefore, in this case, not with a trimolecular reaction represented by the equation

$$C_2N_2 + 2\ O_2 = N_2 + 2\ CO_2,$$

but with a bimolecular reaction.

The trimolecular reactions with which we are at present acquainted will be more fully treated later. At present it may be mentioned that their number is small.

---

[1] Journ. Chem. Soc. 1894. 603.

THE COURSE OF CHEMICAL CHANGE.

SECOND PART.

DISTURBING ACTIONS.

Chapter I.

Disturbing actions in liquids.

I. EFFECT OF THE MEDIUM ON THE VELOCITY OF REACTION. ACTION OF CONTACT.

It is only in rather rare cases that a chemical change takes place in the simple way indicated. The influences to which it is subject are so manifold, that the study of the course of a reaction resolves itself to a great extent into that of the disturbing effects. For this reason these secondary actions will be separately considered here.

In this special chapter such obvious causes of irregularity as lack of homogeneity of the reacting substances, evolution of heat by the reaction, occurrence of secondary transformations and so on, will not be considered.

Attention will rather be directed to less evident disturbances. As we have chosen the normal course of change for our point of departure, we shall first turn to the reactions which take place in liquids in order to study these phenomena, because in liquids the influences under consideration are very little felt and are easily eliminated, whilst the study of the gases presents much greater difficulties in this respect and can only be taken up later.

If a reaction take place in a liquid there is only one cause of irregularity which merits special attention here, namely the *influence of the medium* on the velocity of the reaction.

It is evident that if this influence really exist, the data relating to the reaction will not be comparable with each other in the different periods of its course, because the medium is gradually modified in consequence of the accumulation of the products of the reaction.

Such an influence of the medium on the velocity of the reaction quite certainly exists, and is of considerable magnitude even in those cases in which a chemical, or any analogous process which might be supposed to produce such effects, appears to be excluded; that which is called action of contact, therefore, really exists.

The numerous observations which have been made on the influence of the medium on the velocity of a reaction can be referred in the majority of cases to actions which are due to the nature af the medium; they do not in the least compel us to admit the reality of the mysterious action of contact.

Thus the following two categories of observations appear to be wholly unsuited to solve the question.

(1) There are in the first place those actions of the medium which are evidently of a chemical nature.

(2) We have secondly those observations in which the reacting bodies were not in a homogeneous condition; these cannot be regarded as decisive.

The effects produced by spongy platinum may perhaps be classed with these, though this is a point which is not yet completely elucidated.[1]

Further, (and this remark applies to the experiments of Boguski[2] on the rate at which marble is dissolved by dilute acids), an alteration of the medium (such as the addition of certain salts to it) may favour the renewal of the decomposed acid near the marble and thus may influence the velocity of the reaction in a way differing entirely from a contact action.

The following observations, against which the objections mentioned cannot be raised, seem to establish the action of the medium in virtue of its presence alone: —

---

[1] See also Ostwald, Lehrbuch der Allgem. Chemie, II. 512 et seq.

[2] Berichte 9, 1646, 1876; see also Spring, Zeit. phys. Chem. 1, 209, 1887.

(1) Berthelot and Péan de St. Gilles[1] found that an excess of alcohol retards the etherification of acetic acid in such a way that a gram molecule of it was transformed in 4 hours at 100°

$$\text{to the extent of} \left\{\begin{array}{l} 28 \text{ per cent} \\ 18 \quad ,, \\ \;\,1 \quad ,,\text{[2]} \end{array}\right\} \text{by} \left\{\begin{array}{r} 2 \\ 5 \\ 10 \end{array}\right\} \text{molecules of alcohol.}$$

(2) A thorough investigation of the subject has recently been made by Menschutkin[3], who has shown by means of an extended series of experiments, that the so called chemically indifferent solvents influence the velocity of chemical reactions in very different degrees.

Whilst for example the combination of triethylamine and ethyl iodide takes place with a velocity = 1 when they are dissolved in hexane, the same combination occurs with benzyl alcohol for solvent with a velocity which is 742.2 times greater.

It may therefore also happen that one of the liquid bodies which is taking part in the reaction is itself an unfavourable medium.

An excess of aniline for example retards its own action on acetic acid in such a way that, of a gram. molecule of acetic acid

$$\left.\begin{array}{l} 35 \text{ per cent} \\ 29 \quad ,, \end{array}\right\} \text{is changed by} \left\{\begin{array}{c} 1 \\ 2 \end{array}\right\} \text{molecules of aniline}$$

into acetanilide in 15 minutes at 155°.

(3) L. Meyer[4] has drawn attention to the fact that the velocity of nitration of benzene increases proportionately to the square of the quantity of nitric acid used, whereas it is diminished by excess of benzene.

Along with these phenomena we may here mention the researches of Landolt[5] on the change in the optical rotatory power of a substance when it is dissolved in liquids with which there is little probability of a chemical reaction, for example turpentine dissolved in alcohol, benzene, or acetic acid.

---

[1] Ann. Chim. Phys. (3), 66, 90, 1862.

[2] Schwab, Inaugural Dissertation p. 37; cf. p. 17.

[3] Zeit. phys. Chem. 1. 627, 1887; 6, 41, 1890; Berichte, 15, 1618, 1882.

[4] Zeit. phys. Chem. 2. 713, 1888; Berichte, 22, 18, 1889.

[5] Das optische Drehungsvermögen.

To those who regard the rotativity as a function of the constitution of the molecule, (without regard to any special hypothesis), an alteration in it will be an indication of some displacement of the molecular equilibrium.

The velocity of a reaction is very much affected by such small displacements; the slow course of the monomolecular reactions proves, for example, that the different molecules, although apparently placed in identical conditions, still differ from each other in such a way that in a given time only a part of them undergoes change.

LANDOLT expresses himself as follows: —

"It is conceivable that when molecules of a foreign body (alcohol) come between the molecules of an active substance (turpentine) a certain modification is produced in the structure of the latter, so that in each molecule the distances between the atoms, their arrangement in space, and also the nature of the atomic movements are changed."

In connexion with the experiments which he has recently made MENSCHUTKIN[1] says: —

"This behaviour shows that a certain contact action occurs between the so called indifferent solvent and the dissolved body, in consequence of which solutions of a body exhibit different chemical behaviour with regard to the changes in the velocity of chemical reactions taking place in such solutions, according to the composition and structure of the indifferent solvent."

On the whole, experience forces us to admit that contact action exists, that is, that the medium may by its mere presence influence the velocity of a reaction. The greatest attention must therefore be paid to this influence in studying the course of a reaction.

---

[1] Zeit. phys. Chem. I, 627 et seq. 1887; 6. 41 et seq. 1890.

II. INFLUENCE OF PRESSURE ON THE VELOCITY OF REACTION.

That the rate of reaction is influenced by pressure is proved by many of the researches which have been made on the subject.

Reicher [1] has shown that the transformation of monosymmetric into rhombic sulphur takes place at 96°.2 under a pressure of 16 atmospheres, whilst at atmospheric pressure the change in the opposite direction occurs at this temperature. Later, Spring and van 't Hoff found that copper calcium acetate, which decomposes into its constituents at 77° under atmospheric pressure, undergoes this same decomposition at 40° when the pressure is 6000 atmospheres.

Spring [2] has prepared compounds of sulphur and arsenic with various metals by using very high pressures. A great number of reactions may be brought about by sudden pressure [3].

These effects of pressure will, however, be considered below, for the present it is sufficient to point out their existence.

The influence of pressure on the rate of reactions taking place in liquid media has only been examined in a few cases.

Berthelot and Péan de St. Gilles [4] could find no difference in the rate of etherification of an alcohol by an acid at different pressures.

Van 't Hoff also found that the rate at which dibromsuccinic acid, when dissolved in water, is transformed at 100°, is independent of the pressure.

Finally some recent experiments by Röntgen [5] may be mentioned, in which the influence of pressure on the rate at which cane sugar is inverted by hydrochloric acid was studied. The pressure used was 500 atmospheres, whilst Berthelot and Péan de St. Gilles worked at 50, and van 't Hoff at 6 atmospheres. Röntgen concludes that the rate of inversion is diminished by pressure. He is, however, not justified in drawing this conclusion from his experiments.

---

[1] Groth's Zeitschrift für Krystallographie, Vol. 8. p. 593, 1884. Inaugural Dissertation, Amsterdam, 1883.

[2] Bulletins de l'Académie royal de Belgique, [2] vols. 45 and 49. Berichte 15. 595, 1882.

[3] Meyer. Dynamik der Atome. 1883, 393.

[4] Ann. Chim. Phys. (3) 66. 45, 1862.

[5] Wied. Ann. 45, 98, 1892.

For if the velocity constants for the inversion be calculated from his numbers, it is found that the values of the constants obtained in different experiments with the same solution differ from each other more considerably, than do the constants obtained with solutions which have undergone inversion on the one hand at the ordinary pressure, on the other under a pressure of 500 atmospheres.

The differences observed by Röntgen in the course of the inversion under different pressures are accordingly smaller than the errors in the experiments, which are of not inconsiderable magnitude, and which can be completely accounted for by the variations of the temperature of the solutions[1].

A measurable acceleration of the reaction should however occur with weak acids or acids of intermediate strength, as in such cases, according to the calculations of Tammann[2], the external pressure exerts a very considerable influence on the degree of electrolytic dissociation of the acid.

Chapter II.

Disturbing actions in gaseous systems.

I. THE ORDER OF MAGNITUDE OF THE DISTURBING ACTIONS IN GASEOUS SYSTEMS.

While it is fairly easy to eliminate the disturbances which occur in the course of reactions in liquid systems, and to lay bare the true character of the course of the reaction in all its simplicity, so that reactions of this kind form the most convenient material for studies in chemical dynamics, it is quite different with gaseous systems. There the irregularities of the reactions are of such importance that it is frequently difficult to realise the normal course of the reaction.

When this work originally appeared there was in existence a number of researches, by other chemists, on the course of reactions in liquid systems, the results of which agreed more or less with the requirements of the equations which have been deduced above.

---

[1] See Tammann, Zeit. phys. Chem., 14, 444, 1894.

[2] See Tammann, Zeit. phys. Chem., 17, 725, 1895.

This was the case with the researches of BUCHANAN[1] on the decomposition of chloracetic acid by caustic soda, and of aqueous solutions of chloracetic acid; with those of URECH on the birotation of milk sugar[2] and on the inversion of cane sugar[3]; and also with those of WARDER[4] on hydrolysis; since then they have become innumerable.

The position is, however, quite different when we turn to chemical reactions in gaseous systems; the only researches in this department, which up to the present time have been brought to a satisfactory conclusion are those on the rate of change of arsine and phosphine (VAN 'T HOFF, KOOIJ), and of hydriodic acid (BODENSTEIN). On the other hand our experimental knowledge of the disturbances which affect reactions in gaseous systems has greatly increased without any comprehensive explanation of the greater part of the phenomena having, so far, been given.

The following observations appear to point to a contact action of the medium, though other hypotheses have been proposed to account for them.

(1) The rate of oxidation of phosphorus is affected in a remarkable way by various gases.

For example the oxidation in air is prevented by mixing the air with $^1/_3$ of its volume of H_2S, $^1/_{50}$ of ether vapour, $^1/_{450}$ of ethylene, $^1/_{1000}$ of PH_3, $^1/_{1820}$ of petroleum vapour, or $^1/_{4444}$ of turpentine vapour[5].

(2) In recent years a great number of cases have been investigated, more especially by DIXON and BAKER, in which the influence of minute traces of aqueous vapour on chemical changes is apparent[6].

---

[1] Berichte 4, 863, 1871.

[2] „ 15, 2457, 1882.

[3] „ 16, 2270, 1883.

[4] Amer. chem. Journ. 3, 1881—82; Berichte 14, 1361, 1881.

[5] According to GRAHAM, Phil. Mag. 5, 408, 1834, liquid hydride of phosphorus shows a similar behaviour.

[6] The literature of this subject is given in the Journal of the Chemical Society 1894. (Trans.) p. 623.

According to Dixon[1] a perfectly dry mixture of carbon monoxide and oxygen cannot be exploded at all, or only with great difficulty, by the electric spark. If a minute trace of moisture be brought into the mixture, the explosion occurs at once without difficulty. The explosion may also be induced by other gases such as H_2S, NH_3, HCl, C_2H_4, *i.e.*, such as contain hydrogen, while SO_2, CS_2, CO_2, C_2N_2 are without action.

Furthermore the quantity of the aqueous vapour present has a very great effect on the velocity with which the explosion is propagated.

It is in place, however, to point out here that in other reactions the presence of aqueous vapour may retard the change; the rate of decomposition of ammonia at high temperatures according to Than[2] is diminished by about 98 per cent by the presence of aqueous vapour, and according to van de Stadt[3] the rate of oxidation of gaseous phosphine is also diminished by it.

Among Baker's numerous observations, the experiment in which phosphorus was found not to burn in very carefully dried oxygen even when heated to 150°, may be pointed out as particularly interesting; it was only after the admission of a small quantity of moist air that inflammation occurred.[4] Similar results were obtained with sulphur, carbon, etc.

(3.) Whilst studying the action of hydrogen on chlorine under the influence of light, Bunsen and Roscoe[5] found that the rate of change was diminished

$$\text{to the extent of}\left\{\begin{array}{l} 37.8 \text{ per cent} \\ 9.7 \qquad ,, \\ 60.2 \qquad ,, \end{array}\right\}\text{by}\left\{\begin{array}{l} {}^{3}/_{1000} \text{ of hydrogen,} \\ {}^{5}/_{1000} \text{ of oxygen,} \\ {}^{10}/_{1000} \text{ of chlorine.} \end{array}\right.$$

Pringsheim[6], Dixon and Harker[7], and also Baker[8] have further

---

[1] Phil. Trans. 1884, 618.

[2] Lieb. Ann. 131, 121, 1864.

[3] Zeit. phys. Chem. 12, 329, 1893.

[4] Baker unfortunately does not mention the pressure of the oxygen used. See Ewan's experiments on p. 68.

[5] Pogg. Ann. 100, 499, 501, 502, 1857. Also Ostwald's Klassiker der exact. Wissenschaften, No. 34. p. 81.

[6] Wied. Ann. 32, 384, 1887.

[7] Manchester Lit. and Phil. Soc. 1890. Owens College Researches, 1.

[8] Journ. Chem. Soc. 1894, p. 623.

ESE LIBRAR

shown that this change takes place much more slowly when aqueous vapour is excluded than when it is present.

(4.) The formation of ozone by the electric discharge is completely stopped by the addition of traces of chlorine, while nitrogen, hydrogen, and fluoride of silicon are favourable to it[1]. In this case aqueous vapour has no effect according to Shenstone[2] and Baker[3].

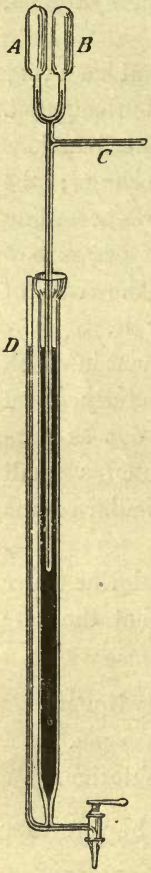


Fig. 7.

A reaction which was carefully studied by van 't Hoff is closely allied to these so called catalytic actions; he found that the formation of ammonium carbamate was accelerated by the presence of aqueous vapour whilst alcohol vapour retards it.

It is to be noticed that the acceleration produced by the aqueous vapour is not be ascribed to the simultaneous formation of ammonium carbonate though this certainly occurs.

Special experiments on this point have shown that the mixture of steam, ammonia, and carbon dioxide which may be obtained according to the equation

$$NH_4.HCO_3 = CO_2 + NH_3 + H_2O,$$

by volatilising ammonium carbonate, forms in the first place ammonium carbamate with very great velocity,

$$CO_2 + NH_3 = NH_2.COOHN_4,$$

and then, very slowly, ammonium carbonate,

$$NH_2.COONH_4 + H_2O = NH_4.HCO_3 + NH_3.$$

The apparatus which was used in the observations on the acceleration produced by aqueous vapour and the retarding effect of alcohol vapour is represented in figure 7.

---

[1] Compt. Rend. 91, 762, 1880.

[2] Journ. Chem. Soc. 1888, 53.

[3] Ibid. 1894, 617.

The side tube C was filled with carbamate und closed before the blowpipe. The whole apparatus was then filled with mercury and placed in position in the burette D which also contained mercury.

On heating the salt, the mixture of carbon dioxide and ammonia produced displaces the mercury from the vessels A and B. When a sufficient quantity of the mixture is obtained the formation of the carbamate may be allowed to begin, and the velocity with which it takes place in the two vessels compared.

This is done by determining the pressures of the gaseous mixture in the two vessels from time to time, the volume being maintained constant. This is accomplished by allowing mercury to flow out of the burette whenever it is on the point of rising into A or B.

If the apparatus has been properly filled, the velocities of the reaction in the two divisions of it are found to be exactly equal.

A small quantity of water is then introduced in a little glass bulb into A. The quantity used is that which can evaporate at the ordinary temperature into the space available (0.0004 gram, or 4 per cent. of the carbamate employed).

Both vessels are then warmed in an air bath so as to decompose the carbamate which has deposited on their walls. In this way the mixture of carbon dioxide and ammonia is regenerated in A and B, but with the difference that water vapour is now present in A.

When the two divisions of the apparatus are brought back to the initial temperature a decided difference in the rates at which the reaction occurs in them is evident.

The rate in A is approximately doubled by the introduction of the aqueous vapour.

The retarding influence of alcohol vapour was established in a similar way, while air had no effect even when present in fairly large quantities.

Since the existence of these disturbances in the course of a reaction is proved experimentally in such a variety of cases, it is not surprising that the greater part of the reactions occurring in gaseous systems which have been studied up to now do not follow the equations which we have deduced.[1] This is the case with the experiments of **Berthelot** and **Péan de Saint Gilles** on etherification, and with those of **Lemoine** on the formation and decomposition of hydriodic acid.

---

[1] See the exceptions on p. 32.

The following changes also, which were investigated by **van 't Hoff**, lead to similar results: —

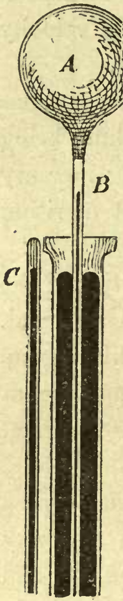


Fig. 8.

1. The polymerisation of formaldehyde.
2. The polymerisation of cyanic acid.
3. The transformation of moist electrolytic gas into water.
4. The transformation of dry electrolytic gas into water.

1. *Polymerisation of formaldehyde.*

Through the researches of **Hofmann**[1] we know that gaseous formaldehyde possesses the formula CH_2O, and that this body gradually changes into a solid polymeric substance, the formula of which is very probably $C_3H_6O_3$.

This reaction was investigated as it is of special interest, being probably trimolecular.

The apparatus used (fig. 8) consists of a large round flask A, attached to a barometer tube B. After evacuating it as far as possible with the air pump, (to about 2.01 mm.), the gaseous formaldehyde, evolved by heating the compound $C_3H_6O_3$ in a small retort, was admitted over mercury.

Having thus filled the apparatus it is placed in position in the mercury of the burette C[2]; the volume is maintained constant and the pressure of the unchanged formaldehyde measured from time to time. The numbers obtained are given in the following table[3].

---

[1] Berichte, 2, 156, 1869.

[2] Compare with D in fig. 7, page 34.

[3] The total pressure, reduced to 0°, is corrected for the initial pressure of the air in the apparatus (2.01 mm.).

Time.	Pressure of the formaldehyde.
0	23.6 mm.
2.3 hours.	22.1 ”
67.5 ”	20.6 ”
6 days.	18.8 ”
34 ”	16.8 ”
50 ”	15.0 ”
82 ”	11.8 ”
3 months.	9.5 ”
4 ”	4.9 ”
5 ”	2.9 ”

The course of this change does not correspond in any way with that required by the equations which we have proposed.

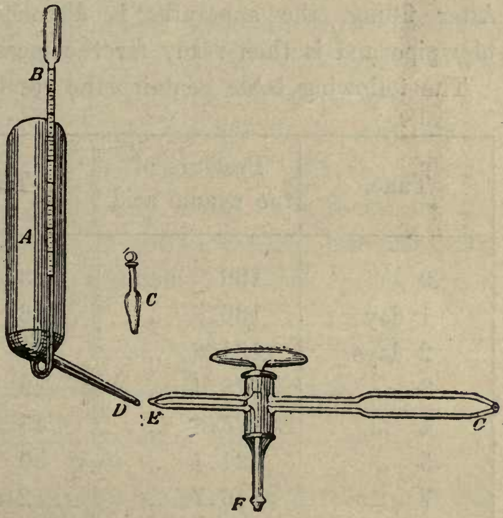


Fig. 9.

The same result was always obtained when the experiment was repeated.[1]

2. *Polymerisation of cyanic acid.*

The change of cyanic acid into cyamelide, which occurs in the liquid acid with explosive violence, takes place in the gaseous acid so slowly that it is specially well suited for a dynamical study.

---

[1] The reaction does not take place so smoothly as might be desired, for simultaneously with the formation of the polymer, its decomposition takes place, and a final maximum pressure is therefore obtained. This is in agreement with the fact that the polymer sublimes (Tollens, Berichte, XV, 1629, 1882). The deviations observed are however too large to be ascribed wholly to this cause.

The apparatus used in this investigation consisted of a cylindrical vessel A (fig. 9) to which a small manometer B was attached. The liquid cyanic acid which was employed in filling it was prepared by heating anhydrous cyanuric acid in the retort H, and condensing it in the cooled receiver J, (fig. 10). The liquid acid is poured into the small, well cooled bottle C, which is then connected with the tap F, by means of which its contents may be put in communication with the air pump. The air still remaining in the bottle having been pumped out, it is put in communication with the apparatus A B which has previously been fused to E by means of the side tube D, and is vacuous. After filling, the apparatus is disconnected by means of the blowpipe and is then ready for the measurements of pressure.

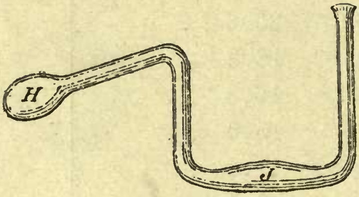


Fig. 10.

The following table contains the results which were obtained.

Time.	Pressure of the cyanic acid.	Time.	Pressure of the cyanic acid.
0	139 mm.	23 days	89.1 mm.
1 day	136.8 ,,	26 ,,	85.5 ,,
2 days	131.8 ,,	27 ,,	84.1 ,,
3 ,,	128.4 ,,	29 ,,	82.3 ,,
4 ,,	125.4 ,,	45 ,,	68.4 ,,
5 ,,	121.4 ,,	50 ,,	65.9 ,,
7 ,,	116.7 ,,	2 months	56.5 ,,
9 ,,	112.2 ,,	4 ,,	44.1 ,,
12 ,,	106.1 ,,	5 ,,	39.7 ,,
13 ,,	104.1 ,,	6 ,,	33.3 ,,
16 ,,	99.2 ,,	8 ,,	30.3 ,,
19 ,,	94.7 ,,	10 ,,	27.6 ,,
21 ,,	91.5 ,,	20 ,,	13.0 ,,

Here, also, the measurements do not agree at all with any of the equations proposed. The experiment, repeated several times, always yielded the same result.

3. *The transformation of moist electrolytic gas into water.*

The transformation of electrolytic gas into water was found to take place at 440° sufficiently slowly to admit of its course being followed; this change, especially attractive on account of its simplicity, was therefore carefully studied.

The apparatus which was employed with moist electrolytic gas resembled a large thermometer; it was filled by means of the gas burette[1] A (fig. 11) which contained the electrolytic gas. By means of the tap B the part of the apparatus to be filled (shown in the figure in a horizontal position) may be connected either with the air pump through D, or with A; in this way it is first evacuated and then filled with the gaseous mixture, after which, the tap C being closed, it is sealed off between C and B. Some mercury is now introduced into the part of the tube to the left of the tap, which is then opened so as to obtain a short index of mercury shutting off a column of air of suitable length in the capillary tube of the apparatus (L in fig. 12). The tube is finally sealed up before the blowpipe.

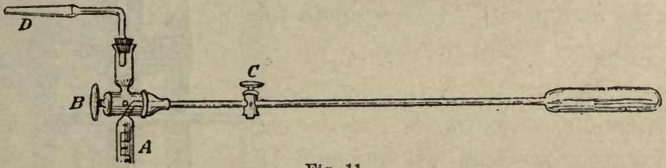


Fig. 11.

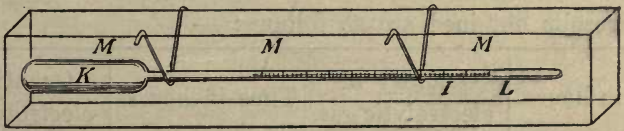


Fig. 12.

The bath in which the apparatus was heated (fig. 13) consists of an iron cylinder A, containing boiling sulphur. Two windows of mica, one of which is visible at C, permit the height of the sulphur vapour to be observed.

---

[1] This was constructed in the way described by Bunsen, Gasometrische Methoden, 1877, p. 76.

The bath was heated in a Perrot's gas furnace provided with a gas regulator D[1].

The quantity of the gaseous mixture remaining after the heating had been continued for a known interval of time, was determined by placing the apparatus in a horizontal position in the water M, (fig. 12), so as to equalise the temperature in all its parts. The length of the column of air, L, was then measured on the scale which is shown in the figure. This length is inversely proportional to the pressure, and thus to the quantity of the residual gas[2].

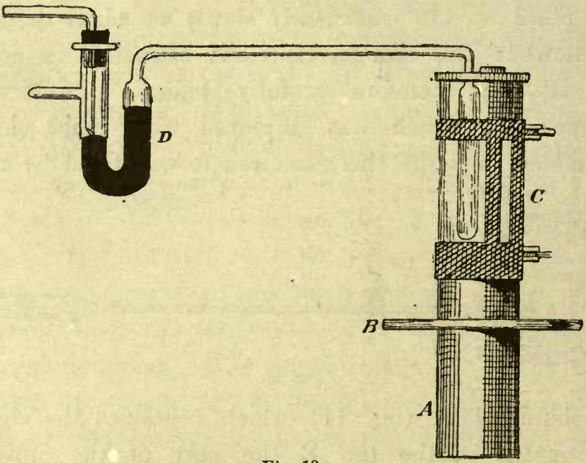


Fig. 13.

The results obtained are as follows: —

Time in hours.	Quantity of electrolytic gas.	Time in hours.	Quantity of electrolytic gas.
0	1	54	0.871
6	0.974	61	0.863
13	0.951	68	0.853
20	0.931	75	0.846
27	0.915	82	0.839
34	0.902	89	0.831
41	0.893	116.5	0.808
47	0.881		

---

[1] Constructed by Herr Claessen.

[2] Both the electrolytic gas and the column of air are saturated with aqueous vapour.

The results of this experiment, which was repeated several times, also do not agree with our equations.

4. *The transformation of dry electrolytic gas into water.*

For these experiments the following alterations were made in the apparatus just described; the reservoir A[1], in figure 14, is filled in the same way as formerly through E, but it is now made to communicate with the parts C, D and F, which are united by means of a flexible tube containing mercury.

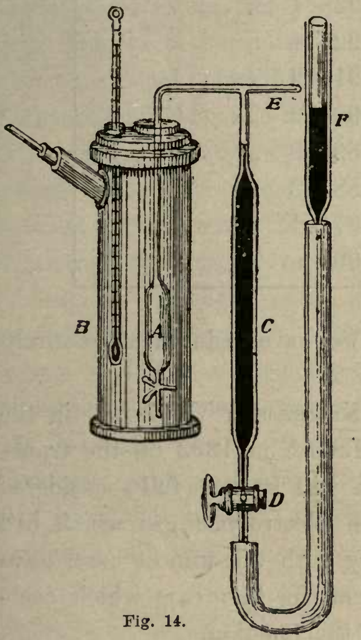


Fig. 14.

This arrangement allows a portion of the gaseous mixture to be transferred from A to C, (by lowering F), in order to dry it by contact with sulphuric acid contained in C over the mercury.

While the apparatus is being heated in the sulphur bath (not in the apparatus B shown in the figure, which will be mentioned later) the whole of the gaseous mixture is contained in A, and the tap D is closed.

When the mixture has been heated for the time desired, the tap is opened and the tube F raised and lowered about a hundred times so that the gas is dried while it is cooling.

The quantity of the gaseous mixture remaining is then determined by means of its pressure at constant temperature and volume[2].

The results are the following: —

---

[1] The lower part with the three side pieces serves to prevent A from coming in contact with the iron cylinder in which the sulplur in boiled.

[2] The reservoir A is placed in water from the water supply, and the temperature, the height of the barometer, and the difference in level between the mercury in C and F when the gas occupies a given volume, read off by means of the cathetometer.

Time in hours.	Pressure of the electrolytic gas.
0	997.7 mm.
5	980 „
12	965.6 „
20	953.2 „
29.5	938.4 „
38.5	926.4 „
47.75	914.9 „
57	905.2 „
67.5	894.9 „
78.5	885.3 „
99.5	871.1 „
126.66	860 „

Here also the equations which we have deduced are entirely at fault.

The researches carried out by Krause and V. Meyer[1] in the year 1891, and by Askenasy and Meyer[2] in 1892 on the transformation of electrolytic gas, which will be more fully considered later, and which were made with electrolytic gas which had been prepared in a state of purity with the utmost care, gave the same results; disturbances occur in this case which completely mask the normal course of the reaction.

The experiments described justify the conclusion that while the course of a reaction in a liquid medium is normal, even when no special precautions are adopted, that is, it agrees with the equations which we have deduced, this is, in general, by no means the case with gases.

[1] Lieb. Ann. 264, 85, 1891. Naturwissenschaftliche Rundschau, VI, 349.

[2] Lieb. Ann. 269, 49, 1892.

II. THE NATURE OF THE DISTURBING ACTIONS IN GASEOUS SYSTEMS. ACTION OF THE WALLS OF THE VESSEL.

Formation of cyamelide and of water; decomposition of phosphine.

Since the deviations from the normal course of change in gaseous systems appeared be of a secondary nature, the question as to their cause presented itself.

It was found possible to prove by experiment the existence of disturbing actions in the cases which have been described.

Turning in the first place to the disturbing actions in liquid systems, the volume occupied by the reacting substances must be taken into account; this volume must be a vanishing quantity when compared with the whole volume of the system. This condition is satisfied when we are dealing with gases under atmospheric pressure; the other condition, that the nature of the medium shall remain unchanged during the reaction is, however, not satisfied in gaseous systems.

It is clear that in a reaction taking place between gaseous substances, as for example the formation of water from electrolytic gas, the medium undergoes a profound change. In the example mentioned, the medium at the beginning of the process is electrolytic gas, at the end, it is the aqueous vapour which has been formed.

In addition to the two disturbing actions which are found in liquid systems, there are two other causes of irregularity which exert their influence more especially in gaseous systems, viz: —

1. The area of the surface of the walls of the vessel.
2. The nature of the surface of the walls of the vessel.

1. *Influence of the area of the surface of the walls of the vessel. Polymerisation of cyanic acid.*

The apparatus shown in figure 15 was used to investigate the effects of the walls of the vessel on the rate of formation of cyamelide[1].

---

[1] On this action, see NAUMANN, LIEB. Ann. 160, 16, 1871.

The divisions A and B have the same volume, but the areas of their walls are in the ratio 6 : 1.

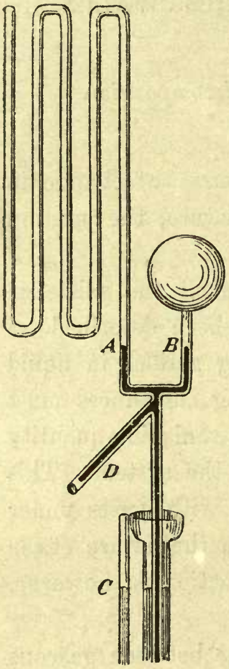


Fig. 15.

A little anhydrous cyanuric acid having been brought into D the apparatus is placed in a burette containing mercury and evacuated by means of the air pump which is attached to it at D. The tube D is then closed before the blowpipe.

By heating D both compartments are filled with gaseous cyanic acid. On lowering the apparatus communication between A and B is cut off, after which the pressure of the unaltered cyanic acid is measured from time to time.

These measurements of the pressure show that the reaction takes place at entirely different rates in the two divisions.

Initial pressure	188.4	mm.	
After one day	146.8	,,	in A.
	157	,,	,, B.

Ratio of the velocities in A and B, —

1.33 : 1.

The velocity in the division with the greater surface is therefore much the greater.

2. *Influence of the nature of the surface of the walls of the vessel.*

Since the superficial area of the walls of the vessel influences the rate of the reaction, it may be surmised that the nature of these walls will also have some action.

This is a matter which is worthy of special attention in dynamical studies in which the reaction itself produces some change in the walls, as for example when a solid product of the reaction is deposited on them.

Although observations of this kind had previously been made [1], it was still thought to be of special importance to study the phenomena more completely, in order that their effects might be eliminated.

---

[1] Naumann, Lieb. Ann. 160, 16, 1871.

Investigations were made on,

a. The polymerisation of cyanic acid.
b. The transformation of electrolytic gas into water.
c. The decomposition of phosphine.

a. *Influence of the nature of the walls of the vessel on the polymerisation of cyanic acid.*

The influence of cyamelide, which is deposited on the walls of the vessel during the polymerisation of cyanic acid, was studied by means of the apparatus represented in figure 7.

The division B was filled with gaseous cyanic acid, in the way which has already been described (p. 35). As soon as the walls had, in consequence of the polymerisation, become coated with cyamelide, the unaltered cyanic acid was divided between A and B by raising the apparatus; the communication between the two vessels was then interrupted by lowering it again, and the measurements of the pressure proceeded with.

The following results were obtained;

Initial pressure . . . . 49.5 mm.
Pressure after one day . . . . $\begin{cases} 44.5 \text{ mm. in A.} \\ 32.4 \;\;\text{,,} \;\;\text{,,}\;\; \text{B.} \end{cases}$

Ratio of the velocities in A and B, —

1 : 3.42.

The rate of the reaction is therefore rather more than trebled in the division the walls of which are coated with cyamelide.

b. *Influence of the nature of the surface of the walls on the transformation of electrolytic gas into water.*

1. Older experiments.

The results obtained in the study of this reaction (p. 40) appeared to point to a disturbance, arising during the progress of the reaction, and retarding it more and more as it proceeded.

The apparatus shown in figure 14, when filled with electrolytic gas, gave the following results,

Initial pressure	997.7 mm.
Pressure after heating to 448° for 5 hours	980 ,,
Diminution of pressure per hour	3.5 ,,

After having been used for 130 hours, the same apparatus, when filled afresh, gave: —

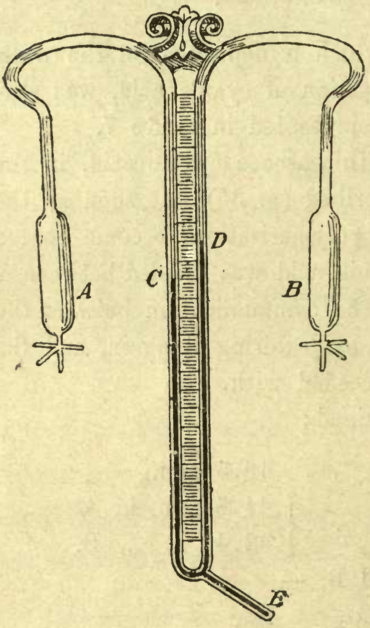


Fig. 16.

Initial pressure	801.1 mm.
Pressure after heating to 448° for 20 hours	788.8 ,,
Decrease of pressure per hour	0.6 ,,

The change in the nature of the walls, produced by heating the vessel for 130 hours, has thus reduced the velocity of the reaction to one sixth of its original value.

This result was confirmed by means of the apparatus represented in figure 16.

The vessel A, which had been used in the experiments just mentioned, and which had therefore been heated for 150 hours, was used along with a second, new vessel B of the same shape. The two were connected by means of a capillary tube C D. After evacuation, through E, both vessels were filled with electrolytic gas, and a column of mercury was introduced into C D in order to interrupt the communication between the vessels, and to measure the pressure in them; E was finally closed before the blowpipe.

The two vessels were heated in the same way, in two Perrot's gas furnaces provided with thermo-regulators (see p. 40). They were immersed in the vapour of boiling sulphur contained in cylinders of the form described on page 39.

The heating was discontinued from time to time, the vessels allowed to cool, and immersed in water from the water supply to bring them to the same temperature.

The height of the mercury column was then read off on the millimetre scale.

Time in hours.	Height of mercury column.		Difference in velocity per hour.
	Old apparatus.	New apparatus.	
0	111.75	111.0	0.63
37.5	100.0	123.0	

The result is clear; the formation of water takes place considerably more slowly in the apparatus which has already been used, than in the new one.

The change which occurs in the walls of the vessels in these experiments, may probably be accounted for by a superficial devitrification owing to the action of the hot aqueous vapour on the glass; although this is scarcely visible to the naked eye, it exerts, as we have seen, an enormous influence on the velocity with which the reaction proceeds.

It is, however, to be noticed that devitrification of the walls of the vessel does not always *retard* the reaction; the experiments of Krause, Askenasy and V. Meyer, which will be considered below, show that the very opposite may occur in the transformation of electrolytic gas into water.

2. More recent experiments.

The laborious experiments of V. Meyer, Krause and Askenasy[1], which were briefly mentioned on page 42, are to be considered here.

---

[1] See literature mentioned on p. 42.

Since **Bunsen** and **Roscoe** had observed that exceedingly small quantities of impurity, have a very great influence on the normal course of the reaction between chlorine and hydrogen[1], **Meyer**, **Krause**, and **Askenasy** took pains to prepare absolutely pure electrolytic gas for use in their experiments. With electrolytic gas containing traces of other gases, they had previously obtained entirely irregular results.

Their experiments were performed as follows: — Small glass bulbs, containing about 20 cc., after being filled with the explosive gas, were heated for a certain time, either in a liquid bath, or in the vapour of a boiling liquid.

The final experiments were made with an extremely pure mixture of oxygen and hydrogen prepared by electrolysis, which, in order to avoid impurity, had been passed for 10—14 days through the bulbs which were to be filled, (the bulbs being united with each other by means of glass capillary tubes). It was found that the normal course of the reaction could not be realised.

For example, two very carefully cleaned glass bulbs were heated simultaneously, for exactly two hours, in the same bath, (phosphorus sulphide, boiling at 518°), after which the quantity of electrolytic gas remaining was determined.

The results are as follows: —

Number of the experiment		I	II	III	IV	V
°/₀ of the electrolytic gas combined	Bulb 1.	26.41	27.83	28.2	53.71	63.29
	„ 2.	19.34	100.00	100.0	57.29	100.00

From these results, the only conclusion possible is, that even the most carefully cleaned glass surfaces possess irregularities which exert a variable influence on the transformation of electrolytic gas, and that the surfaces of two glass bulbs which have been prepared with the greatest care in the same way, may be sufficiently different, or may become so during the reaction, to account for the entire irregularity in the results of the experiments.

The attempt to prepare identical smooth bulbs was abandon-

---

[1] See page 33.

REESE LIBRARY OF THE UNIVERSITY OF CALIFO

ed, and the internal surfaces made completely rough, as it was thought possible that in this way they might be more easily obtained the same. This remedy was however a complete failure, as the following numbers show: —

Etched bulbs[1].

Percentage of electrolytic gas transformed into water.	1.	33.8
	2.	51.1

The exclusion of glass surfaces was also unsuccessful. Glass bulbs coated internally with silver yielded results similar to those obtained with the etched ones.

Silvered bulbs.

		I.	II.	III.
Percentage of electrolytic gas transformed into water	Vessel 1.	19.8	7.5	15.6
	,, 2.	97.7	92.9	35.2

These bulbs were heated in aniline vapour, at 183°, for two hours, it having been found that the change takes place at a considerably lower temperature in contact with a surface of silver, than in glass vessels.

It has already been noticed, that Meyer and Askenasy found that the devitrification, which probably occurs in consequence of the action of the heated aqueous vapour on the walls of the glass vessels, does not always retard the formation of water, as the older experiments of van 't Hoff (p. 47) appear to show, but that the results are completely irregular in this respect also.

		Bulb previously heated to 518° for			
Percentage of electrolytic gas	New bulb	22	24	26	28 hours.
transformed into water at 518°	24.81	21.8	29.3	78.7	37.4

c. *Effect of the nature of the walls of the vessel on the decomposition of gaseous phosphine.*

In the course of an investigation on the decomposition of gaseous phosphine at higher temperatures, D. M. Kooy[2] has also recently observed the effects of the surface of the vessels on the velocity of the reaction. The experiments were made with the apparatus represented in figure 14.

---

[1] Totally irregular results were also obtained in bulbs which had been protected from light. In one series of experiments the percentage of gas which was changed into water varied from 11.3 to 82.3.

[2] Zeit. phys. Chem. 12, 155, 1893. Inaugural Dissertation, Amsterdam, 1892.

The following table contains the experimental results. (Temperature = 446°).

New vessel[1].

Time in hours.	Pressure in mm.	Velocity constant.
0	715.21	—
28.17	765.88	0.00236
33.42	773.89	232
38.50	781.59	232
45.33	793.93	238

Old vessel[2].

Time in hours.	Pressure in mm.	Velocity constant.
0	706.02	—
29.58	830.35	0.00637
33.58	843.76	637
39.58	861.38	636
44.58	876.18	641

It must, however, be regarded as being doubtful, whether the velocity of this reaction is *always* greater in vessels which have already been heated.

III. THE NATURE OF THE DISTURBING ACTIONS IN GASEOUS SYSTEMS.

a. *The rate of oxidation of phosphine.*

According to the equations which represent the relation between the concentration of the reacting substances and the velocity of the reaction, the latter increases when the former increases. There are, however, a number of facts which seem to show that the opposite to this is true.

---

[1] The values of the velocity constant k have been calculated by the equation on p. 3, common logarithms being substituted for those to the base e.

[2] This vessel had already been used for a considerable time in similar experiments.

Fourcroy[1] found that at the ordinary temperature and normal pressure, pure oxygen does not act upon phosphorus, whilst air oxidises it vigorously.

In 1798, van Marum[2] observed that a piece of phosphorus glows much more brightly in diluted air than in air under the normal pressure, and that the phosphorus even takes fire at low pressures if it be wrapped in a little cotton wool.

In 1817, Houton de Labillardière[3] observed, in the course of an investigation on phosphine, a very remarkable phenomenon, which he described in the following words: —

"Le gaz hydrogène protophosphoré se distingue du perphosphoré en ce qu'il n'a pas la propriété de s'enflammer par le contact de l'air. Il est cependant à remarquer qu'on peut enflammer ce gaz dans l'air, à la température ordinaire en le raréfiant. On s'assure de ce fait en introduisant dans une éprouvette très-forte et longue, entourée d'un grillage de fil de fer pour éviter les morceaux si le vase venait à casser, de l'air ou de l'oxigène et de l'hydrogène protophosphoré, en maintenant le mercure dans l'éprouvette au niveau du mercure extérieur; alors, en élevant l'éprouvette de manière que le mercure de l'éprouvette soit à deux décimètres environ au-dessus du mercure du bain lorsqu'on opère à 20° C, il se produit tout-à-coup une détonnation dans l'éprouvette."

This experiment appears to have received no special attention. Dumas[4] repeated it and showed that the presence of an excess of phosphine is necessary for the success of the experiment. (2 vols. PH_3 to 1 vol. O_2.) Davy[5] appears also to have noticed something similar.

He says: — "I found that phosphuretted hydrogen produced a flash of light when admitted into the best vacuum, that could be made by an excellent pump of Nairn's construction."

---

[1] Memoires de l'acad. des Sciences, 1788.

[2] Verhandelingen uitgegeven door Teylers Genootschap. 10, 1798.

[3] Ann. Chim. Phys. (2) 6, 304, 1817.

[4] Ann. Chim. Phys. (2), 31, 119, 124, 1829. See also Rose, Pogg. Ann. 24, 127. 1832.

[5] Phil. Trans. 1817, 49.

To these facts the following similar ones may be added.

Arsenic, and sulphur begin to oxidise, according to Joubert[1], only when the oxygen is sufficiently dilute.

Friedel and Ladenburg[2] found that silicon hydride behaves in a similar way, and according to Berthelot, nickel carbonyl does so also.

Reicher and Jorissen[3], however, found that the last named substance is still spontaneously inflammable in oxygen under a pressure of 13 atmospheres.

Further, according to Engelmann[4], oxygen appears to have a more stimulating action on certain low organisms when its pressure is decreased.

Labillardière's experiment was repeated with the apparatus shown in the accompanying diagram (fig. 17). The tap C being closed, the tube is filled with mercury, the mixture of phosphine and oxygen introduced, and the opening, F, closed with a cork. D is then put in communication with the air pump, and the tap, C, opened. The volume of the mixture of gases increases, and an explosion takes place.

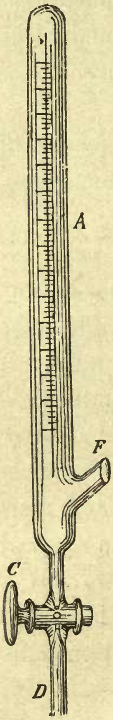


Fig. 17.

The observation of Labillardière having been confirmed in this way, the conditions under which the phenomenon occurs were more carefully investigated. The investigation could not however be begun, until a special cause of the inflammation of the mixture of phosphine and oxygen, had been discovered and eliminated.

It was found that this inflammation may be caused by movements of the mercury which is in contact with the gaseous mixture.

The following experiment shows that the mixture is so sensitive to such movements, that the use of mercury is attended with great difficulties.

---

[1] Thèse sur la Phosphorescence du Phosphore, 1874, Paris.

[2] Ann. Chim. Phys. (4), 23, 430, 1871.

[3] Maandblad voor Natuurwetenschappen, 1894, No. 1.

[4] Botanische Zeitung, 1882, p. 320.

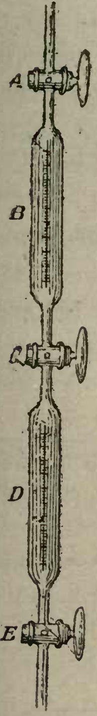


Fig. 18.

The apparatus shown in figure 18 being initially full of mercury, a mixture of 2 vols. of phosphine and 5 vols. of air is brought into it through A, which is then closed; mercury is then pumped out through C and E, as in the previous experiment, so that the mixed gases are expanded until they fill the whole apparatus. (75 vols.)

The taps C and B are now closed, the dilute gas filling the two separate divisions B and D, in one of which a globule of mercury has been left Combustion is now produced by the slightest shock in the division containing the globule of mercury. The reason of this may possibly be found in local dilutions of the gas, produced by the mobile mercury. (See the explanation given below.)

In order to avoid this cause of combustion, the mercury was replaced by a viscid solution of calcium chloride in most of the experiments which follow.

Using the apparatus in figure 17, it was proved that *the explosion is not produced by expansion alone.* No change is produced by a sudden, and much more considerable expansion than that which gave rise to the explosion in the former experiments; the gaseous mixture may be preserved in this dilute condition without undergoing any change whatever; the explosion is produced, however, by the diminution of volume which takes place when the tap is opened, after D has been brought below the surface of the calcium chloride solution.

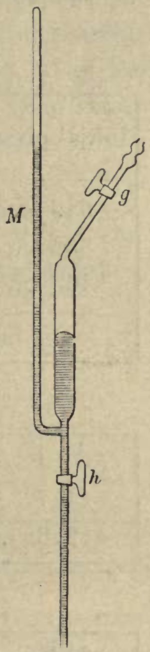


Fig. 19.

Investigation of the rate of oxidation of phosphine near the explosive limit.

Having cleared up the nature of the reactions which occur in the slow oxidation of phosphine, J. D. van de Stadt[1] made a careful study of the rate of oxidation.

For this purpose he used the apparatus represented in figure 19. M serves as a manometer; the apparatus having been completely filled with mercury, with the help of an air pump, the gases are admitted through g, mercury flowing out through h; the volume of the gas is obtained by weighing the latter. The pressure was read with a cathetometer, and the gas was in contact with calcium chloride solution.

First series of experiments. After filling the apparatus, it was heated to 50° in a water bath, for periods of one hour; at the end of each period the pressure was diminished by about 100 mm. by running mercury out through h.

No. 1. 2.64 cc. PH_3 and 1.55 cc. O_2.

Initial pressure.	Final pressure.	Diminution per hour.	$^0/_0$-age of the initial pressure.
649 mm.	640 mm.	9 mm.	1.4
553 ,,	546 ,,	7 ,,	1.2
463 ,,	459 ,,	4 ,,	0.9
On further dilution the explosion occurs.			

No. 2. 2.46 cc. PH_3 and 2.54 cc. O_2

589.4 mm.	588.0 mm.	1.4	0.24
524.7 ,,	521.9[2] ,,	1.4	0.26
419.6 ,,	418.4 ,,	1.2	0.28

No. 3. 2.65 cc. PH_3 and 1.58 cc. O_2.

623 mm.	612 mm.	11 mm.	1.8
521 ,,	510 ,,	11 ,,	2.1
446 ,,	439 ,,	7 ,,	1.6
364 ,,	Explosion at 50°.		

---

[1] Zeit. Phys. Chem. 12, 322, 1893. See also p. 20.

[2] Duration of this experiment = 2 hours.

It follows from these data,

1. That temperature, pressure, and quantity remaining approximately the same, the velocity of change varies considerably; viz. from 0.2 in No. 2 to 2.0 in No. 3.

2. That the explosion is not preceded by any well marked acceleration of the reaction, but that large velocities may occur without any explosion (No. 3), while small ones may be followed by an explosion. (No. 1).

Second series of experiments. In the experiments No. 1 and No. 3, the explosion took place during an operation, — in No. 1 on diluting, and in No. 3 while bringing the apparatus into the water bath; in order to avoid these external influences completely, the artificial decrease of the pressure at the end of each hour was abandoned, and the apparatus simply left to itself at 50°, so as to bring about spontaneous inflammation if possible. Some calcium chloride solution was again added, as in the first series. All the pressures given relate to the temperature 50°, at which they were measured.

No. 4. 1.99 cc. PH_3, and 1.03 cc. O_2.

Time in hours.	Pressure at 50°.	Decrease of pressure p. hour.	%-age of the initial pressure.
0	763 mm.	—	—
1	739	24	3.2
2	716.5	22.5	3.0
3	694.5	22	3.1
4	671	23	3.3
5	643.5	27.5	4.1

The explosion took place some minutes later.

No. 5. 2.14 cc. PH_3 and 1.12 cc. O_2.

0	765 mm.	—	—
2	757	4	0.5
8	737	3.3	0.5
12	724	3.2	0.5
21	696.5	3	0.4
25	685.5	2.8	0.4
31	665	3.4	0.5
34	655	3.3	0.5

The explosion occurred.

No. 6. 1.44 cc. PH_3 and 1.48 cc. O_2.

Time in hours.	Pressure at 50°.	Decrease of pressure of hour.	$^{\circ}/_{0}$-age of the initial pressure.
0	708.5	—	—
2	705	1.8	0.2
6	696	2.3	0.3
15	675	2.3	0.3
19	664.5	2.6	0.4
25	648	2.8	0.4
31	633	2.5	0.4
36	621	2.4	0 4
42	606	2.5	0.4
The explosion took place after several hours.			

The result is the same as in the first series; unexpectedly large variations in the velocity are found, — on the one hand 4.0 in No. 4, on the other, 0.4 in No. 6. The explosion is not preceded by any noticeable acceleration; it may occur when the velocity is small (for example, 0.4 in No. 6) or it may not occur when the velocity is large, (for example, 3.0 in No. 4).

It may therefore be regarded as proved, that although dilution causes the explosion, yet the latter is not the culmination of an acceleration of the reaction produced by the dilution. The dilution seems rather to act in such a way that suddenly something new comes into play; this conclusion is in accordance with the results obtained by IKEDA[1] in the oxidation of phophorus, which have been confirmed by EWAN.[2] Both found that within certain limits of pressure the process is quite normal, its velocity being proportional to the pressure of the oxygen.

Regarding the limiting pressure at which explosion occurs, two cases must be distinguished according as we are dealing with dry, or with moist mixtures of gases.

1. *The explosive limit for dried mixtures.*

There is, in this case, an upper limiting pressure of oxygen above which the explosion does not occur.

[1] Journ. Coll. Science. Imp. Univ. Japan, VI, 43. 1893.

[2] Zeit. phys. Chem., 16, 315, 1895.

The determination of this limit is, as VAN DE STADT found, extremely difficult, if the gases be completely dried.

The phosphine usually burns when it comes in contact with the oxygen, with a visible flame, or formation of a dense cloud, complete combustion taking place.

At the ordinary temperature, a definite result could only be obtained in a few experiments.

The observations were made in a thick walled tube closed at both ends by taps. This was first filled with mercury, after which the gases were introduced through the upper tap, the mercury displaced through the lower one being weighed in order to measure the volume of the gases. After closing the upper tap and mixing the gases, they were caused to expand by allowing mercury to flow from the lower tap into a vacuous space; this was done very slowly and without shaking, (compare page 53), for which purpose the lower tube was drawn out to a capillary.

Only one of the many experiments in which the gases were dried over phosphorus pentoxide was successful.

2.09 cc. O_2; 0.51 cc. PH_3; Volume at the explosion 21.9 cc.

$$\text{Pressure of oxygen } \frac{2.09}{21.9} = 0.1 \text{ atmosphere. } (10^\circ)$$

After drying over soda-lime the following experiment was successfully carried out without any cloud being formed.

0.54 cc. O_2; 0.95 cc. PH_3; Volume at the explosion 5 cc.

$$\text{Pressure of the oxygen } \frac{0.54}{5} = 0.11 \text{ atmosphere.}$$

The upper limit of pressure was also found to be 0.1 atmo. after drying over crystallised glycerine.

A lower limit of pressure does not exist in the case of dry gases. The explosion always occurs when working with dry gases, even at the greatest dilution.

2. *The explosive limit with moist gases.*

VAN 'T HOFF determined the volume at which a mixture of 1 cc. of phosphine, and 0.5 cc. of oxygen explodes, by means of the apparatus shown in figure 18. The mercury was covered by a layer of calcium chloride solution.

The explosion was produced sometimes by expansion, sometimes by compression following on a sudden expansion, (compare p 53.) The volume of the gas at the moment at which the explosion took place, was measured on the scale on the tube A; the reddish-brown deposit which covers the walls of the tube after the explosion, facilitates the reading considerably.

The following table contains the values of the volumes, (in cc.) occupied by 1—5 cc. of the mixture at the time of the explosion; the corresponding pressures of the oxygen are also given.

Expansion.		Compression.	
Volume of the mixture.	Pressure of oxygen in atmos.	Volume of the mixture.	Pressure of oxygen in atmos.
3.5 cc.	0.14	9.5 cc.	0.05
5.1 ,,	0.1	6.8 ,,	0.07
7.35 ,,	0.068	3.9 ,,	0.13
11.7 ,,	0.04	8.9 ,,	0.06
—	—	9.9 ,,	0.05
—	—	5.5 ,,	0.09
—	—	3.3 ,,	0.15
—	—	5.6 ,,	0.09

With moist gases, there are therefore, two limits to the oxygen pressures at which the explosion takes place; an upper one, which as the table shows, lies between 0.04 and 0.14 atm. in these experiments, and a lower one, which varies between 0.05 and 0.15 atm. To what is this lower limit, which as we have already seen does not exist when the gases are dry, to be ascribed?

Special experiments were made by VAN DE STADT on this point, which showed that moisture retards the reaction. Since the gaseous mixture was preserved over an aqueous solution of calcium chloride, the proportion of aqueous vapour in it must obviously increase when it is expanded, and its retarding influence, therefore become more pronounced, thus giving rise to a lower limit.

The fact that traces of aqueous vapour completely stop the change at great dilutions, is of some interest, since the experiments of Dixon, Baker, and others have shown that the presence of water is absolutely necessary in many reactions.[1]

If the PH_3 had been dried over phosphorus pentoxide, soda-lime, or crystallised glycerine, it frequently took fire spontaneously in the air, as if it were P_2H_4. This fact explains the curious behaviour of mixtures of phosphine and oxygen, which, as Rose[2] and van 't Hoff observed, often explode only after standing for some days.

Van 't Hoff brought together 130 cc. of phosphine and 8 cc. of oxygen and noticed, that as the diffusion progressed, a cloud was formed, this being followed, on one occasion after two hours, on another after 20 hours, by an explosion.

If the oxygen be replaced by air the same phenomenon occurs as soon as the oxygen has reached the necessary pressure. 15.5 cc. of air and 49 cc. of phosphine being mixed, for example, the explosion did not occur until 30 hours had elapsed.

As soon as the hygroscopic substances HPO_2 and H_3PO_3[3], which are formed at first by the slow oxidation, have taken up the moisture present, and thus dried the gases, the explosion takes place.

The table on the preceding page shows that when two limits of pressure exist, they lie close together.

The upper limit of pressure has been accurately determined by van 't Hoff at the ordinary temperature, and by van de Stadt at 50°.

Van 't Hoff used the apparatus shown in figure 17. By means of the pipette, (fig. 20), the gases were brought into the apparatus in measured quantities.

The pipette was filled with mercury and connected to the oxygen gasholder, the tubes by which the connection was made having first been freed from air by filling

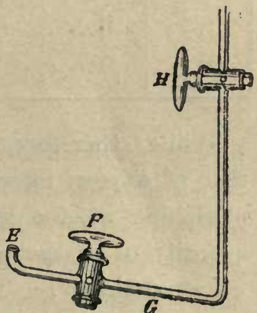


Fig. 20.

---

[1] See p. 33.

[2] Pogg. Ann. 24, 158, 1832.

[3] See p. 20.

them with mercury. The taps F and H were then opened so as to fill the pipette with gas up to a mark near G, which is not shown in the figure. The taps were then closed, and the pipette, containing 0.5 cc. oxygen between F and G, disconnected. The tube between E and F was then filled with mercury, and F brought into the lateral opening of the explosion apparatus A, which had previously been filled with a viscid solution of calcium chloride.

The phosphine was introduced in the same way, after which the expansion was brought about in the manner described previously. (page 52).

In this way, mixtures containing 0.5 cc. oxygen and varying quantities of phosphine were examined. The following table contains the results obtained.

PH_3 cc.	O_2 cc.	Volume at which the mixture exploded.	Explosion pressure in atmospheres of the	
			PH_3.	O_2.
0.5	0.5	5	0.1	0.1
1	0.5	3.3—11.7	0.19	0.096
1.5	0.5	4 — 8.5	0.28	0.092
2	0.5	4.3— 7	0.38	0.095
2.5	0.5	5 — 9.8	0.38	0.075
3	0.5	9.5—14	0.27	0.045
3.5	0.5	6.2—14	0.41	0.059
6	0.5	9.6	0.62	0.052

While, therefore, the ratio of the quantity of phosphine to that of oxygen increases from 1 to 12, and the pressure of the phosphine at the moment of the explosion increases with the quantity of it, the pressure of the oxygen remains approximately $^1/_{10}$ atmosphere[1].

Van de Stadt found, that also at 50° the upper explosive limit corresponds to a definite pressure of the oxygen, which however, is at this temperature considerably higher, viz. 180 mm. approximately. This result is analogous to that obtained by JOUBERT, who found that the pressure above which phosphorus ceases to be luminous in oxygen gas, rises with rising temperature.

---

[1] It is to be noticed that the same limit was obtained with dry mixtures at the ordinary temperature (p. 57).

If the gases are saturated with moisture, and at the ordinary temperature, the limiting pressure is depressed somewhat, owing to the presence of the water vapour, (as it is also by increasing the quantity of the phosphine, see the foregoing table). The following table shows the effect of moisture.

cc O_2.	cc. PH_3.	Final volume.	Pressure of oxygen.	Temp.
1.16	3	17.9	0.065	14°
0.9	2.05	13.1	0.069	11°
1.02	2.1	12.6	0.071	14°
1.01	1.9	13.9	0.088	11°

b. *The rate of oxidation of Phosphorus, Sulphur, and Aldehyde.*

I. PHOSPHORUS.

The slow oxidation of phosphine having been found to be unsuitable for the study of the connexion between the velocity of the change and the concentration of the oxygen, owing to the explosion which occurs preventing further measurements, phosphorus, sulphur, and aldehyde were studied from this point of view by T. EWAN.[1]

1. Phosphorus in moist oxygen.

a. *Rate of oxidation in air.*

This had already been studied by IKEDA[2]. EWAN first repeated some of the experiments described by IKEDA. The apparatus used consisted of a bottle of 1½ to 2 liters capacity with two necks, into one of which a test-tube was fitted by means of a cork, while the other communicated with a manometer. The test tube reached to about the middle of the bottle, and its lower, closed end was surrounded by a cylinder of phosphorus, which was kept cool by a current of water of the same temperature as the water bath in which the apparatus stood. The experiments were made as follows: — The bottle, containing air, and a little water, was placed in the thermostat, connected with the manometer, and allowed to stand until it had assumed the temperature of the bath.

---

[1] Zeit. phys. Chem. 16, 315, 1895. Phil. Mag. (5). 38, 505, 1894.

[2] See p. 56.

The phosphorus was then quickly placed in position in the apparatus, and the pressure noted. The readings of the pressure were then repeated at suitable intervals of time. Since the phosphorus is very little acted on during an experiment, the area of its surface may be regarded as remaining unchanged.

The numbers which were obtained are given in the following table. In it, k_1 is the velocity constant of the oxidation, calculated from the expression

$$-\frac{dp}{dt} = k_1 p \ldots\ldots \quad (1)$$

which on integration becomes,

$$k_1 = \frac{1}{t} \log \frac{p_1}{p_t} \ldots\ldots\ldots \quad (1^a)$$

where p_1 is the partial pressure of the oxygen initially,

p_t ,, ,, ,, ,, ,, ,, ,, after partial oxidation of the phosphorus,

and t is the time.

The values of k_1 which were obtained increase slightly, showing that the rate of oxidation of phosphorus in moist air decreases somewhat more slowly than the partial pressure of the oxygen. IKEDA had also drawn this conclusion from his experiments.

Phosphorus in moist air.

Temperature . . . . = 20°.2 — 20°.4
Pressure of the aqueous vapour = 17.8 mm.
,, ,, phosphorus ,, = 0.113 mm[1].

---

[1] JOUBERT, Thèse, 1874. (cf. p. 52).

Time in minutes t.	Pressure. P.	Partial pressure of the oxygen. p.	k_1.	k.
0	773.1	157.8	—	—
25	750.6	135.3	0.00267	42.0
50	729.7	114.0	0.00282	43.1
75	714.3	99.0	0.00271	40.1
100	697.4	82.1	0.00284	42.3
130	682.2	66.9	0.00286	42.1

Since the values of k_1 are calculated on the assumption that the velocity of oxidation is proportional to the oxygen pressure, the fact that they increase shows, that at smaller pressures, the reaction takes place somewhat faster than this assumption leads us to expect. The reason of this, is perhaps to be found in the fact that bodies evaporate more quickly into a gas at a lower pressure, than at a higher one.

The reaction, in the case under consideration, probably takes place between the vapour of phosphorus and oxygen; it was therefore natural to assume, that the rate of oxidation would be proportional to the rate of evaporation of the phosphorus.

The rate at which a liquid of constant temperature and constant surface area evaporates into a gas depends, according to Stefan [1], on the pressure of the gas, the connexion being

$$V = c \log \frac{P}{P - p_1}.$$

In this equation

V is the rate of evaporation,
P is the total pressure of gas and vapour,
p_1 is the partial pressure of the vapour,

and c is a constant.

If now, in accordance with the assumption made above, $-\frac{dp}{dt}$ in equation (1) be taken to be also proportional to V, we obtain,

[1] Sitzungsber. Wiener Akad. der Wissenschaften, 68, 385 1873.

$$-\frac{dp}{dt} = k\ p \log \frac{P}{P - p_1} \ldots\ldots (2)$$

This equation states, that the rate of oxidation of phosphorus is not only proportional to the pressure of the oxygen, but also to the rate of evaporation of the phosphorus.

In order to calculate the values of k, equation (2) must be integrated.

If *a* be the sum of the partial pressures of the nitrogen and aqueous vapour in the mixture of gases, and therefore a constant quantity, we have $p = P - a$. Substituting this value in (2), and developing the logarithm in a series, we obtain

$$-kdt = \frac{dP}{P-a}\left[\frac{P}{p_1} - \frac{1}{2} - \frac{1}{12}\frac{p_1}{P} - \frac{1}{24}\frac{p_1^2}{P^2} - \ldots\ldots\right].$$

Integrating between the limits P_1 and P_t, and neglecting small terms[1], this gives,

$$k = \frac{1}{t}\frac{P_1 - P_t}{p_1} + \frac{1}{t}\left(\log\frac{P_1 - a}{P_t - a}\right)\left(\frac{a}{p_1} - \frac{1}{2}\right) \ldots\ldots (2a)$$

The values of k in the table on page 63 are calculated by means of this equation; they are more nearly constant than the values of k_1; we may therefore conclude, that *the rate of oxidation of phosphorus in moist air is really proportional to the pressure of the oxygen.*

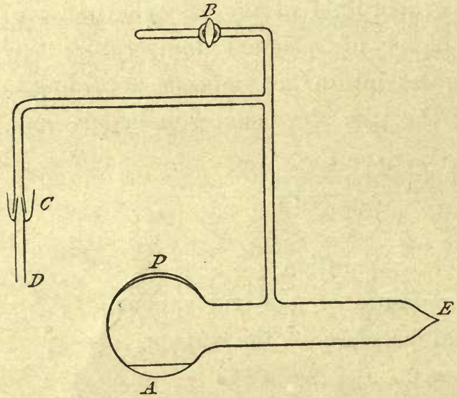


Fig. 21.

This, however, can only be true within certain limits, for it is well known that oxidation of phosphorus does not take place in oxygen at higher pressures.

b. *Rate of oxidation at higher pressures.*

By means of the apparatus shown in the accompanying drawing, measurements were now made at all pressures at which the oxidation occurs.

---

[1] With phosphorus p_1 is small compared to a at the ordinary temperature.

The glass vessel EPA, the volume of which was 50--70 cc., communicates, by means of capillary tubes of 0.5 mm. internal diameter, with the tap B and with a manometer at D. The junction at C was made, either by a ground glass joint luted with mercury, or by a short length of thick-walled indiarubber tubing.

The manometer was arranged so that the mercury always stood at the same height in the tube D; the volume of the apparatus therefore remained constant. A mercury manometer was usually employed, though in a number of experiments a brom-naphthalene manometer was substituted for it; the latter could be read more accurately, and the vapour of the brom-naphthalene had no effect on the course of the reaction. The phosphorus was purified by melting it under a weak solution of potassium bichromate and sulphuric acid, and washing it.

A piece of this phosphorus was brought into the apparatus through E, melted at P, (in an atmosphere of carbon dioxide, or *in vacuo*,) and spread out over the upper surface of the bulb in as thin a layer as possible, after which it was allowed to solidify. A little water having been brought into the apparatus at A, the opening E was sealed up before the blowpipe.

The apparatus, prepared in this way, was placed in a constant temperature water bath, after which it was evacuated and oxygen allowed to enter. The latter operations were repeated four or five times. In doing this it is of importance to keep the phosphorus at a sufficiently low temperature, as otherwise it is very apt to take fire when the oxygen is admitted to the vacuous apparatus. The inflammation takes place particularly easily when the pressure is low and the phosphorus dry. With oxygen which had been dried over phosphorus pentoxide, it occurred even at 0°, under a pressure of about 1 mm.

The greater part of the experiments were made at 20° [1]. Two experiments, which were made at 20°, on the limiting pressure above which no oxidation takes place, gave the following results; the reaction just began in one case when the pressure of the oxygen was 696 mm., in another case it began at 671 mm., but not at 723 mm. We may therefore conclude that phosphorus only oxidises in moist oxygen, at 20°—21°, under pressures which are less than about 700 mm.

---

[1] See the complete tables given in the Zeit. phys. Chem. 16 p. 321, 1895, or Phil. Mag. (5), 38, 512, 1894.

It is of interest to notice, that Joubert, who has published

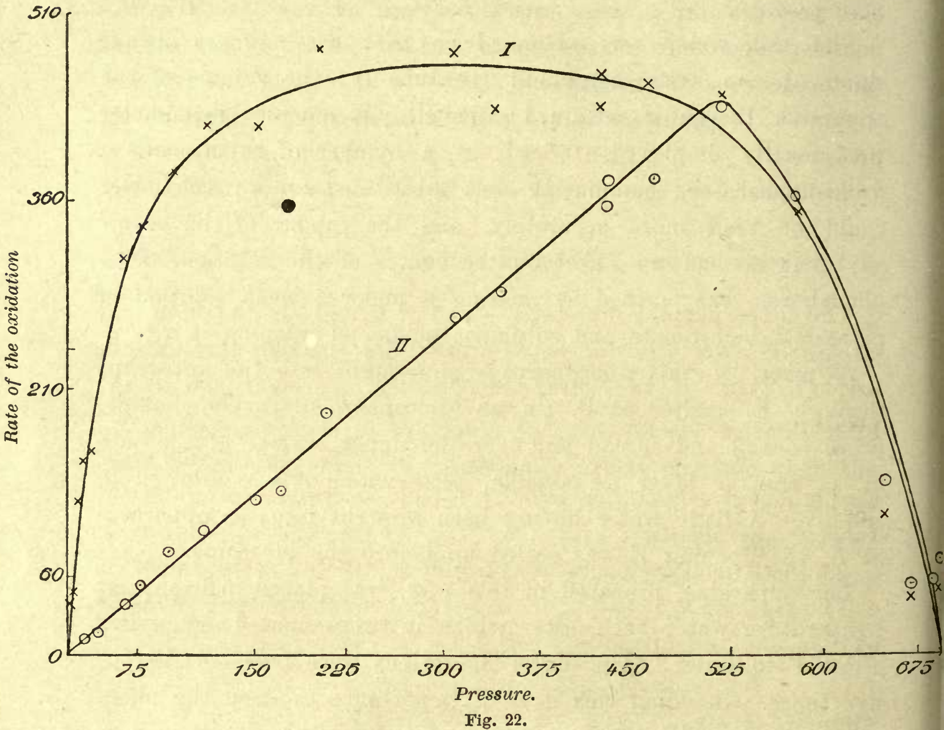


Fig. 22.

two series of experiments on the pressures at which phosphorus just becomes luminous in oxygen, finds, at 20°.2, in the first series 787 mm., in the second 666 mm., as the pressure at which luminosity is first visible.

The pressure found here seems, therefore, to agree with those obtained by Joubert, from which it follows that the pressure at which the oxidation begins is the same as that at which the phosphorus becomes luminous.

The curve, (fig. 22), illustrates the connexion between the rate of oxidation of phosphorus in moist oxygen (at 20°), and the pressure of the oxygen. In curve I, the values of $\frac{dp}{dt}$ are taken as ordinates, those of the mean partial pressures of the oxygen as abscissae.

Curve I shows that the velocity of the reaction beginning with the value 0 at 700 mm. increases at first very rapidly as the pressure falls, then varies between narrow limits over a considerable range of pressure (viz., from 500—100 mm.), and finally decreases again rapidly.

Curve II represents graphically the connexion between the pressure of the oxygen and the rate of oxidation, the rate of volatilisation of the phosphorus being supposed constant, viz.,

$$\frac{dp}{dt} : \log \frac{P}{P - p_1}.$$[1]

The experimental numbers — represented in the figure by circles — evidently lie on a straight line passing through the origin. That is, the corrected velocity is proportional to the pressure of the oxygen.

This is however only true up to a pressure of about 520 mm.; at higher pressures the velocity rapidly decreases, reaching the value 0 at 700 mm.

At the ordinary temperature, therefore, the following connexion exists between the rate of oxidation of phosphorus in moist oxygen and the pressure: —

$$-\frac{dp}{dt} = kp \log \frac{P}{P - p_1}.$$

Above a certain limiting pressure — which probably varies with the temperature — this ceases to be true, the reaction taking place very much more slowly.

2. Phosphorus in dried oxygen.

Quite a different result is obtained in this case. The experiments were made in the same way as those with moist oxygen, except that phosphorus pentoxide was substituted for the water in A (fig. 21).

---

[1] The data from which the curve is drawn are contained in the paper already cited. Phil. Mag. Dec. 1894. p. 505.

Two experiments were made; in the first the oxygen was left in contact with the phosphorus pentoxide for a week, in the second for two days.

The reaction now first began at a much lower pressure than with moist oxygen. Under a pressure of oxygen of 377 mm. no reaction occurred, at 202 mm. it went forward very slowly.

The connexion between the pressure of the oxygen, and the rate of oxidation is represented graphically in curve I (fig. 23).

Setting out from the pressure of 200 mm., the velocity of the reaction appears to increase continuously as the pressure falls, without reaching a maximum value as is the case when the gas is moist. (Compare the curve in fig. 22).

Curve II represents the rate of oxidation in dry oxygen when the rate of evaporation of the phosphorus is constant. It is obtained by dividing the values used in drawing curve I by the corresponding values of the rates of evaporation of the phosphorus. The numbers obtained in this way are very irregular; it appears however, that the rate of oxidation between 0 and 70 mm. is proportional to the square root of the pressure of the oxygen.

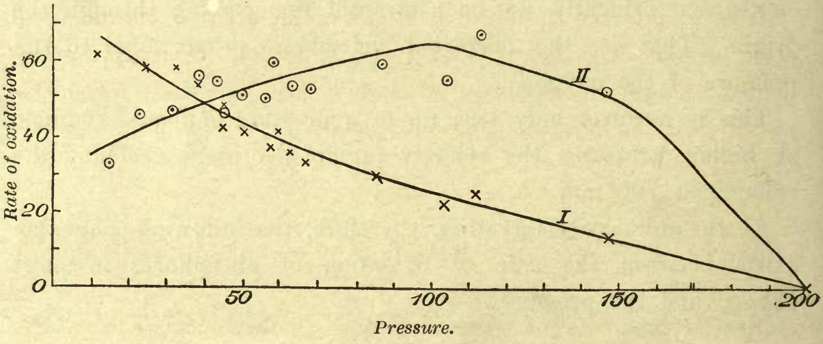


Fig. 23.

We may therefore write: —

$$- \frac{dp}{dt} = k_1 . p^{1/2} . \log \frac{P}{P - p_1} \quad \dots\dots\dots (3)$$

After expanding the logarithm in a series, and integrating, we obtain — neglecting small terms —,

$$k_1 = \frac{1}{t}\frac{2}{3\,p_1}\left[(P_1 - a)^{3/2} - (P_t - a)^{3/2}\right] + \frac{1}{t}\left(\frac{2a}{p_1} - 1\right)\left[(P_1 - a)^{1/2} - (P_t - a)^{1/2}\right] \quad (3^a.)$$

The values of k_1 calculated by means of this equation from the experiments, remain approximately constant below 60—70 mm., at higher pressures they decrease.

The irregularity of the results obtained in these experiments is probably due, in part at any rate, to the deposition of a coating of oxide on the surface of the phosphorus. We may therefore say, that, the rate of evaporation of the phosphorus being supposed constant, the rate at which it is oxidised by dry oxygen is proportional to the square root of the pressure of the latter. This is only true (at 20°) up to a pressure of 60—70 mm., above this pressure the velocity is smaller.

It is of interest that the maximum velocity of oxidation — at constant rate of evaporation of the phosphorus — occurs at a pressure of $^1/_{10}$ atmosphere; this pressure is also the most favourable to the reaction between phosphine and oxygen (p. 60).

II. Sulphur.

As we have seen, the deposition of phosphorus pentoxide on the surface of the phosphorus introduces a difficulty into the study of the rate of oxidation of this substance. The process takes place more regularly when sulphur is used as the oxidisable substance, because the product of the reaction is volatile.

The apparatus shown in figure 24 was used in these experiments; by means of it the pressure may be kept constant during the measurements, the volume being variable. It consists of a glass tube S, on which two bulbs are blown, and having a capacity of 60—70 cc. One bulb, S, contains 1—2 grams of sulphur, the other 5—6 grams of soda-lime. A constant temperature of about 160° is maintained by immersing the apparatus in the vapour of boiling turpentine, which is contained in the flask.

The measuring tube A is graduated in $^1/_{10}$ cc., and contains mercury the level of which may be adjusted by means of the reservoir B. C is a three way tap, D a small gauge containing bromnaphthalene which allows the pressure in the part of the apparatus to the left of D to be made equal to that in the bottle F.

By means of the tap E, these two parts of the apparatus may be put in communication with each other.

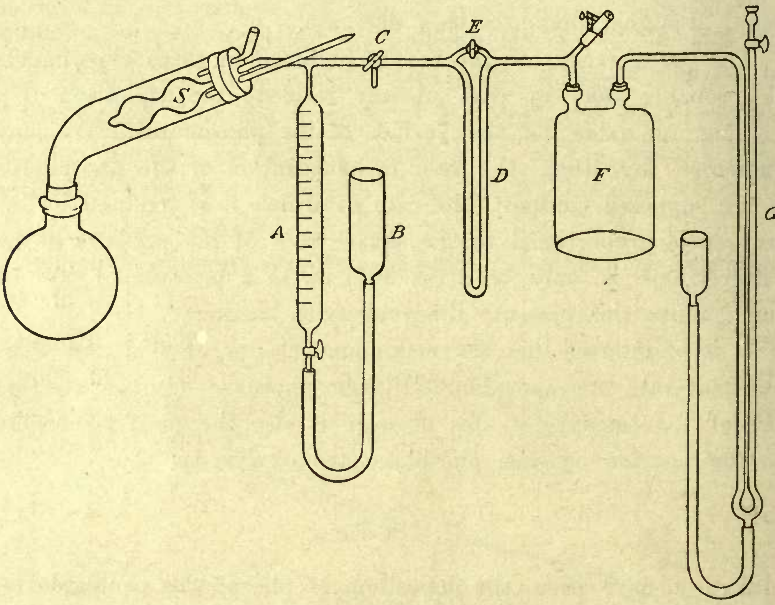


Fig. 24.

The reservoir F, which serves to keep the pressure constant, is in communication with the manometer G and with an air pump.

The part of the apparatus which is seen in the figure to the left of D, was first filled with oxygen at a somewhat greater pressure than that existing in F, the tap E opened for a moment to equalise the pressure on both sides of D, and the position of the mercury in A read off. By raising B it is easy to maintain the pressure constant, and equal to that in F.

The diminution of volume per minute, when reduced to some standard pressure, is then proportional to the velocity of the reaction.

When the velocity has become constant, the pressure in F is reduced, the tap E opened to equalise the pressure again, and further readings made at the new pressure.

The following table contains the results.

In it $\frac{\Delta v}{\Delta t}$ is the diminution of the volume per minute, the volume being measured at pressure P.

$\frac{dv}{dt}$ is the rate of change of the volume, calculated for a pressure of 819.7 mm., and is proportional to the quantity of oxygen which is converted into sulphur dioxide per minute, that is to the rate of the reaction.

Pressure P.	$\frac{\Delta v}{\Delta t}$.	$\frac{dv}{dt}$.	Temperature.	k_1.	k.
809.8	0.0176	0.0174	158°	0.0985	0.0035
587	0.0244	0.0175	158	0.0841	0.0035
380.6	0.0459	0.0213	158	0.0820	0.0042
198.5	0.147	0.0356	159	0.0975	0.0069
105.6	0.456	0.0588	159	0.118	0.0056
43.8	1.77	0.0946	159	0.108	0.0163
819.7	0.0149	0.0149	158	0.085	0.0030
578.7	0.0243	0.0172	159	0.082	0.0034
422.2	0.0349	0.0180	159	0.088	0.0043
306	0.0653	0.0244	159.5	0.084	0.0048
194	0.133	0.0315	159.2	0.085	0.0061
147.3	0.222	0.0399	„	0.093	0.0077
95.9	0.455	0.0532	159.4	0.098	0.0100
41.8	1.84	0.0938	„	0.104	0.0161

The constant k_1 is calculated from the following equation, which is essentially identical with equation 3: —[1]

$$-\frac{dv}{dt} = k_1 P^{1/2} \log \frac{P}{P - p_1},$$

---

[1] In the calculation p_1 has been taken as 11.5 mm. (at 158°—159°). This value, which does not pretend to any great accuracy, was determined by a special experiment. It is also to be noticed that an error in p_1 has very little influence on the value of k_1 or of k.

while k is calculated by the formula

$$-\frac{dv}{dt} = k\ P \log. \frac{P}{P - p_1}.$$

As the table shows, the experimental results are in much better agreement with the first of these equations, in which the rate of oxidation is put proportional to the square root of the pressure, than with the second, in which it is supposed to be proportional to the pressure itself.

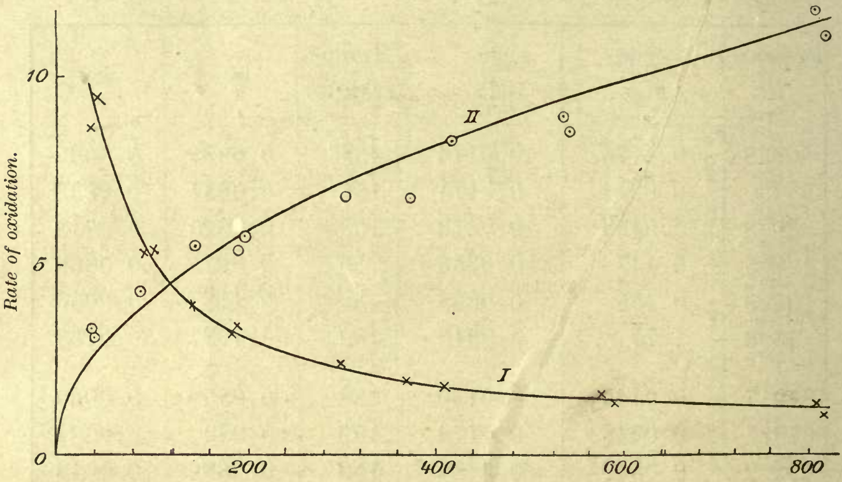


Fig. 25.

The curves in fig. 25 represent the connexion between the rate of oxidation and the pressure.

Curve I is drawn with the values of $\frac{dp}{dt}$ as ordinates, and those of the pressure as abscissae. It has a strong general resemblance to that which was obtained with phosphorus and dried oxygen, (fig. 23); in both cases, the velocity increases continuously as the pressure falls.

Curve II is drawn with ordinates proportional to the square roots of the corresponding pressures. The experimental values of the velocity of oxidation corrected for the rate of evaporation of the sulphur, viz. $-\frac{dv}{dt} : \log \frac{P}{P-p_1}$, are represented in the figure by circles.

The theoretical curve represents these points with fair approximation.

It is of interest that the whole curve here, up to 800 mm., corresponds to the part of the curve for phosphorus and dried oxygen between 0 and 70 mm.[1] Whether a maximum velocity such as was observed with phosphorus and oxygen, occurs also with sulphur and oxygen at higher pressures, must be decided by further experiments.

III. Aldehyde.

In experiments with solid or liquid bodies, such as phosphorus or melted sulphur, the rate of evaporation has such a great influence on the velocity of the oxidation, that it is not easy to determine with perfect certainty what influence the concentration of the oxygen has upon it.

It appears, however, from the foregoing experiments, very probable that the rate of oxidation in dried oxygen is proportional to the square root of its pressure. In order to further test the truth of this result, experiments were made with oxygen and aldehyde-vapour.

The reaction was found to take place with convenient speed at 20°. It was assumed that aldehyde-vapour at 20°, and under pressures which do not exceed about 550 mm., may be considered, with sufficient approximation, as a perfect gas.

Numerous attempts were made to absorb the acetic acid formed, by means of some solid substance without action on aldehyde; PbO, ZnO, $BaCO_3$, anhydrous $KC_2H_3O_2$, were tried, but all produced a more or less rapid diminution in the quantity of aldehyde-vapour. The experiments were therefore made without any such absorbent, and by means of apparatus similar to that represented in fig. 14, p. 41.

---

[1] Compare fig. 23 on page 68.

The oxidation takes place in the bulb A (fig. 26), which is kept at a constant temperature in a thermostat; its volume is 60—70 cc. The pressure of the gas is determined by means of the manometer B C D. By raising or lowering the tube C, the level of the mercury is always brought to the mark B before a reading is made. The pressure, BD, may then be measured on a vertical millimeter scale or by means of a cathetometer. CD is a barometer dipping below the mercury at C; the air-trap E serves to retain any air bubbles which may leak through between the glass and rubber tubes.

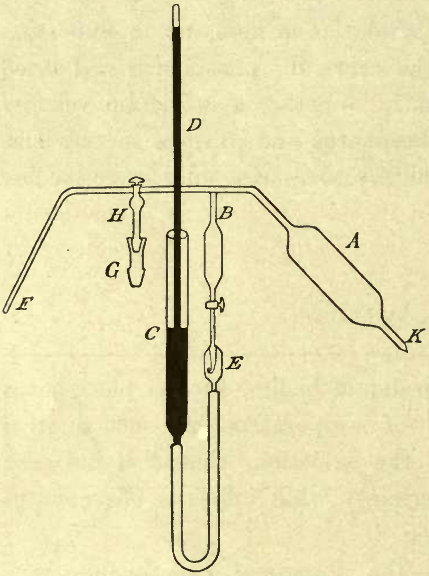


Fig. 26.

By means of the three-way tap H the apparatus may be connected either with an air-pump through F, or with a little vessel containing liquid aldehyde, G, which is ground to fit the lower limb of the tap. The aldehyde-vapour is admitted by putting the apparatus — evacuated as far as possible — in communication with the liquid aldehyde in G; by repeating these operations the air is completely replaced by aldehyde-vapour. The tap H is then closed, the apparatus placed in the thermostat, and the pressure observed.

G is then removed, F connected up to the oxygen gas holder, and a current of oxygen, dried over $CaCl_2$, led for some time through F H. The tap H is then quickly opened to admit the oxygen to the apparatus, closed again, and the pressure observed. Further readings are then made from time to time until the reaction is ended.

Since the gases do not mix immediately, the velocity is frequently rather small at the beginning of the reaction.

The calculation of the rate of oxidation from the experiments, requires a knowledge of the composition of the gas remaining in the apparatus at the end of an experiment.

As soon as the last reading of the pressure had been made, therefore, a very dilute solution of caustic potash — used in order to be polymerise the aldehyde — was allowed to flow into the apparatus from a weighed flask. The difference between the volume of the apparatus — determined by weighing it full of water — and the volume of the caustic potash solution drawn into it, gave the volume of the oxygen and nitrogen contained in the residue. The oxygen was absorbed by alkaline pyrogallol[1].

The experiments were made in the dark, special experiments having shown that light has some influence on the velocity of the reaction.

The following table contains the results, —

Time in minutes. t	Pressure of oxygen. p_1	Pressure of aldehyde. p_2	Total pressure. P	$k \times 10^5$
0	225.8	536.0	785.0	—
67	210.3	499.1	744.5	2.91
117	200.5	466.9	702.5	2.94
190	188.1	427.3	651.5	2.81
259	177.1	395.8	608.0	2.84
270	174.6	388.8	598.5	2.93
296	167.2	368.7	571.0	3.16
332	161.4	353.5	550.0	3.19
386	150.7	324.7	510.5	3.43
476	136.6	292.3	464.0	3.57
673	118.3	251.6	405.0	3.40
1303	83.8	183.1	302.0	3.29

Temperature 20°.1 — 20°.32.
Partial pressure of oxygen at end of experiment. 83.4 mm.
,, ,, ,, nitrogen. . . . . 23.7 ,,
Total pressure at the end of the experiment . . 301.0 ,,
Vapour-pressure of acetic acid at 20°.2. . . . . 11.4 ,,[2]
$k_1 = 0.002873$

---

[1] It was found necessary to cover the surface of the mercury with a layer of brom-naphthalene, in order to avoid the action of the mixture of oxygen and aldehyde on the mercury of the manometer.

KAHLBAUM, Zeit. phys. Chem. 13, 35. 1894.

Time in minutes. t	Pressure of oxygen. p_1	Pressure of aldehyde. p_2	Total pressure. P	k × 10^5
0	489.6	291.2	799.0	—
72	485.3	281.7	790.5	0.96
98	480.6	273.2	781.0	1.52
132	475.5	251.2	766.5	1.81
163	470.0	249.2	749.0	2.05
229	457.2	220.5	707.5	2.87
325	441.6	186.1	657.5	2.94
464	424.2	159.5	603.5	3.11
617	409.1	119.1	558.0	3.18
1330	376.5	57.2	463.5	3.00

Temperature 20°.5 — 20°.7.

Total pressure of residual gas . . . . . . 473.5 mm.
Partial pressure of residual oxygen . . . . 376.5 „
„ „ „ nitrogen. . . . 18.2 „
Vapour pressure of acetic acid at 20°.6. . 11.6 „

$k_1 = 0.00103.$

Time in minutes. t	Pressure of oxygen. p_1	Pressure of aldehyde. p_2	Total pressure. P	k × 10^5
0	595.7	270.0	878.0	—
146	—	—	878.0	—
0	533.2	241.6	785.7	—
136	532.3	239.9	783.1	—
1163	532.3	239.7	782.9	—
0	373.0	178.5	559.3	—
353	346.8	122.8	488.8	2.82
421	344.6	118.2	481.8	2.59
501	342.7	114.2	476.1	2.34

Temperature 20°.8.

Total pressure of residual gas . . . . . . 442.6 mm.
Partial „ „ oxygen . . . . 331.9 „
„ „ „ nitrogen . . . . 7.8 „

$k_1 = 0.001767.$

In order to calculate, from the decrease of pressure, the quantities of oxygen and aldehyde which have undergone the change, it is necessary to take account of the solvent action of the liquid acetic acid which is formed on the aldehyde.

Let the initial pressure of the aldehyde be a mm., that of the oxygen b mm., and of the nitrogen N mm. Further, call the total pressure of the gaseous mixture after t minutes have elapsed, P_t, and suppose that x mm. of oxygen have combined with 2x mm. of aldehyde. At first the acetic acid formed remains in the condition of vapour, and since its density at 20° is double the normal value, we shall have 2 volumes of aldehyde-vapour and 1 volume of oxygen combining to form 1 volume of acetic acid vapour.

The pressure and volume of the acetic acid are, therefore, the same as those of the oxygen from which it is formed.

The pressure of the mixture is therefore

$$P_t = (a - 2x) + (b - x) + x + N = a + b - 2x + N$$

The pressure at the beginning of the experiment was $P_1 = a + b + N$, so that

$$2x = P_1 - P_t.$$

After a time the acetic-acid vapour will attain its maximum pressure, m mms., after which liquid acetic acid will be deposited, and its quantity will be proportional to x — m.

If we assume that the quantity of aldehyde dissolved in the acetic acid follows Henry's law, it will be proportional to the pressure of the aldehyde, p_2, and also to the quantity of liquid acetic acid.

The pressure of the aldehyde is therefore

$$p_2 = a - 2x - k_1 (x - m) p_2,$$

or

$$p_2 = \frac{a - 2x}{1 + k_1 (x - m)}.$$

Here, 2 x is the diminution of pressure due to the transformation of aldehyde into acetic acid, $k_1 (x - m) p_2$, that which is produced by the solution of aldehyde in the liquid acid, and k_1 some constant.

If the assumption that aldehyde-vapour dissolves in acetic acid according to Henry's law is not strictly accurate, no great error will arise, since the quantity dissolved is small.

Putting the total pressure equal to the sum of the partial pressures of the different gases, we obtain, —

$$P_t = (b - x) + p_2 + m + N.$$

Substituting in this the value of p_2 found above, it becomes

$$P_t = (b - x) + \frac{a - 2x}{1 + k_1 (x - m)} + m + N.$$

From this equation x — the diminution in the oxygen pressure — may be obtained when k_1 is known. The analysis of the gas at the end of an experiment gives an independent determination of x, from which k_1 may be found.

The connexion between the rate of oxidation of aldehyde vapour by oxygen, and the concentrations of the gases — or their partial pressures, which are proportional to the concentrations — is expressed by the equation

$$-\frac{dp_1}{dt} = kp_1^{1/2}\,p_2 \quad \dots\dots\dots \text{(A)}$$

p_1 is the partial pressure of the oxygen, p_2 that of the aldehyde.

In order to integrate this equation, substitute (see p. 77)

$$p_2 = \frac{a - 2x}{1 + k_1 (x - m)};\ p_1 = (b - x);\ \text{and} - \frac{dp_1}{dt} = \frac{dx}{dt}.$$

This gives

$$\frac{dx}{dt} = k\,(b - x)^{1/2}\left(\frac{a - 2x}{1 + k_1 (x - m)}\right),$$

from which we obtain, after performing the integration,

OF THE
UNIVERS
OF CALIFORN

$$k = \frac{1}{t}\,\frac{2\,k_1 m - k_1 a - 2}{2\left(\frac{2b - a}{2}\right)^{1/2}}\,\log\frac{(b - x)^{1/2} - \left(\frac{2\,b - a}{2}\right)^{1/2}}{(b - x)^{1/2} + \left(\frac{2\,b - a}{2}\right)^{1/2}}$$

$$+ \frac{1}{t}\,k_1\,(b - x)^{1/2} + \text{const.}\ldots(B)$$

The value of the constant is obtained from the condition that $x = 0$, when $t = 0$.

This form of the equation can only be used when $(2\,b - a)$ is positive.

When excess of aldehyde is used, and $(2\,b - a)$ is therefore negative, the integrated equation may be transformed into

$$k = \frac{1}{t}\,\frac{2\,k_1 m - 2 - k_1 a}{2\left(\frac{a - 2b}{2}\right)^{1/2}}\,\tan^{-1}.\,\frac{(b - x)^{1/2}}{\left(\frac{a - 2b}{2}\right)^{1/2}} + \frac{1}{t}\,k_1\,(b - x)^{1/2} + \text{const.}\ldots\ldots(C)$$

The values of k in the tables on pp. 75—6 are calculated by means of equations B and C. They show that, up to an oxygen pressure of 450 mm., these equations are in harmony with the experimental results.

When the partial pressure of the oxygen is higher than about 450 mm., however, the values of k decrease. This appears to point to the existence of an upper limit of pressure, above which the reaction either stops altogether, or goes forward with a velocity very much smaller than that which would be deduced from equation A.

As a matter of fact, no oxidation took place when the pressure of the oxygen exceeded 530 mm., as may be seen from the numbers tabulated.

The experiments show, therefore, that the oxidation of aldehyde vapour by oxygen takes place with a velocity which is proportional to the pressure of the aldehyde-vapour and to the square root of the pressure of the oxygen, and further that there is probably a certain pressure of the oxygen above which the reaction takes place more slowly, — about 450 mm. of mercury at 20°.

As we have already seen on page 19, the velocity of a polymolecular reaction may be expressed as follows, —

$$-\frac{dC_1}{dt} = k\,C_1^{\,m}\,C_2^{\,n}\ldots\ldots\ldots(D)$$

where m and n are the numbers of the different kinds of molecules taking part in the reaction. It will be shown later, p. 99, that the values of m and n may be calculated from measurements of the velocity of the reaction in cases in which they are unknown.

Applying this to the reaction between aldehyde and oxygen, we have $-\frac{dC_1}{dt}$ proportional to $-\frac{dp_1}{dt}$ (page 78). C_1 is proportional to the pressure of the aldehyde, C_2 to that of the oxygen. Making these substitutions in equation D, we obtain

$$-\frac{dp_1}{dt} = kp_2^{m}p_1^{n}.$$

Comparing this with equation A we find

$$m = 1, \text{ and } n = 1/2,$$

that is the reaction takes place between aldehyde *molecules* and oxygen *atoms*, and is to be written in the following way: —

$$C_2H_4O + O = C_2H_4O_2.$$

The supposition that a certain small number of oxygen atoms exists normally in oxygen gas, is in accordance with our present knowledge of the subject.

The mathematical theory of reactions between gases, which was published in 1884 by J. J. Thomson[1], is also in agreement with the results obtained with aldehyde and oxygen.

It is probable, on other grounds, that oxygen gas contains free atoms; there can be little doubt that the oxygen molecule would, at a sufficiently high temperature, be dissociated into its atoms. Equilibrium between the dissociated and undissociated molecules will be established when the concentration of the atoms has reached a value determined by the equation

$$C_{(O_2)} = k\,C^2_{(O)},$$

where $C_{(O_2)}$ is the concentration of the oxygen molecules, $C_{(O)}$ that of the atoms, and k a constant the value of which depends on the temperature[2].

---

[1] Phil. Mag. (5), 18, 233, 1884.

[2] This is treated fully further on.

Since the heat of formation of the oxygen molecule from its atoms is probably positive, the equilibrium well be displaced, in such a way that at lower temperatures the concentration of the oxygen atoms will be smaller than at higher temperatures. It will, however, probably never become zero, and we shall have therefore at the ordinary temperature

$$C_{(o)} = k \sqrt{C_{(o_2)}}.$$

We may take the concentration of the oxygen molecules as being proportional to the pressure of the gas; the concentration of the oxygen atoms is therefore proportional to the square root of the pressure.

If we assume that the oxygen atoms alone take part in the oxidation of the aldehyde, the rate of oxidation must also be proportional to the square root of the oxygen pressure.

Although the results obtained with aldehyde may be explained in this way, it is doubtful whether this is also the case with phosphorus and sulphur.

It is possible that the reaction between oxygen and phosphorus or sulphur takes place in different stages, for example,

$$P_4 + O = P_4 O$$[1].

The velocity of each of these partial processes would then be proportional to the concentration of the oxygen atoms. This view is also in agreement with the fact that when phosphorus is burnt with a limited supply of oxygen, the lower oxides, such as P_4O_6, are formed.

The fact that the presence of moisture accelerates the oxidation of phosphorus and sulphur[2] is also in accordance with the view that the oxidation is due to the action of oxygen atoms, for J. J. THOMSON[3] has found that the electric discharge (without electrodes) passes much more easily through the moist, than through the dry gas; the moisture apparently favours the formation of the atoms which carry the electricity.

---

[1] The existence of this oxide, discovered by LE VERRIER, is rendered probable by the work of REINIZER and GOLDSCHMIDT (Berichte 13. p. 845. 1880).

[2] Compare the experiments of BAKER and of DEWAR. See also page 33.

[3] British Association, Oxford, 1894.

It must, however, be pointed out that the above hypothesis does not explain the formation of ozone which accompanies the oxidation of phosphorus, not only in moist oxygen but also, according to MARCHAND, in the dry gas.

We have, so far, always spoken of oxygen atoms as taking part in the oxidation of aldehyde, etc. The question, however, arises whether we are dealing here with atoms, or with ions, that is with positively or negatively charged atoms. VAN 'T HOFF[1] has investigated this question.

According to the commonly received view on the subject, one half of the oxygen molecule may be regarded as employed in the slow oxidation, while the other half brings about the formation of ozone.

From EWAN'S experiments, which show that the rate of oxidation is proportional to the square root of the pressure of the oxygen, it would follow that the dissociation of the oxygen molecule is not a consequence of the oxidation, but that it exists previous to it.

If we are really dealing with the equilibrium[2]

$$O_2 \rightleftarrows 2\,O,$$

and if the atoms are oppositely charged, it is conceivable that the oxidisable substance should show preference for those with one kind of charge, the remainder giving an electrical charge to the oxygen which is finally removed by some secondary reaction such as the formation of ozone, or the decolourisation of indigo.

Some indications that this may be the case are to be found in the literature of the subject. The white fumes formed during the oxidation of phosphorus, for example, are due chiefly to the condensation of steam, and persist in air which, after being in contact with phosphorus, has been freed from ozone by means of potassium iodide.[3] They therefore, resemble the cloudiness which was observed by R. v. HELMHOLTZ in electrified steam.[4]

---

[1] Zeit. phys. Chem. 16, 411. 1895.

[2] The meaning of equations written in this way is explained later.

[3] MEISSNER, Untersuchungen über den Sauerstoff. 1863, 20, 218.

[4] Wied Ann. 32, 1, 1887; also MEISSNER, loc. cit.

We shall also see that in oxygen made active by contact with phosphorus the primary product is not ozone, because it stops the luminosity of phosphorus, while ozone favours it;[1] it might be electrically charged oxygen.

The maximum quantity of oxygen taking part in the secondary actions which accompany a slow oxidation was first determined, in order to compare it with the quantity of oxygen employed in the oxidation itself.

The determinations of SCHÖNBEIN[2], and LEEDS[3] give very different results.

SCHÖNBEIN's method was modified, so as to allow of quantitative determinations, in the following way: — A small stick of phosphorus was placed in a large flask together with a very dilute solution of indigo, either as indigo sulphate, or as commercial sodium sulphindigotate, the oxidation value of which had been determined by means of a standard permanganate solution by SKALWEIT's[4] method.

It was found in some preliminary experiments that it is necessary to use small quantities of phosphorus, and that it is absolutely essential to keep the temperature low during the oxidation (40°), and to shake the flask vigorously.

21.3 mgrs. of phosphorus were used; to obtain such quantities easily, the phosphorus was cast in thin sticks about 1 mm. in diameter by drawing it up while melted into a thick walled glass tube.

These sticks were easily removed from the tube, after which they were cut into pieces of known length by bringing them into a short piece of the same tube, which had been ground flat at both ends, and cutting off the projecting parts with a knife.

First experiment. 60 cc. of indigo solution, to which 10 cc. of sulphuric acid had been added, were shaken with 21.3 mgrs. of phosphorus and excess of air, until the phosphorus had disappeared. It was then found that an equal volume of the indigo solution was brought to the same greenish tint as that acquired in the experiment by treatment with 79.5 cc. permanganate solution, (0.00987 N).

---

[1] CHAPPUIS, Bull. Soc Chim. 35, 419, 1881.

[2] Journ. prakt. Chem. 53, 501, 1851.

[3] LIEB., Ann. 200, 295, 1880.

[4] Repertorium der analyt. Chemie. 4, 247.

During the oxidation of 21.3 mgrs. of phosphorus, therefore, 79.5 × 0.00987 × 8 = 6.28 mgrs. of oxygen had taken part in the secondary reaction. The atomic ratio is thus $P : O_{0.57}$.

Second experiment. This was carried out in a similar way, except that the phosphorus was introduced gradually in four parts. The 60 cc.[1] of indigo solution were now almost completely decolourised, loosing the green tinge. 6 × 1.11 = 6.66 mgrs. of oxygen were therefore used in the secondary reaction, or $P : O_{0.6}$.

In some further experiments without sulphuric acid it was noticed that the acid accelerates the reaction considerably, the ratio between the phosphorus and the oxygen, however, remained unchanged. A final series of experiments was now made in the dark so as to avoid the possible oxidation of indigo by the action of the light. Sodium sulphindigotate was used, and the slow combustion of the phosphorus conducted in a special way. The phosphorus was brought into a condition of fine division in the same way as in the earlier experiments, by warming the flask until the phosphorus melted, and then shaking it thoroughly.

From this point the experiment was conducted in a somewhat different way, because it was seen in the dark that the oxidation took place in two different stages. The well known phosphorescence is first seen; phosphoric acid is practically the only product formed in this stage when such small quantities of phosphorus are employed. Secondly, if the particles of phosphorus are completely covered by the liquid, luminosity is seen throughout the whole flask, and phosphorous acid is also formed.

To give an example, the flask was placed in water at 50°, taken out and shaken well about thirty times, and replaced in the water, after this the luminosity was seen. On repeating these operations the same results were obtained.

9.18 mgrs. of phosphorus were used, and after 277 repetitions of the shaking and luminosity, 40 cc. of indigo solution had been decolourised; on standing in the cold an additional 4 cc. of indigo were gradually decolourised, and the phosphorus totally disappeared.

---

[1] 10 cc. of this indigo solution required 14.1 cc. permanganate, or 14.1 × 8 × 0;00987 = 1.11 mgrs. oxygen.

50 cc. of the indigo solution were equivalent to 40.73 cc. of 0.00987 N permanganate solution, so that the quantity of oxygen used in decolourising 44 cc. of indigo is $44 \times \frac{40.73}{50} \times 8 \times 0.00987 = 2.83$ mgrs. The ratio between phosphorus and oxygen is thus $P : O_{0.6}$.

It is therefore probable that when an atom of phosphorus is oxidised, it converts approximately half an atom of oxygen into the active condition, independently of whether phosphorous or phosphoric acid is formed.

The difference between the quantity of oxygen actually found and 0.5 appears to be real, and may be due to the fact that the oxidation of phosphorus appears to take place in two directions, — first and chiefly, with formation of phosphorous and phosphoric acids, and secondly, to the extent of about 15 per cent according to Salzer, with formation of hypophosphoric acid; it is perhaps possible that the latter process produces a larger amount of active oxygen.

It may also be pointed out here that in the oxidation of phosphorus, ozone does not appear to be formed at first. The luminous phenomena just described show that something was present in the atmosphere of the flask which prevented the oxidation of the phosphorus; oxygen was obviously present in sufficient quantity, and there was no lack of phosphorus vapour since on opening the flask phosphorescence was seen in contact with the air. The experiments of Chappuis show that ozone promotes the phosphorescence.

This inhibitory action, which may be due to the electric charge, or to the excess of positive or of negative oxygen ions, is removed by shaking with indigo solution, in which process sulphuric acid has a marked accelerative effect, possibly on account of its conductivity.

That the effect of the shaking, viz., rendering possible a renewed appearance of the phosphorescence, is not due merely to a renewed saturation of the air with phosphorus vapour, is proved by the fact that the characteristic phosphorescence is not seen when phosphorus, air, and water alone are used, without indigo.

It is also to be noticed that the substance exercising the inhibitory action disappears very gradually when the flask is not shaken, so that a spontaneous outburst of luminosity appears, which is repeated at intervals of a few hours. In this way the intermittent phosphorescence which was noticed by JOUBERT[1] may be explained.

Chapter III.

Elimination of the disturbing actions.

I. METHODS OF ELIMINATING THE DISTURBING ACTIONS. FORM AND DIMENSIONS OF THE APPARATUS. USE OF A SOLVENT. MOISTENING THE WALLS OF THE VESSEL.

The object of the preceding studies was not only the discovery of the disturbing actions but also their elimination.

The secondary actions which have been examined may now be enumerated together with the methods which may be adopted in order to avoid them. These methods will then be more fully explained.

Disturbing actions.

1. The influence of the volume of the bodies undergoing change.
2. The effect of a change in the nature of the medium during the reaction.
3. The influence of the walls of the apparatus.
4. The influence of changes in the walls of the apparatus occurring during the reaction.

---

[1] See note p. 52.
[Also BAKER, Phil. Trans. 1888, p. 583; THORPE and TUTTON, Chem. Soc. Journ. p. 569, 1890. T. E.]

Methods of eliminating the disturbing actions.

1. Form and dimensions of the apparatus.
2. Use of a solvent.
3. Moistening the walls of the vessel.

1. *Form and dimensions of the apparatus.*

Any action which is connected with the walls of the vessel will evidently be diminished in intensity by diminishing the internal surface of the apparatus, and therefore, also by increasing its volume.

By using spherical flasks of considerable diameter, both the influence of the walls on the reaction, and the effect which the reaction frequently exerts on the walls, will be diminished.

2. *Use of a solvent.*

One of the most important conditions for obtaining the normal course of change, is that the reacting substances be distributed through a large excess of some substance which does not itself take part in the change. We will call a substance of this kind a "solvent", although it may be a gas when a reaction in a gaseous system is under consideration.

A solvent of this kind serves several different ends.

First, by its use we obtain the dilution which is often necessary in order to reduce the influence of the volume of the reacting substances to a negligible quantity, secondly, the change in the nature of the medium which is caused by the accumulation of the products of the reaction is diminished by the presence of the solvent.

Further, special experiments have shown that the influence of the three other disturbing actions which have been mentioned is reduced to a great extent by the use of a solvent, although it is not totally eliminated.

Since the disturbing actions are most prominent in gaseous systems, the effect of a solvent on them was studied in such systems.

In order to prove that the effect of the walls of the vessel is diminished by the addition of a solvent gas, the apparatus represented on p. 44 was used; by means of it the ratio between the rates of polymerisation of cyanic acid in the two divisions A and B can be determined

1, when the acid is alone present,
2, when it is mixed with excess of dry air.

1. *Cyanic acid alone.*

Initial pressure . . . . 209.9 in A, 210.3 in B.
Pressure after 19 hours 190.0 in A, 198.0 in B.
Ratio between the velocities in A and B: — 1.6 : 1.

2. *Cyanic acid with an excess of dry air.*

Initial pressure . . . . 677.2 in A and B.
Pressure after 41 hours 661.5 in A, 662.9 in B.
Ratio of the velocities in A and B: — 1.1 : 1.

From these numbers it will be seen that the velocities tend towards the same value; that is, the influence of the walls, to which the difference in the velocities is due, is diminished by the addition of air.

In order to show that *the effect of the changes which the walls of the vessel undergo is diminished by the presence of a solvent gas*, a similar series of experiments was made with the apparatus shown in fig. 7, page 34.

After depositing a coating of cyamelide on the wall of B, the ratio of the rates of polymerisation of cyanic acid in A and B, was determined,

1, when the acid alone was present,
2, when it was mixed with an excess of dry air.

1. *Cyanic acid alone.*

Initial pressure . . . . . 89.8 in A and B.
Pressure after 3 days . . 88 in A, 85.3 in B.
Ratio between the velocities in A and in B: — 1 : 2.5.

2. *Cyanic acid after addition of dry air.*

Initial pressure . . . . . 542.3 in A and B.
Pressure after 15 days. . 532.4 in A, 529.3 in B.
Ratio of the velocities in A and in B: — 1 : 1.3.

3. *Cyanic acid alone.*

Initial pressure . . . . . 77.4 in A, 79.4 in B.
Pressure after three days 74.5 in A, 71.6 in B.
Ratio of the velocities in A and in B: — 1 : 2.7.

Here, also, the velocities tend towards the same value; that is, the influence of the deposit of cyamelide, which accelerates the change, is diminished by the addition of air. The explanation of the action of the solvent gas is to be found in the formation of a protecting layer of it near the walls. The change, which occurs most rapidly in the neighbourhood of the walls, removes the cyanic acid from the gaseous mixture existing there, so that the influence of the walls cannot be exerted until the cyanic acid has been replaced by diffusion in the layer of gas in contact with them.

3. *Moistening the walls.*

This artifice diminishes the influence of the deposits which are formed in certain changes in a very remarkable way; by using it we shall become acquainted with the surprising magnitude of the disturbing actions which come into play in these reactions.

The apparatus shown in fig. 7, p. 34, was also used in this case. The walls of one of the two divisions, A for example, were covered internally with a coating of valvolin. The effect of this coating on the rate of formation of ammonium carbamate and of trioxymethylene was then investigated.

The manipulation of the experiment is the same as that already described, so that it is only necessary to say that there is an enormous difference between the rates of the reaction in the two divisions, owing to the influence of the liquid coating. The velocity in B, the walls of which were not moistened, was greater than that in A, both with the carbamate and with trioxymethylene, the ratios of the velocities being 6 : 1, and 16 : 1. This difference shows, therefore, that moistening the walls diminishes the accelerative influence of the deposits of carbamate and of trioxymethylene. The reason of this is probably that the pores of the substances deposited are filled up by the liquid.

It must also be pointed out that special care is required in the choice of the liquid with which the walls are covered; it must be viscid, have a very small vapour pressure, and dissolve the reacting gases as sparingly as possible.

The question now arises, whether it is possible to realise the normal course of the reaction in the different cases which have been considered, by making use of the methods which have been described for eliminating the disturbing actions.

In answering this question, it is necessary to differentiate between reactions taking place in liquids, and those taking place in gaseous systems.

In liquid systems, the use of a solvent in large excess does certainly suffice to practically eliminate the disturbing actions. But in the case of gases, a gaseous solvent cannot be used to the same extent, because great difficulties are introduced by the large volume needed.

As we shall see, however, it has proved possible to realise the normal course of the reaction in several cases.

The greatest difficulty is found in those cases in which the gases undergo a change which produces a deposit on the walls of the vessel which increases in quantity as the reaction progresses.

How this difficulty is to be avoided will be shown in a subsequent chapter; here, we may remark that it is very considerable even in liquid systems where, as we have already seen, the conditions are much more favourable to a normal course than with gases. The following experiments may be mentioned as yielding additional evidence in support of this.

Urech [1], while studying the action of Fehling's solution on invert sugar, found that the velocity of the change increased in a curious way when vessels with a larger internal surface were used, he also noticed that the rate of change increased during the first period of the reaction reaching a maximum value, he observed, in short, although in a lesser degree, all the irregularities which have been described in the polymerisation of cyanic acid, and which are due to the accelerative action of the deposit of cyamelide. This indicates that the phenomena observed by **Urech** had a similar cause, namely, the formation of cuprous oxide.

---

[1] Berichte, 15, 2687, 1882.

This experiment should serve as a warning to investigators who are engaged with the study of reactions in gaseous systems; whenever a deposit of a solid substance which accelerates the reaction is formed, the difficulties to be expected are such that even under the favourable conditions existing in liquids, considerable irregularities may be found.

II. THE FIRST PERIOD OF CHEMICAL CHANGE.

Chemical induction.

The first period of a chemical change is of special interest in chemical dynamics. An exceedingly curious phenomenon is frequently encountered in it, viz. the velocity of the reaction increases during this period, finally attaining a maximum value.

The names "chemical induction", and "initial acceleration" have been given to this phenomenon.

Since an acceleration of this kind is incompatible with the views which have been put forward in this book, it was submitted to experimental examination. This showed that the cause of the phenomenon is to be found in the disturbing actions which have already been mentioned. It showed also what importance must be attached to the occurrence of an initial acceleration in studies of this kind.

The existence of an initial acceleration is established by the following observations.

1. **Bunsen** and **Roscoe**, to whom the term "chemical induction" is due, observed the acceleration in question on exposing a mixture of chlorine and hydrogen to light. In one of their

experiments the quantity of change in the eighth minute was ten times that which occurred in the first.[1]

They observed a similar acceleration of the action of bromine on tartaric acid, light being excluded, and expressed themselves with regard to the phenomenon in general in the following way: —[2]

"The occurrence of such a maximum appears, therefore, to depend, not on some special peculiarity in the action of light, but on the mode of action of the force of affinity itself."

2. Baeyer[3], working in Bunsen's laboratory, found another instance of chemical induction in the action of bromine on lactic acid in presence of hydrobromic acid.

3. Wright, Luff, and Rennie[4], again, found the same phenomenon while studying the reduction of certain metallic oxides by hydrogen and carbon monoxide; they say: —

"In all cases for a length of time the action is so slight as to be almost or quite imperceptible, after which it goes on at an accelerating rate until a maximum rate is attained, when it again diminishes.... it is evidently a case of the chemical induction studied by Bunsen and Roscoe."

4. The expression "initial acceleration" is due to Berthelot and Péan de Saint Gilles;[5] they noticed it in the process of etherification and considered it to be of a specific character. They say: —

"Pour concevoir l'acceleration initiale il faut admettre une sorte d'inertie, de résistance à vaincre qui retard la combinaison dans les premiers instants."

---

[1] Pogg. Ann. 100, 488, 1857. Ostwald's Klassiker der exacten Wissenschaften, 34, p. 93.

[2] Pogg. Ann. 100, 513, 1855. Ostwald's Klassiker. 34, p. 93.

[3] Lieb. Ann. 103, 178, 1857.

[4] Journ. Chem. Soc. 1879, 495.

[5] Ann. Chim. Phys. (3) 66, 26, 1862.

More recently MENSCHUTKIN[1] made similar observations on the formation of acetanilide, and says: —

"We find here a phenomenon similar to the acceleration of the etherification which BERTHELOT and PÉAN DE SAINT GILLES have observed."

In the course of his researches on tertiary amylacetate he met with the same phenomenon again.[2]

The examples cited have caused the phenomenon of initial acceleration to be regarded as a characteristic feature of chemical change.

Another interpretation of these phenomena may, however, be given; they may be regarded as due to secondary actions.

BUNSEN and ROSCOE found a sufficient explanation of the acceleration observed in the action of light on mixtures of chlorine and hydrogen, in the fact that the light, when it is absorbed by the mixture of chlorine and hydrogen, brings about what might be called a "dislocation" of the molecules, which does not produce chemical change until it has reached a certain magnitude.

In consequence, however, of their observation that a similar phenomenon occurs with tartaric acid when light is excluded, they expressed the view which has already been quoted.

HARCOURT and ESSON[3] appear to incline to the opposite opinion; having observed an initial acceleration of the reaction between potassium permanganate and oxalic acid in the presence of sulphuric acid and manganese sulphate, they considered it to be due to a secondary action, and found that this was really the case, the reaction taking place in the two stages

$$2\,KMnO_4 + 3\,MnSO_4 + 2\,H_2O = K_2SO_4 + 2\,H_2SO_4 + 5\,MnO_2,$$

and $MnO_2 + H_2SO_4 + H_2C_2O_4 = MnSO_4 + 2\,H_2O + 2\,CO_2$.

It is the second reaction which is actually observed and which exhibits the acceleration; this is hardly surprising, since the MnO_2 which enters into the second reaction is a product of the first.

---

[1] Berichte, 15, 1616, 1882.

[2] Berichte, 15, 2512, 1882. KONOWALOW, Zeit. phys. Chem. 1, 63, 1887. See also SPRING on this subject. Zeit. phys. Chem. 1, 217, 1887; 1, 468, 1887.

[3] Phil. Trans. 1866, 201.

Naumann[1] also appears to regard the initial acceleration as secondary; having observed an acceleration in the conversion of a mixture of ammonia and carbon dioxide into ammonium carbamate he did not hesitate to ascribe it to the accelerative action of the solid ammonium carbamate formed.

Urech[2], finally, having observed the phenomenon in the case of the action of bromine on fatty acids, says: —

"These results would be incomprehensible from a theoretical point of view, if the action of the bromine consisted of a simple substitution, for then the maximum velocity must occur at the beginning of the reaction."

Spring[3] also found an example of chemical induction in the solution of marble in dilute mineral acids, and **Spring** and **van Aubel**[4] another, in the action of dilute acids upon zinc (containing 0.6 per cent. of lead).

The following experiments were made in order to discover whether the initial acceleration is something essential to a chemical change, or whether it is merely a result of secondary actions.

The experiments were made on

1. The change of rhombic, into monosymmetric sulphur.
2. The formation of water.
3. The polymerisation of cyanic acid.

1. *The initial acceleration of the change of rhombic sulphur into monosymmetric sulphur.*

The experiments were made by T. L. **Reicher**[5], the expansion which occurs during the change being measured. The apparatus used — a dilatometer — has the form of a large thermometer (fig. 27); the bulb A contains a quantity of rhombic sulphur together with sufficient sulphuric acid (sp. gr. 1.77) to fill the bulb and part of the capillary tube, the whole was heated in boiling water.

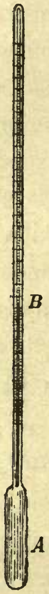


Fig. 27.

---

[1] Lieb. Ann. 160, 21. 1876.

[2] Berichte, 8, 539, 1875.

[3] Zeit. phys. Chem. 1, 217, 1887.

[4] „ „ „ 1, 465, 1887.

[5] Groth's Zeitschrift für Krystallographie, 8, 593, 1884. Inaugural Dissertation, Amsterdam 1883, 45.

The expansion produced by the rise of temperature being at an end, a further slow expansion indicates the progress of the change. The expansions, which were read off every five minutes, were as follows: —

1, 2, 4, 5, 8, 11, 13, 15, 18, 17, 17, 16, 14, 12, 9, 7, 5, 4, 3, 2, 1.

The velocity of the change therefore increases at first, reaching its maximum value when approximately one half of the rhombic sulphur has been converted into the monosymmetric modification.[1]

It has been found that this acceleration is simply due to the well known influence which the presence of monosymmetric sulphur exerts on the change.

2. *Initial acceleration in the formation of water.*

While studying the course of the transformation of electrolytic gas into water at 440° in presence of nitrogen, 13.8 cc. of electrolytic hydrogen, and 32.7 cc. of purified air were introduced into the reservoir K of the apparatus represented in figure 12, page 39; the mixture of gases was separated by an index of mercury I, from the column of air L, the length of which, L_t, measured in the way already described, gives the pressure of the gas which is being examined. Calling the quantity of the mixture of oxygen and hydrogen present at the beginning of the experiment unity, and the quantity which has undergone change at the time t, n, we obtain[2]

$$46.5\ (L_t - L_o) = 20.34\ n\ L_t,$$

L_o and L_t being the lengths of the column of air, L, at the beginning of the experiment, and at the time t.

Therefore

$$1 - n = 2.28\ \frac{L_o}{L_t} - 1.28.$$

---

[1] There is a remarkable similarity in this respect to the change of tertiary amyl acetate studied by **Menschutkin**. Berichte, 15, 2512, 1882.

[2] See appendix, note 2.

The results are given in the following table.

Time in hours.	Quantity of $2H_2 + O_2$ unchanged.	Diminution in the quantity of $2H_2 + O_2$ per hour.
0	1	—
6	1	0
13	0.956	0.006
20	0.899	0.008
27	0.826	0.010
34	0.749	0.011
41	0.669	0.011
55	0.525	0.010
69	0.399	0.009
83	0.317	0.006
111	0.173	0.005
139	0.102	0.003
181	0.060	0.001

The initial acceleration is very noticeable, but it is easy to see that it is of a secondary character. The experiments on page 40 show that the acceleration disappears when the nitrogen is omitted. It is well known that oxides of nitrogen are formed when electrolytic gas explodes in the presence of nitrogen [1], the acceleration observed in this experiment is, therefore, evidently to be referred to the formation of these substances.

3. *Initial acceleration in the polymerisation of cyanic acid.*

An initial acceleration of the change of cyanic acid into cyamelide occurs, as may be seen from the experiments on page 38, and also from the following table.

Time in hours.	Pressure in mm.	Decrease of pressure per hour.
0	201.6	
		0.31
48	186.7	
		0.52
73	173.7	
		0.42
96	164	

---

[1] Chem. News 49, 237, 1884, in which LEEDS states that NH_4NO_2 is formed.

The cause of the acceleration in this case was found in the fact that the cyamelide which is formed promotes the change of the cyanic acid in a very marked way, as we have already seen.

The following experiment gives a further proof that the acceleration is conditioned by the change in the walls of the vessel, since it may be produced at any period of the change, and is not by any means confined to the initial period. The apparatus shown in fig. 7 was used in the experiment, the reservoir B was filled with cyanic acid vapour, A with mercury, and the pressure of the acid (at constant volume) measured from time to time.

Time in hours.	Pressure in mm.	Decrease of pressure per hour.
0	282.9	
		1.44
8	271.4	
		1.55
25	245	
		1.07
48	220.4	

As may be seen the initial acceleration has taken place. The remaining part of the cyanic acid was now divided between the two vessels A and B by raising the apparatus, after which they were separated from each other by lowering it again.

The acceleration was again observed, but this time only in the reservoir A, the walls of which were not coated with cyamelide.

Time in hours.	Pressure and decrease of pressure.			
	Reservoir B		Reservoir A	
0	108.8		110.6	
		0.14		0.044
25	105.3		109.5	
		0.136		0.094
48.5	102.1		107.3	
		0.104		0.076
120.5	94.6		101.8	

The experiments which have been described show that chemical induction, or initial acceleration, may be referred to secondary actions, and therefore the phenomenon may be of service in investigations relating to chemical dynamics, since it indicates, in a way which is not to be undervalued, that some necessary precaution has been omitted.

THE COURSE OF CHEMICAL CHANGE.

THIRD PART.

APPLICATIONS.

I. DETERMINATION OF THE NUMBER OF MOLECULES WHICH TAKE PART IN A CHEMICAL REACTION.

A. METHOD IN WHICH THE VOLUME REMAINS CONSTANT.

Decomposition of arsine and phosphine.

The difference which is found in the course of chemical reactions in which different numbers of molecules take part may be employed in the solution of an interesting problem. In the first part of this book the course of a reaction was deduced from the number of molecules taking part in it; in this part, inversely, the number will be determined from the observed course of the reaction.

The principle on which the determination depends is very simple, for the course of a polymolecular reaction is represented by the equation

$$-\frac{dC}{dt} = kC^n,$$

where n is the number of molecules taking part in the reaction, and we have to determine this quantity experimentally.

Since this can be done in different ways, we shall first develop those methods which depend on the investigation of the course of the reaction at constant volume.

The integrals of the differential equation which has just been given will be used, viz: —

$$\log \frac{1}{C} \text{ or } \frac{1}{C^{n-1}} = kt + \text{constant},$$ [1]

---

[1] The value of k is (n—1) times that which it has in the differential equation. Cf. p. 19.

and we shall have to find which of these equations represents the experimental results.

The decomposition of phosphine has been investigated with this object. We have to decide, by experiment, whether this decomposition really takes place in accordance with the equation which is usually assumed to represent it, viz. —

$$4\ PH_3 = P_4 + 6H_2,$$

that is whether four molecules of phosphine really produce, by their mutual action, one molecule of phosphorus and six molecules of hydrogen.

The experiment was made by measuring the pressure, at constant volume, of a quantity of phosphine at different stages of its decomposition.

We have then $$C_t = C_o \left(3 - \frac{2\ P_t}{P_o}\right),$$

where C_o and P_o are pressure and concentration initially, C_t and P_t the same quantities after partial decomposition.[1] The apparatus used was that which is described on page 41, only in place of the boiling diphenylamine which was used in a copper bath for maintaining a constant temperature of 310° in the very similar experiments with arsenic hydride described on p. 2, sulphur boiling at 440° was employed here.[2]

The following table contains the results of the experiment.

Time in hours.	Pressure in mm. P	$\frac{1}{t}\log\frac{P_o}{3\ P_o - 2\ P_t}$	$\frac{1}{t}\left[\left(\frac{P_o}{3\ P_o - 2\ P_t}\right)^3 - 1\right]$
0	758.01	—	—
4	769.34	0.00759	0.055
9	781.46	0.00709	0.055
14	795.57	0.00746	0.060
24	819.16	0.00732	0.066
35.9	843.71	0.00713	0.073
46.3	865.22	0.00718	0.085

---

[1] Cf. p. 2.

[2] The heating apparatus is described on p. 40.

The steady increase of the numbers given in the last column shows that the course of the reaction does not correspond to the quadri-molecular equation

$$\frac{1}{C^3} = kt + \text{const.}$$

and that the decomposition, therefore, is not represented by the equation

$$4\ P\ H_3 = P_4 + 6\ H_2.$$

On the other hand the values of

$$\frac{1}{t} \log \frac{P_o}{3\ P_o - 2\ P_t}$$

are strikingly constant.

From this result we are justified in concluding that the change is monomolecular, that is, that each molecule of phosphine decomposes independently of the others, according to the equation

$$PH_3 = P + 3H,$$

and that the molecules P_4 and H_2 are formed subsequently by the combination of the atoms of phosphorus and hydrogen.

II. DETERMINATION OF THE NUMBER OF MOLECULES WHICH TAKE PART IN A CHEMICAL REACTION.

B. Method in which the volume varies.

While the method of determining the number of molecules taking part in a reaction which has just been described depends on the investigation of the course of the reaction at constant volume, that which is about to be considered depends on the influence of a change of volume on the velocity of a reaction.

This influence depends on the number of molecules taking part in the reaction. This is shown by the equations,

$$-\frac{d\ C_1}{dt} = k\ C_1^n, \text{ and } -\frac{d\ C_2}{dt} = k\ C_2^n,$$

therefore,

$$\frac{d\ C_1}{dt} : \frac{d\ C_2}{dt} = C_1^n : C_2^n$$

or

$$n = \frac{\log\left[\frac{dC_1}{dt} \div \frac{dC_2}{dt}\right]}{\log \frac{C_1}{C_2}}.$$

The calculation of n from this differential equation cannot, however, lay claim to any great degree of accuracy.

For if we substitute for the differentials dC_1 and dC_2, the very small changes of concentration which take place at the very beginning of the reactions, for example, the result will be inaccurate on account of the magnitude of the experimental error due, partly, to the smallness of the changes of concentration measured, and partly, to the initial disturbances to which the reactions are subject.

If, again, we substitute a large change of concentration the result is still inaccurate, since we assume implicitly that the rate of the reaction, $\frac{d\ C}{dt}$, remains constant while the concentration undergoes a considerable diminution. This error is partially eliminated owing to the fact that the same assumption is made with respect to both the differentials dC_1 and dC_2; it is, however, difficult to say to what extent this occurs. It is much better to deduce the strictly accurate integrated equation, from which, under certain circumstances, it is possible to calculate n exactly.[1]

According to what is said on page 19 we have for an n-molecular reaction,

$$-\frac{d\ C}{dt} = k\ C^n$$

---

[1] I am indebted to Mr. A. A. Noyes of Boston for this calculation in a somewhat different form. [E. Cohen].

or, after integration,

$$\frac{1}{C^{n-1}} = kt + \text{const.}^{1} \quad . \quad . \quad . \quad . \quad (1)$$

By making two independent experiments, in which we will call ${}_1C_a$ and ${}_1C_e$ the concentrations in the first experiment at the times ${}_1t_a$ and ${}_1t_e$, and similarly, ${}_2C_a$ and ${}_2C_e$ the concentrations in the second experiment at the times ${}_2t_a$ and ${}_2t_e$, we obtain, introducing these values into equation (1), and eliminating the integration constant,

$$\frac{\left({}_1C_e^{\,n-1} - {}_1C_a^{\,n-1}\right) {}_2C_a^{\,n-1} \,.\, {}_2C_e^{\,n-1}}{\left({}_2C_e^{\,n-1} - {}_2C_a^{\,n-1}\right) {}_1C_a^{\,n-1} \,.\, {}_1C_e^{\,n-1}} = \frac{t_1}{t_2} \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{where } t_1 = {}_1t_a - {}_1t_e, \text{ and } t_2 = {}_2t_a - {}_2t_e.$$

If now the change of concentration is, in both experiments, the same fraction of the initial concentration, that is

$$\frac{{}_1C_a - {}_1C_e}{{}_1C_a} = \frac{{}_2C_a - {}_2C_e}{{}_2C_a} = m,$$

and therefore,

$$\frac{{}_1C_e}{{}_1C_a} = \frac{{}_2C_e}{{}_2C_a}, \text{ and } \left(\frac{{}_2C_e}{{}_1C_e}\right)^{n-1} = \left(\frac{{}_2C_a}{{}_1C_a}\right)^{n-1},$$

equation (2) assumes the following simple form : —

$$(n-1) \log \frac{{}_2C_a}{{}_1C_a} = \log \frac{t_1}{t_2},$$

and therefore

$$n = 1 + \frac{\log (t_1 / t_2)}{\log ({}_2C_a / {}_1C_a)} \ldots\ldots (3)$$

Under the conditions specified, n may be calculated from this equation with complete accuracy.

---

[1] k in this equation is (n—1) times greater than it is in the differential equation.

We have here a method which is not merely similar to that described in the preceding section, but one which is considerably more simple, and in which the measurements can be made with greater certainty.

The method described in the preceding section becomes valueless in cases in which disturbing actions occur ; for example, in those cases, so frequently observed, in which the products of the reaction accelerate or retard the change. If the change be retarded by the products of the reaction, the value obtained for n will be too great, if it be accelerated, the value found will be too small.

These influences may be avoided by means of the method in which the volume is variable.

This advantage of the method is due to the fact that the same change of volume produces very different changes in the velocities of different reactions, according to the number of molecules taking part in them ; for example, if the volume be doubled, the velocity of a mono-molecular reaction is reduced to one half, that of a bimolecular reaction to one fourth that of a trimolecular reaction to one eighth. Where such great differences exist the disturbing actions become less noticeable.

The value of this method is clearly seen in the researches of Noyes and Scott[1]. They show that the method at constant volume leads to completely inaccurate results, in many cases, owing to the occurrence of disturbing actions, while the true nature of the reactions is brought to light by the application of the method with variable volume. Noyes and Scott found, for example, that while the reaction between hydriodic acid and hydrogen peroxide appears to be trimolecular when examined by the first method, a more careful investigation by means of the second shows it to be bimolecular. A similar result was obtained with the action of bromic acid on hydriodic acid ; the reaction, which according to the results of the first method is to be regarded as trimolecular, is really bimolecular.

Finally, the decomposition of potassium hypoiodite in presence of a small quantity of iodine, which was studied by Schwicker[1], by means of the first method, and which he considered to be trimolecular, turns out on examination by the second method to be really monomolecular under certain conditions.

---

[1] Zeit. phys. Chem. 18, 118, 1895.

The method with variable volume was also used in the investigation of: —

1. The action of bromine on fumaric acid.
2. The polymerisation of cyanic acid.
3. The action of stannous chloride on ferric chloride. (Noyes.)

1. *Action of bromine on fumaric acid.*

The formation of dibromsuccinic acid by the addition of bromine to fumaric acid in aqueous solution exhibits certain irregularities which make it impossible to apply the method at constant volume. These irregularities are due to the partial conversion of the dibromsuccinic acid formed into brommaleïc and tartaric acids.

The method at variable volume, however, at once yields satisfactory results.

The experiments were made by Reicher by means of the apparatus shown in fig. 28, the advantage of which is that the solution of bromine and fumaric acid, contained in A, cannot lose bromine by evaporation.

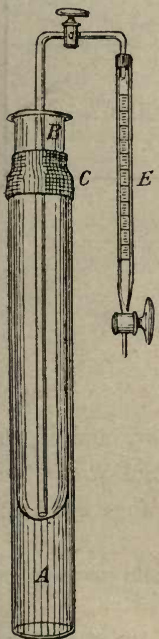


Fig. 28.

The apparatus is completely filled with the solution, which contains 2.3 grams of fumaric acid, and an equivalent quantity of bromine, per litre; this can be caused to flow out through the tap by depressing the cylinder B into A, after which a known volume, measured by means of the small burette E, can be brought into a solution of potassium iodide. The iodine liberated is titrated by means of sodium thiosulphate, the concentration of the system, which is to be determined, being proportional to the quantity of thiosulphate employed. The result of the experiments is contained in the following table.

---

[1] Zeit. phys. Chem. 16, 303, 1895.

Time in minutes. t.	Concentration.[1] C_1	$\frac{dC_1}{dt}$[2]
0	8.88	0.0106
95	7.87	

The volume is then changed by introducing water into the apparatus by means of the tap and mixing it with the solution, after which further determinations of the titre are made.

Time in minutes.	Concentration.	$\frac{d\,C_2}{dt}$
0	3.81	0.00227
132	3.51	

The value of n calculated from the equation

$$n = \frac{\log\left(\frac{dC_1}{dt} : \frac{dC_2}{dt}\right)}{\log\,(C_1 : C_2)}$$

is found to be 1.87[3].

If the reaction were mono-, bi-, or tri-molecular, and if no disturbing action were at work, the value of n found would be 1, 2, or 3; since, however, a disturbing action does exist in this case we must expect to find a number differing more or less from an integer. The result obtained, 1.87, therefore, makes it permissible to regard the reaction under consideration as bimolecular.

---

[1] Since the choice of the units has no influence upon the result, the concentration has been taken as equal to the number of cc. thiosulphate required.

[2] The value of $\frac{dC_1}{dt}$ has been replaced in the calculation by the ratio of the finite differences, viz. $\frac{8.88-7.87}{95}$. (cf. p. 102).

[3] The mean values have been taken for the concentrations, for example $C_1 = \frac{8.88 + 7.87}{2}$.

2. *Polymerisation of cyanic acid.*

The course of this change, also, exhibits irregularities which make it impossible to employ the method at constant volume. The irregularities in this case originate in the accelerative action of the cyamelide which is formed.

We are thus opposed here by the greatest difficulties which are to be met with in the study of the course of a reaction; the experiments of Urech, to which reference has already been made, have shown that the formation of a deposit having an accelerative action on the change may be very troublesome even in liquid systems; in a gaseous system, with which we have to deal in the case of cyanic acid, this difficulty becomes very much more serious.

It is for this reason that the question as to the number of molecules of cyanic acid which take part in the formation of cyamelide formed the subject of a very protracted research, extending, with intervals, over several years and in the course of which more than five hundred experiments were made. The method with variable volume, the advantages of which have been pointed out, has to be improved, in this case, by the realisation of a special condition.

This consists in comparing the velocities of the reaction, at very different concentrations, and in vessels the walls of which are as far as possible identical.

The experiments may be arranged in three groups, according as,

a. The initial velocities were compared in clean vessels.

b. The velocities were compared in different parts of the same apparatus, the walls of which were covered by a layer of cyamelide.

c. The velocities were compared in the same vessel, the condition of the walls being the same as in *b.*

A synopsis of the results is first given, after which the apparatus used is described.

No.	Time in hours. t	Concentration.[1] C	$n = \frac{\log\left(\frac{d\ C_1}{dt} : \frac{d\ C_2}{dt}\right)}{\log\left(C_1 : C_2\right)}$
1	23	I 188.84 153.46	2.9
	20	II 79.07 76.04	
2	72	I 126.44 117.66	3.3
	48	II 221.2 189.15	
3	24	I*a* 356.72 320.68	2.9
	48	II 160.34 152.33	
	24	I*b* 304.66 280.56	
4	23	I 244.97 220.37	2.8
	47	II 111.03 105.3	
5	24	I 533.77 514.23	2.9
	73	II 261.31 253.96	
6	48	I 568.7 555.56	3
	353	II 283.36 271.47	
7	17	I 271.43 244.97	3.2
	23½	II 109.48 107.28	
		Mean value	3

---

[1] Since the choice of units does not influence the result, the pressure of the cyanic acid, reduced to 0°, is taken in place of the concentration to which it is proportional.

a. *Comparison of the initial velocities in perfectly clean vessels.*

The object of this part of the investigation being to compare the initial velocities at different concentrations in vessels of the same form, the apparatus represented in fig. 29 was employed. The lower extremity of the apparatus having been placed under mercury, the compartments A and B were evacuated, and the tap separating them closed. The division B was then filled with cyanic acid in the way described on page 38, and the initial velocity of polymerisation determined. (Experiment 1, I. in the table.) When at least half of the cyanic acid had disappeared, the tap was opened, the apparatus depressed in the burette so as to transfer the cyanic acid to A, and the initial velocity again determined at the smaller concentration which obtained in the apparatus. (Experiment, 1, II). Result, n = 2.9.

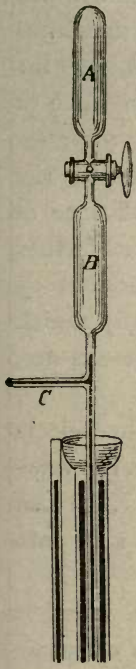


Fig. 29.

b. *Comparison of the velocities in different parts of the same apparatus, the walls being covered by a layer of cyamelide.*

For this purpose a globe (fig. 8) was used which was evacuated, and filled with cyanic acid. (Experiment 2, I.)

The globe was then depressed so that the mercury entered it and doubled the concentration of the cyanic acid, after which the rate of polymerisation was again determined (Experiment 2, II.) This experiment gave n = 3.3.

In another experiment of this kind the apparatus shown in fig. 29 (with omission of the tap) was used. The cyanic acid was first contained entirely in the compartment A, the mercury filling B; then by raising the apparatus the acid was distributed equally through A and B; finally the original condition was restored. The results are given under experiment 3 in the table, and lead to the value n = 2.9.[1]

---

[1] C_1 and $\frac{dC_1}{dt}$ are the mean values of the first and third observations.

c. *Comparison of the velocities in the same apparatus, the condition of the walls being the same as in b.*

The apparatus shown in fig. 7 was used in this case. Both compartments were completely evacuated, and one of them, A, filled with cyanic acid, the rate of polymerisation of which was then determined. (Experiment 4, I.) By raising the apparatus half of the cyanic acid was transferred from A to B, and the velocity in A again measured. (Experiment 4, II.) The value of n obtained was 2.8.

The experiment was repeated, dry air being added to the cyanic acid in one case, in order to diminish the influence of the walls of the vessel (Experiment 5), in another the further precaution was taken of keeping the temperature constant by means of a current of cold water from the water supply which circulated round the vessel A. (Experiment 6.) The results are, $n = 2.9$ and $n = 3$.

This apparatus is also suitable for comparisons of the velocities in clean vessels, at different concentrations. The initial velocity was measured in this way in A, (Experiment 7, I.) and then in B after transferring the half of the residual acid into it. (Experiment 7, II.) Result, $n = 3.2$.

From the results obtained, — the mean value of n found is 3 — it appears very probable that the polymerisation of cyanic acid is a tri-molecular reaction which takes place according to the equation

$$3\,CNOH = C_3N_3O_3H_3.$$

All doubt on the subject would be removed, if it were not that the experiments on the effect of moistening the walls described on page 89 have shown how very large the disturbing action of the deposit of cyamelide formed during the reaction may be.

3. *The action of stannous chloride on ferric chloride.*

The reaction which occurs between stannous chloride and ferric chloride has been carefully investigated recently by

A. A. Noyes[1], in order to determine the number of molecules taking part in it. According to the equation

$$2\ FeCl_3 + SnCl_2 = 2\ FeCl_2 + SnCl_4$$

it should be trimolecular.[2]

The data which are contained in the memoir referred to will be used in order to show how the method which was explained on p. 103 may be applied in solving the problem which we are considering.

A solution of ferric chloride, as neutral as possible, was placed in flasks of 500—800 cc. capacity, which stood in a water bath the temperature of which was maintained constant at 25°. The air in the flasks was first expelled by carbon dioxide. The neutral solution of stannous chloride[3] was then quickly added from a pipette with a wide opening, the time was noted, and the flasks thorougly shaken. From time to time portions of the liquid were removed by means of a pipette and mixed with excess of mercuric chloride solution, by which means the reaction was at once stopped;[4] the time at which the mixture took place was noted.

The ferrous salt formed was then titrated by means of $N/_{10}$ potassium bichromate solution, potassium ferricyanide serving as indicator.

The initial volume of the liquid in which the reaction occurred was usually 300, sometimes 600 cc., the portion titrated varied, according to the concentration, from 25 to 100 cc.

The following table contains the experimental results obtained by Noyes. C_a is the initial concentration of the ferric chloride solution employed, in gram equivalents per litre, $C_a—C_e$ gives the number of equivalents of ferric chloride reduced at the time t. The times are given in minutes.

---

[1] Zeit phys. Chem. 16, 546, 1895.

[2] Further proofs that this is really a trimolecular reaction are to be found in the original memoir.

[3] The concentration of this solution and also that of the solution of ferric chloride were determined with $N/_{10}$ potassium bichromate solution.

[4] The mercuric chloride oxidises the remaining stannous chloride.

I. $C_a = 0.1$		II. $C_a = 0.0625$		III. $C_a = 0.05$		IV. $C_a = 0.025$	
Time. t	$C_a - C_e$	Time. t	$C_a - C_e$	Time. t	$C_a - C_e$	Time. t	$C_a - C_e$
0.75	0.0359	1	0.01434	1	0.00944	2	0.00450
1	0.0419	1.75	0.01998	1.5	0.01191	4	0.00637
1.5	0.0510	3	0.02586	2	0.01365	5	0.00692
2.5	0.0618	4.5	0.03076	3	0.01681	6	0.00755
4	0.0700	7	0.03612	4	0.01882	10	0.00929
6.5	0.0770	11	0.04102	5	0.02073	12.5	0.00991
20	0.0866	17	0.04502	7	0.02366	15	0.01084
—	—	25	0.04792	10	0.02693	22	0.01210
—	—	40	0.05058	16	0.03091	26	0.01272
—	—	—	—	25	0.03402	30	0.01338
—	—	—	—	40	0.03708	43	0.01483
—	—	—	—	60	0.03915	50	0.01538
—	—	—	—	—	—	60	0.01627
—	—	—	—	—	—	80	0.01732
—	—	—	—	—	—	91	0.01788

The following table gives the values of n which have been calculated in different ways from the above data.

The values of n, calculated by means of equation (3) on p. 103 for $m = 1/3$, are to be found under n_1; the values calculated by the same formula for $m = 1/2$ are tabulated under n_2. The values of the time, t_1 and t_2, are obtained by graphical interpolation.

	n_1 ($m = 1/3$)	n_2 ($m = 1/2$)
From I and II	3.22	3.54
,, I ,, III	3.20	3.51
,, II ,, IV	2.56	2.79
,, III ,, IV	2.37	2.58
Mean	2.84	2.90

The reaction is therefore trimolecular.

III. RECOGNITION OF MIXTURES.

Decomposition of dibromsuccinic and isodibromsuccinic acids.

A further application of the study of the course of a reaction is to be found in the possibility of determining by it whether a given substance is a single compound or a mixture of isomers. Suppose, for example, that a monomolecular reaction takes place in a mixture of two isomeric substances, the course of the reaction will not correspond to the equation

$$-\frac{dC}{dt} = kC,$$

because, owing to the fact that the substance is a mixture, two changes will take place simultaneously, in accordance with the equations

$$-\frac{dC_1}{dt} = k_1 C_1, \text{ and } -\frac{dC_2}{dt} = k_2 C_2.$$

Supposing we were unaware that we were dealing with a mixture, it would only be possible to take account of the variation of the total concentration $C = C_1 + C_2$, and it would be found that it did not follow the equation

$$-\frac{dC}{dt} = kC,$$

but rather an equation of the form

$$-\frac{dC}{dt} = k_1 C_1 + k_2 C_2 \text{ [1]}.$$

In order to test this experimentally the course of the change was investigated in the following three cases: —

1. The decomposition of dibromsuccinic acid.
2. The decomposition of isodibromsuccinic acid.
3. The decomposition of a mixture of the two.

Since both the iso-acid and its isomer split off a molecule of hydrobromic acid, the course of the decomposition was easily followed by titrating the aqueous solution of the acid after heating it in sealed tubes at 50°.

---

[1] The two equations give the same result only when $k_1 = k_2$, that is when both isomers decompose at the same rate. No account is taken, in these considerations, of any catalytic action of the one isomer on the rate of change of the other.

The following table contains the results.

	Time in minutes. t	Titre. T	Velocity constant. k
1. Dibrom-succinic acid			$k = \frac{1}{t}\log\frac{T_0}{3\,T_0 - 2\,T_n}$
	0	10.095 (T_0)	—
	214	10.37	0.000114
	380	10.57	0.000113
2. Iso-dibrom-succinic acid.			$k = \frac{1}{t}\log\frac{3\,T_0 - 2\,T_1}{3\,T_0 - 2\,T_n}$
	0	9.94 (T_1)	—
	60	10.45	0.00081
	150	11.11	0.00081
	300	11.93	0.00077
3. Mixture of both acids.			$k = \frac{1}{t}\log\frac{T_0}{3\,T_0 - 2\,T_n}$
	0	9.87 (T_0)	—
	60	10.31	0.00068
	155	10.76	0.00056
	300	11.23	0.00047

The tabulated numbers show plainly that the values of k remain constant with the pure acids, while with the mixture of acids they decrease.

With regard to the iso-dibromsuccinic acid, it is to be noticed that the decomposition which it undergoes in aqueous solution at the ordinary temperature must be taken into account in calculating k. The titre of the solution of the acid, immediately after it was made up, was $T_0 = 9.83$.

The constant k was obtained by eliminating x from the equations

$$k = \frac{1}{x}\log\frac{T_0}{3\,T_0 - 2\,T_1}, \text{ and } k = \frac{1}{x+t}\log\frac{T_0}{3\,T_0 - 2\,T_n},$$

where x is the unknown time which would be needed for the titre to increase from T_o to T_1 and t the time during which the reaction had proceeded, reckoned from the time at which the titre was T_1.

After eliminating x we find,

$$k = \frac{1}{t} \log \frac{3\ T_o - 2\ T_1}{3\ T_o - 2\ T_n}.$$

IV. COMPARISON OF THE VELOCITIES OF DIFFERENT REACTIONS.

a. *Hydrolysis of esters by bases.*

If the velocities of different reactions are to be compared together it is essential that their normal courses, free from any disturbances, should be realised. If this condition be not fulfilled the results obtained will not be comparable, on the other hand, when it is fulfilled, perfectly definite values of the velocity constant k may be obtained.

In order to determine the hydrolysing power of different bases the rate at which they bring about hydrolysis has been determined by Reicher,[1] and more recently, and very comprehensively, by Ostwald.[2]

Reicher's work was carried out by the method and with the apparatus which have been fully described on page 6. It will, therefore, be sufficient to give here the rates of hydrolysis of ethyl acetate which were found when different bases were used.

Hydrolysis of ethyl acetate at 9°.4.

Base.	*k*
Sodium hydroxide	2.370
Potassium „	2.298
Calcium „	2.285
Strontium „	2.204
Barium „	2.144

---

[1] Lieb. Ann. 228, 275, 1885.

[2] Journ. prakt. Chem. (2), 35, 112, 1887.

The influence of the nature of the alcohol and acid forming the ester was also investigated by Reicher in a similar way. The base used was sodium hydroxide.

Influence of the nature of the alcohol. Temp. = 9°.4.

Ester.	*k.*
Methyl acetate	3.493
Ethyl ,,	2.307
Propyl ,,	1.920
Isobutyl ,,	1.618
Isoamyl ,,	1.645

Influence of the nature of the acid. Temp. = 14°.4.

Ester.	*k*
Ethyl acetate	3.204 [1]
,, propionate	2.816
,, butyrate	1.702
,, isobutyrate	1.731
,, isovalerate	0.614
,, benzoate	0.830

It appears, therefore, that the greater the number of atoms in the molecule of an ester the smaller is the velocity with which it is hydrolysed.

b. *Hydrolysis of esters by acids.*

The catalytic action of the hydrogen ion having been established by Ostwald's classical researches on the hydrolysis of methyl acetate, it appeared to be of interest to investigate the action of acids on the esters mentioned in the preceding section.

This investigation was carried out by A. de Hemptinne [2] in the following way: —

Flasks, capable of containing about 1/2 litre, were filled with N/10 hydrochloric acid and placed in a water bath the temperature of which was maintained constant at 25°. In order to diminish, as far as possible, the error arising from the solubility

[1] Warder found 3.240.

[2] Zeit. phys. Chem. 13, 561, 1894.

of the glass, the flasks were previously filled with strong hydrochloric acid and allowed to stand for several days. That the error was thus reduced to negligible dimensions was proved by titrations.

A quantity of ester, such that when it was dissolved in the acid, a $^1/_{20}$ to $^1/_{40}$ normal, or if necessary still more dilute solution would result, was then weighed out in a small tube.

This tube, with the ester, was placed in one of the flasks, which was then corked up and well shaken, whereupon 50 cc. of the contents were at once titrated with an approximately $N/_{10}$ baryta solution; in this way the exact quantity of base required to neutralise the hydrochloric acid was obtained.

Since 50 cc. of the solution were removed for each titration, the empty space in the flask increased rapidly; in order to avoid this the contents of the flask were distributed among a number of smaller flasks of about 60 cc. capacity, which were then securely corked up. Errors arising from evaporation were avoided in this way.

At suitable intervals 50 cc. of the liquid contained in the flasks were removed and titrated. Two burettes were used for this purpose; from the first a quantity of $N/_{10}$ baryta solution, exactly equivalent to the hydrochloric acid present, is run in, by means of the second the excess of acid is titrated with $N/_{20}$ baryta solution.

The velocity constant is calculated from the equation[1]

$$-\frac{dC}{dt} = kC.$$

After integration and elimination of the integration constant we obtain

$$k = \frac{1}{t} \log \frac{C_o}{C_t},$$

where C_o is the concentration of the ester at the beginning of the experiment, and C_t its concentration after partial decomposition.

The degree of purity of the ester having been determined beforehand by decomposing a weighed quantity of it with baryta, the concentration C_0 is known, and, therefore, k can be calculated from the titrations without awaiting the completion of the hydrolysis which in this case requires a rather prolonged time.

---

[1] Compare pp. 2 and 3.

Some preliminary experiments with acetic acid showed that it does not possess a catalysing power which is at all comparable with that of hydrochloric acid. Using a $N/_{20}$ solution of ester, the acceleration produced by the acetic acid set free during the hydrolysis may be neglected during a considerable part of the change. A small acceleration becomes perceptible only when 60 to 70 per cent of the ester has been decomposed. The following results were obtained with methyl acetate.

Time.[1]	Percentage of the ester decomposed.	$\log \frac{C_0}{C_t}$[2]	k.
60	17.96	0.0860	0.001433
280	60.18	0.3999	0.001428
350	68.29	0.4987	0.001425
		Mean =	0.001428
70	18.88	0.0908	0.00144
290	61.68	0.4164	0.001436
350	68.59	0.5030	0.001437
		Mean =	0.001437

The mean of the two experiments is 0.001432.

In order to determine the influence of the nature of the alcohol and acid forming the ester on the velocity with which it undergoes hydrolysis, R. Löwenherz[3] has extended Hemptinne's work to other esters.

The following table contains the whole of the experimental results obtained by DE HEMPTINNE and LÖWENHERZ expressed in the same units[1] as the numbers obtained by REICHER for the rate of hydrolysis by caustic soda, which are also included in the table to facilitate comparison.

---

[1] The unit of time used here is 5 minutes.

[2] If we make $C_0 = 100$, then $C_t = (100-17.96) = 82.04$, and so on.

[3] Zeit. phys. Chem. 15, 389, 1894.

1. Influence of the nature of the alcohol.

Hydrolysis of different esters of the same acid at 25°.

Table A.

Ester.	k for hydrolysis with hydrochloric acid.	k for hydrolysis with caustic soda.
Methyl acetate	0.0066 2)	9.66
Ethyl ,,	0.0068	6.38
Propyl ,,	0.0067	5.31
Phenyl ,,	0.0040	—
Glyceryl ,,	0.0031	—
Methyl propionate	0.0071	—
Ethyl ,,	0.0073	5.61
Propyl ,,	0.0072	
Methyl butyrate	0.0039	—
Ethyl ,,	0.0042	3.39
Propyl ,,	0.0041	—
Methyl monochloracetate	0.0043	—
Ethyl ,,	0.0040	—

---

[1] The numbers obtained by REICHER (at 9°.4 and 14°.4) and by LÖWENHERZ (at 40°) have been calculated for 25° by means of the equation $\frac{d \log k}{dT} = \frac{A}{T^2} + B$, which will be explained later. REICHER used the minute as unit of time; the unit of concentration of the ester, as explained on p. 13, does not affect the value of k, the reaction being monomolecular; REICHER also calculated the values of k for normal caustic soda solutions, and used natural logarithms, so that the numbers in table A are obtained by multiplying HEMPTINNE's numbers by $\frac{10 \times 2.3025}{5}$.

[2] OSTWALD found 0.00689. That k is here found somewhat smaller is doubtless due to the greater dilution.

2. The influence of the nature of the acid.

Hydrolysis of different esters of the same alcohol at 25°.

Table B.

Ester.	k for hydrolysis by hydrochloric acid.	k for hydrolysis by caustic soda.
Ethyl formate	0.13 [1]	—
,, acetate	0.0068	6.38
,, monochloracetate	0.0040	—
,, dichloracetate	0.0064	—
,, propionate	0.0073	5.61
,, butyrate	0.0042	3.39
,, isobutyrate	0 0041	—
,, valerate	0.0014	—
Methyl benzoate [2]	0.00004 [1]	—

The differences between the rates at which the esters formed from the same acid and different alcohols are hydrolysed (table A) are very small compared with the differences which are found between the rates of hydrolysis of the esters of the same alcohol with different acids, (table B).

While the differences between the velocity constants for the esters of methyl and ethyl alcohols with the same acid scarcely exceed the experimental error, the constants for the ethyl esters of two similar acids, such as formic and acetic, are approximately in the ratio 20 : 1.

The extreme values of the constants obtained when the alcohol is varied are nearly in the ratio 2 : 1, (methyl alcohol and glycerin), while when the acid is varied the ratio is approximately 3300 : 1 (Formic and Benzoic acids).

The following table, which is taken from table A, shows that if the velocities of hydrolysis of the esters of acetic acid be known, the corresponding values for the esters of any other acid may be approximately calculated from them, when the value for one of the series has been determined.[1]

---

[1] This number makes no pretension to exactitude, it merely gives the order of magnitude correctly.

[2] This ester was used in place of the ethyl ester because it is more readily soluble.

Ester.	Ratio of rates of hydrolysis.	Ester.	Ratio of rates of hydrolysis.	Ester.	Ratio of rates of hydrolysis.
Methyl acetate	0.971	Methyl propionate	0.972	Methyl butyrate	0.928
Ethyl „	1.015	Ethyl „	1.014	Ethyl „	1.024
Propyl „		Propyl „		Propyl „	

It is also to be seen from the table that the hydrolysing power of the hydroxyl ion is very much greater than that of the hydrogen ion, (about 1000 times). The activities of the two ions do not appear to be proportional to each other, for while the velocity of hydrolysis by caustic soda decreases with increasing molecular weight of the ester hydrolysed, this is not the case with hydrolysis by acids.

---

[1] There are two errors in HEMPTINNE's table I, p. 565 loc. cit. The ratio of the velocities of methyl and ethyl butyrate should be 0.944 instead of 0.9736, and of ethyl and propyl butyrate should be 1.024 instead of 1.004.

THE INFLUENCE OF TEMPERATURE ON CHEMICAL CHANGE.

FIRST PART.

THE RELATION BETWEEN THE VELOCITY CONSTANT K AND THE TEMPERATURE.

a. *Application of thermodynamics.*

We shall employ here a formula the strict proof of which will be given later in the chapter dealing with chemical equilibrium.

Taking the chemical equilibrium which occurs with nitrogen peroxide as a concrete example, we may represent it in the following way,

$$N_2O_4 \rightleftarrows 2\ NO_2.$$

We are dealing here with two changes taking place in opposite directions, namely

$$N_2O_4 = 2\ NO_2, \text{ and } 2\ NO_2 = N_2O_4.$$

At any given temperature the velocity constant of each of these changes has a perfectly definite value, which we will call k_1 for the first, and k_2 for the second change.

It may be proved, by means of thermodynamics,[1] that the values of k_1 and k_2 must satisfy the following equation: —

$$\frac{d \log k_1}{dT} - \frac{d \log k_2}{dT} = \frac{q}{2T^2} \quad . \ . \ . \ . \ (1)$$

T is the absolute temperature, and q the quantity of heat, in calories, which would be evolved by the transformation of unit quantity (in this case 92 kgrms.) of the first system into the second at constant volume.

---

[1] The proof of this equation is given on p. 148 et seq.

Although this equation does not directly give the relationship between the constants k and the temperature, which we are seeking, it shows that this relationship must be of the form

$$\frac{d \log k}{dT} = \frac{A}{T^2} + B \ . \ . \ . \ . \ (2) \ \text{(van 't Hoff)}$$

where A and B are constants.

If we put A = 0, we obtain

$$\frac{d \log k}{dT} = B \ . \ . \ . \ . \ . \ . \ (3) \ \text{(Berthelot).}$$

This equation corresponds to the expression $k = ab^t$, which was proposed by Berthelot in connexion with his experiments on etherification.

As will be shown later, the results of experiment are often in good agreement with the formula when we put B = 0, and consequently

$$\frac{d \log k}{dT} = \frac{A}{T^2} \ . \ . \ . \ . \ (4) \ \text{(Arrhenius)}^1$$

By integration of (4) we obtain

$$\log k = -\frac{A}{T} + \text{constant.}$$

So far, we have assumed that q is independent of the temperature. This is, however, certainly not allowable when the equation is applied to considerable intervals of temperature. The quantity of heat evolved by a reaction changes with the temperature to some extent.

Taking this into account, and writing $q_T = q_o + bT$, where b is the difference between the specific heats of the two systems,[2] we obtain, in place of equation (4),

$$\frac{d \log k}{dT} = \frac{A + BT}{T^2} \ . \ . \ . \ . \ (5) \ \text{(Kooy).}^3$$

---

[1] Zeit. phys. Chem. 4, 226, 1889.

[2] Appendix, note 3.

[3] Inaugural Dissertation, Amsterdam 1893. Zeit. phys. Chem. 12, 155, 1893.

From this equation, we obtain by integration,

$$\log k = -\frac{A}{T} + B \log T + \text{constant}.$$

If we put $A = 0$ in equation (5), we obtain

$$\frac{d \log k}{dT} = \frac{B}{T}, \quad \ldots \quad (6)$$ (Harcourt and Esson)[1]

or after integration

$$\log k = B \log T + \text{constant}.$$

Equation (4), p. 123, which in many cases is in good agreement with the observations which have been made, makes it possible to calculate the effect of a given change of temperature on the velocity of a reaction.[2]

Berthelot's equation reproduces the chief characteristic of the relation between velocity of reaction and temperature, which is that if the temperatures form an arithmetical series the rates of change at these temperatures will form a geometrical series.

By integration between the limits T_1 and T_2, we obtain from equation (4)

$$\log \frac{k_1}{k_2} = A \frac{T_1 - T_2}{T_1 T_2},$$

k_1 and k_2 being here the velocity constants at the temperatures T_1 and T_2 respectively.

For a rise of temperature of 10 degrees, therefore,

$$\log \frac{k_1}{k_2} = A \frac{10}{T_1 T_2}.$$

We see from this, and on this point all the functions which have been proposed are in agreement, that at higher temperatures the increase in the ratio of the velocity constants produced by a rise of temperature of 10 degrees will be smaller than at lower temperatures.

---

[1] Proc. Roy. Soc. 58, 112, 1895. Harcourt and Esson express, in this paper, the connexion between the rates of reaction α_1 and α_2 at the temperatures T_1 and T_2, as follows

$$\frac{\alpha_1}{\alpha_2} = \left(\frac{T_1}{T_2}\right)^m.$$

[2] D. M. Kooy, loc. cit.

The great majority of cases which have as yet been investigated in this direction have been studied in the interval of temperature lying between 0° and 184°, and it is very striking that the ratio of the velocity constants for two temperatures differing by 10 degrees has a value between 2 and 3 approximately. In other words, a rise of temperature of 10° doubles or trebles the velocity of a reaction.

The following table will serve to illustrate this.[1]

Reaction.	Interval of temperature.	Mean ratio of velocities at T and (T + 10).
Sodium ethylate + methyl iodide[2]	0°—30°	3.34
$HPO_3 + H_2O = H_3PO_4$[3]	0°—61°	3.00
Hydrolysis of ethyl acetate[4]	3°.6—30°.4	2.03
" " "[5]	9°.4—44°.94	1.89
$KClO_3 + FeSO_4 + H_2SO_4$[6].	10°—32°	2.44
$C_4H_4O_4Br_2 = HBr + C_4H_3O_4Br$[7]	15°—101°	2.65
Decomposition of ethylene hydrochloride into hydrochloric acid and ethylene[8]	24°.5—43°.6	2.87
Decomposition of methylethylene hydrochloride	24°.5—43°.6	2.68
Decomposition of dimethylethylene hydrochloride[8]	24°.5—43°.6	2.66
Decomposition of trimethylethylene hydrochloride[8]	24°.5—43°.6	2.70
Decomposition of α-dichlorhydrine[8]	24°.5—43°.6	2.79
Inversion of cane sugar[9]	25°—55°	3.63
Hydrolysis of acetamide by acids[10]	65°—100°	2.12
Action of caustic soda on sodium chloracetate[11]	70°—130°	2.54
$C_2H_3ClO_2 + H_2O = C_2H_4O_3 + HCl$[12].	80°—130°	2.55
Hydrolysis of tertiary amylacetate[13]	156°—184°	2.19

It is also of interest that similar phenomena are, according to the researches of CLAUSEN [1], to be observed in the respiration of plants. The quantities of carbon dioxide expired in equal intervals of time increase rapidly when the temperature rises between 0° and 25°. A rise of temperature of 10° increases the quantity 2.46 times (on the average) with wheat, 2.45 times with lupins, and 2.47 times with syringa (lilac).

---

[1] Kooy, Zeit. phys. Chem. 12, 155, 1893.

[2] Hecht and Conrad, Zeit. phys. Chem, 3, 473, 1889. also p. 133.

[3] Sabatier, Compt. Rend. 106, 63, 1888.

[4] Warder, Berichte, 14, 1365, 1881.

[5] Reicher. Lieb. Ann., 232, 111, 1885. also p. 130.

[6] Hood, Phil. Mag. (5) 20, 185, 1885. also p. 132.

[7] Page 127.

[8] Evans, Zeit. phys. Chem. 7, 356, 1891.

[9] Spohr, Zeit phys. Chem. 2, 195, 1888.

[10] Ostwald. Journ. prakt. Chem. (2), 27, 1, 1883.

[11] Page 129.

[12] Page 130.

[13] Konowalow, Zeit. phys. Chem. 1, 64, 1887.

Above 25° the increase in the rate of the metabolic changes is smaller, and above 50° it approximates to that which is found at lower temperatures.

With regard to the ratio of the velocity constants at high temperatures, KOOY'S[2] experiments on the decomposition of phosphine at temperatures between 310° and 512° confirm the result which was obtained from the equation

$$\log \frac{k_1}{k_2} = A \frac{10}{T_1 T_2}.$$

The following table contains the velocity constants determined experimentally at different temperatures.

If the ratio of the velocity constants be calculated approximately, for differences of temperature of 10°, in the intervals 310°—367°, 367°—446°, 446°—512°, the value obtained is 1.2, while for the interval of temperature 0°—10° the number 2.92 is obtained, so that at lower temperatures it is of the same order of magnitude as the ratio found already for other reactions at the ordinary temperature.

Decomposition of phosphine.

Temperatures.	Velocity constant. [3]
310°	0.00048
367°	0.0015
446°	0.0057
512°	0.0186

---

[1] Landw. Jahrbücher. 19, 894, 1890.

[2] loc. cit.

[3] That the velocity constant found here does not agree with the number found on page 100, is due to the influence of the walls of the vessel. Any change in the vessel produces a change in the constant. The two series of experiments in question were separated from each other by an interval of about ten years, so that they were made with quite different pieces of apparatus.

b. *Experimental treatment of the subject.*

The influence of the temperature on the velocity of a reaction has been studied in a number of cases which are described in what follows.

1. *Influence of the temperature on the rate of decomposition of dibromsuccinic acid.*

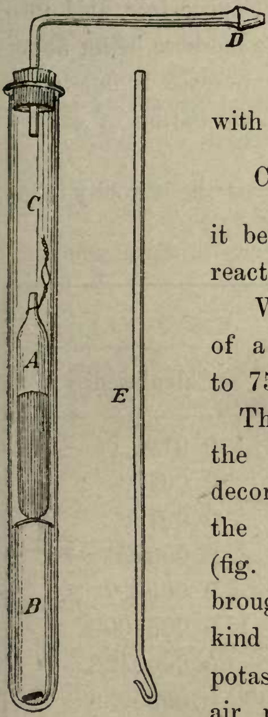


Fig. 30.

Since it was found that dibromsuccinic acid decomposes at 100° in aqueous solution in only approximate accordance with the equation

$$C_4 H_4 O_4 Br_2 = C_4 H_3 O_4 Br + H Br,$$

it became necessary to investigate the secondary reactions which occur at different temperatures.

With this object the increase which the titre of a solution of the acid undergoes on heating to 75°, 100°, 125°, and 150° was determined. The solution was heated in sealed tubes and the carbon dioxide, formed by the secondary decomposition of the acid, removed before making the determinations of the titre. The tubes A (fig. 30) were opened after being heated, and brought, by means of the hook E, into a kind of exsiccator containing a pice of caustic potash at B. This was connected, at D, to the air pump and partially evacuated, the tubes being then allowed to remain in the partial vacuum for 24 hours.[1]

The following table contains the augmentations of the titre produced by heating for different periods of time and at different temperatures.

---

[1] Special experiments had shown that the carbonic acid may be removed in this way without loss of hydrobromic acid.

75°		100°		125°		150°	
Duration of heating in hours.	Ratio of increase to initial titre.	Duration of heating in hours.	Ratio of increase to initial titre.	Duration of heating in hours.	Ratio of increase to initial titre.	Duration of heating in hours.	Ratio of increase to initial titre.
25	0.507	3.3	0.501	0.5	0.464	0.1	0.396
35	0.519[1]	4.3	0.504	0.8	0.462	0.2	0.356

It is evident that below 100° the increase of the titre corresponds to the decomposition of the dibromsuccinic acid into hydrobromic acid and brom-maleïc acid, the increase being about 50 per cent, while above 100° the smaller increase is due to the secondary decomposition of the acids with formation of carbon dioxide.

The following table contains the values of the velocity constants.

Temperature.	k.	
	Observed.[2]	Calculated.
101	0.0138	0.0138
89.4	0.00454	0.00458
80	0.002	0.00183
70.1	0.000734	0.000734
60.2	0.000284	0.000287
50	0.000108	0.000109
40	0.0000375	0.0000422
15	0.0000042	0.0000039

The values given in the third column are calculated by means of the equation

$$\frac{d \log k}{dT} = \frac{A}{T^2} + B.$$

---

[1] This number is somewhat to high owing to an error in the determination of the titre.

[2] Each number is the mean of two observations.

Putting

$$A = 0, \ B = 0.0412, \text{ and } T = t + 273,$$

we obtain

$$\log k = 0.0412 \, t - 6.02219.$$

2. *Influence of the temperature on the rate of the reaction between sodium chloracetate and caustic soda.*

The experiments on this point were made by Schwab in the way which has already been described on page 17.

The following table contains the experimental results, together with those calculated.

Temperature.	k.	
	Observed.[1]	Calculated.
130°	0.217	0.217
120	0.0857	0.0856
110	0.0305	0.0338
100	0.0128	0.0133
90	0.00499	0.0525
80	0.00198	0.00207
70	0.000822	0.000818

The numbers in the third column are calculated by means of the equation

$$\log k = 0.0404 \, t - 5.91554,$$

which is obtained from the equation

$$\frac{d \log k}{dT} = \frac{A}{T^2} + B$$

by putting $A = 0$; $B = 0.0404$; $T = t + 273$.

---

[1] Each number is the mean of from three to six observations.

3. *Influence of the temperature on the rate of change of chloracetic acid in aqueous solution.*

This series of experiments also was carried out by Schwab.

Temperature.	k.	
	Observed [1].	Calculated.
130°	0.00237	0.00237
120	0.00105	0.00102
110	0.000436	0.000424
100	0.000173	0.000167
90	0.0000603	0.0000627
80	0.0000222	0.0000222

If we put

$$B = 0,$$

we obtain

$$\log k = -\frac{A}{T} + 11.695, \text{ where } \log A = 3.76125.$$

4. *Influence of the temperature on the rate of hydrolysis of ethyl acetate by caustic soda.*

Two series of experiments have been made on this subject, one by Warder,[2] the other by Reicher,[3] the values of k obtained agreeing together satisfactorily.

Reicher employed in his experiments the apparatus represented in figure 1, and described fully on page 6, except that the temperature was maintained constant at any desired point by means of a thermostat.

---

[1] Each number is the mean of six observations.

[2] Amer. chem. Journ. 3, 203, 1881. Berichte, 14, 1365, 1881.

[3] Lieb. Ann. 232, 103, 1885.

The results obtained were as follows.

Temperature.	k.	
	Observed.[1]	Calculated.
9.4	2.307	2.307
14.4	3.204	3.2
24.22	6.151	6.151
35.14	12.096	11.97
44.94	21.648	21.648

The numbers in the third column have been calculated, in this case also, by means of the equation

$$\frac{d \log k}{dT} = \frac{A}{T^2} + B.$$

Putting

$$A = 1780, \quad B = 0.00754, \quad T = t + 273,$$

we obtain

$$\log k = -\frac{1780}{T} + 0.00754\ T + 4.53.$$

Arrhenius[2] has shown that many of the observations which have been recorded by different authors may be represented by the formula

$$\frac{d \log k}{dT} = \frac{A}{T^2}$$

This formula is also applicable to the experiments of series 5—9 which follow.

---

[1] The first, third, and fifth numbers have been used in calculating the constants of the equation.

[2] See page 123.

5. *Influence of the temperature on the velocity of the reaction between potassium chlorate and ferrous sulphate in presence of sulphuric acid.*

This reaction has been very carefully investigated by Hood;[1] 0.5637 grams of ferrous sulphate, 0.2057 grams of potassium chlorate, and 3.099 grams of sulphuric acid were brought into a flask, which was kept at the desired temperature by means of a thermostat, and diluted to 260 cc.

The progress of the oxidation was followed by titrating 10 cc. of the liquid with permanganate from time to time. The results are contained in the following table.

Temperature.	k.		Temperature.	k.	
	Observed.	Calculated.		Observed.	Calculated.
10	1.00	1.00	20	2.51	2.54
12	1.21	1.21	22	2.96	3.02
14	1.46	1.46[2]	24	3.59	3.62
16	1.73	1.76	28	5.08	5.08[3]
18	2.11	2.11	30	6.04	6.04
—	—	—	32	7.15	7.11

The values of k are calculated by means of the formula

$$\log k = -\frac{7695}{T} + 27.189.$$

---

[1] Phil. Mag. (5), 20, 323, 1885.

[2] The value of k at 10° is taken as unity.

[3] These values were used in calculating the constants in the equation.

6. *Influence of the temperature on the rate of hydrolysis of ethyl acetate by caustic soda.*

We shall consider here the experiments of WARDER to which reference has already been made. The results are contained in the following table.

Temperature.	k.		Temperature.	k.	
	Observed.	Calculated.		Observed.	Calculated.
3.6	1.42	1.48	27.0	7.24	7.16
5.5	1.68	1.70	28.4	8.03	7.81
7.2	1.92	(1.92)	30.4	8.88	8.82
11.0	2.56	2.51	32.9	9.87	10.24
12.7	2.87	2.82	34.0	10.92	(10.92)
19.3	4.57	4.38	35.0	11.69	11.60
20.9	4.99	4.86	37.7	13.41	13.59
23.6	6.01	5.78	—	—	—

The values of k are calculated by means of the equation

$$\log k = -\frac{5579}{T} + 20.562.$$

7. *The influence of the temperature on the inversion of cane sugar* was investigated by URECH,[1] and more recently by SPOHR.[2] The values of k obtained, in this case also, are well represented by the formula of ARRHENIUS.

The same remark is true with reference to (8) *the influence of the temperature on the action of sodium ethylate on methyl iodide*, which was studied by HECHT and CONRAD,[3] and to (9) *the influence of temperature on the formation of nitriles from syn-aldoxime acetates and on the change of the latter into the anti-modifications*, which were studied by H. LEY.[4]

---

[1] Berichte, 16, 765, 1883; 17, 2175, 1884.

[2] Zeit. phys. Chem. 2, 196, 1888.

[3] „ „ „ 3, 450, 1889.

[4] „ „ „ 18, 376, 1895.

10. *Influence of the temperature on the rate of decomposition of the hydrides of arsenic and phosphorus.*

While the reactions which we have so far considered have been investigated only within rather narrow limits of temperature, we have here a case in which determinations of the velocity have been made over a fairly wide range.

Kooy has determined the velocity constants for the decomposition of arsenic and phosphorus hydrides at temperatures as much as 200° apart.

a. *Arsenic hydride.*

The apparatus used, and the way in which the experiments were made, are described on page 41. The velocity constants were determined at the boiling points of amyl benzoate (256°), diphenylamine (310°), and anthraquinone (373°).

We have already seen (p. 43) that changes in the nature of the walls of the vessel may have a considerable influence on the velocity of a reaction, so that to obtain results at different temperatures which would be comparable with each other it was necessary to avoid disturbances arising from this cause.

This was achieved by making all the determinations of the velocity in the same new vessel and by avoiding prolonged heating. By taking these precautions the nature of the walls changed very little, and the values of k obtained are comparable.

The following table contains the results.

Temperature.	Velocity constant. [1]
256	0 0209
311	0.0506
367	0.202

---

[1] See also p. 2, and note 3 on p. 126.

b. *Phosphine.*

The experiments were made in the same way as those with arsenic hydride, the rate of decomposition being determined at 310° (diphenylamine), 367° (anthraquinone), 446° (sulphur), and 512° (sulphide of phosphorus).

The results have already been given in the table on page 126, moisture had no influence on the value of k.

The agreement between the observed values of k and those calculated by means of the formula of Arrhenius,

$$\frac{d \log k}{dT} = \frac{A}{T^2},$$

is not satisfactory.

In this case the intervals of temperature are large, and the variation of q with the temperature cannot therefore be neglected, so that it is better to employ the formula

$$\frac{d \log k}{dT} = \frac{A + BT}{T^2},$$

or, after integration,

$$\log k = -\frac{A}{T} + B \log T + \text{const. (See page 124.)}$$

The values of k calculated by means of this equation agree better with the observed numbers. The formula of Harcourt and Esson likewise gives fairly correct results, as the following table shows.

Temperature.	k observed.	k calculated from (4) p. 123.	k calculated from (5) p. 123.	k calculated from (6) p. 124.
310	0.00048	(0.00048)[1]	(0.00048)	(0.00048)
367	0.0015	0.0017	0.0014	0.0015
446	0.0057	0.0071	(0.0057)	0.0063
512	0.0186	(0.0186)	(0.0186)	(0.0186)

---

[1] The numbers enclosed in brackets have been used in calculating the constants in the equations.

THE INFLUENCE OF TEMPERATURE ON CHEMICAL CHANGE.

SECOND PART.

THE TEMPERATURE OF IGNITION.

One of the conclusions arrived at in the preceding section requires further consideration, since it appears to be out of harmony with the phenomena of inflammation.

The investigations on the influence of temperature on chemical change, to which attention has so far been directed, led to the conclusion that this influence was a continuous one; the experiments which have been described, and the theoretical considerations which have been advanced agree in this respect. The phenomenon of ignition appears to indicate, however, by its sudden occurrence at a definite temperature, that there are exceptions to this continuity. L. Meyer[1] expresses himself on the subject in the following way: —

"The lowest temperature at which a given chemical reaction occurs, which in the case of combustible substances is known as the temperature of ignition, might be called, in general, the temperature of reaction."

There is here a distinct contradiction of the views which have been advanced as to the influence of temperature on the velocity of reactions. These views do not admit the possibility of any sudden acceleration of the reaction, and require us to suppose that if a reaction occur at any given temperature it will also go forward at any other temperature, although with a different velocity.

---

[1] Dynamik der Atome, 1883, p. 417. Also Bunsen, Gasom. Methode, 1877, p. 336.

A closer study of the subject will, however, show that the phenomena of ignition do not in the least oblige us to admit the existence of a temperature at which the reaction begins; the occurrence of inflammation then falls into line with the ideas which have so far been acquired.

The proof of this statement depends on the fact that there are three conditions fulfilled by every reaction which exibits the phenomenon. By inflammation we shall understand here not only the phenomena of combustion, but also any complete chemical transformation which occurs in consequence of a local elevation of the temperature to the so-called temperature of ignition.

In every change of this kind the following conditions are fulfilled: —

1. The reaction which produces the inflammation evolves heat.
2. The reaction occurs more or less rapidly below the temperature of ignition.
3. The reaction is accelerated by an elevation of temperature.

The necessity of the first condition being sufficiently proved by facts which are generally known, it will suffice to cite the rather sparse observations which lead to the admission of the truth of the second; the third condition appears to be fulfilled equally by all chemical changes so that there is no reason for considering it in more detail.

The following, then, are the observations which appear to show that the reactions occur below the temperature of ignition:

The oxidation of phosphorus, phosphine, arsenic, sulphur, hydrogen[1], hydriodic acid, carbon monoxide, ether, and paraffin, has been observed considerably below the temperature of ignition. The same is true of the chemical transformations undergone by ozone, chloride of nitrogen, cyanic acid, mixtures of chlorine and hydrogen, and of chlorine and hydrocarbons, etc.[1]; they take place more or less slowly at temperatures below those which determine ignition or explosion.

---

[1] A striking example of this is given in the most recent experiments of V. Meyer and W. Raum (Berichte, 28, 2804, 1895) on the effects of prolonged exposure of electrolytic gas to a moderate temperature. At the ordinary temperature the rate of formation of water is so small that it practically cannot be observed. On heating electrolytic gas continuously for 10 days to 300°, the formation of water could not be proved, but on heating day and night for 65 days, to this temperature, a distinct formation of water occurred. It is, therefore, natural to suppose that even at lower temperatures it would be possible to demonstrate the formation of water, by heating for a sufficiently prolonged period of time. In the experiments at 300°, which have been referred to, the following percentages of the electrolytic gas contained in three bulbs (see p. 48) were transformed into water; —

9.5, 0.4, 1.3.

No change could be detected at 100°, after heating for 218 days and nights.

The three conditions mentioned being fulfilled, a phenomenon of the nature of ignition may occur.

To prove this, suppose we have a substance which is not susceptible of chemical change, for example, atmospheric air, and suppose its temperature to be raised locally from 0° to T_1°, (fig. 31). On removing the source of heat, the increased temperature will be communicated to the surrounding gas, and will, therefore, give rise to a kind of hot wave which will be propagated with a certain velocity, its temperature sinking continually towards 0°.

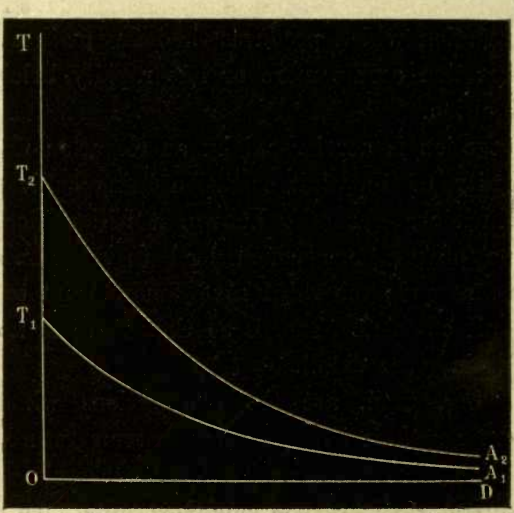


Fig. 31.

---

[1] Bull. Soc. Chim. 13, 1, 1870. Compt. Rend. 78, p. 1853, 1874. Berichte, 15, 2155, 1882; 16, 139 and 478, 1883. Van 't Hoff observed that the slow oxidation of heated paraffin is accompanied by a phosphorescence which is very similar in appearance to a combustion.

The curve T_1A_1, which is obtained by measuring the temperatures along OT and the distances along OD, represents graphically the relation between the temperature of the wave and the distance which it has travelled from the starting point. For brevity we will call $\triangle T$ the diminution in the temperature of the hot wave during the first moments of its progress.

Suppose, now, that a chemical reaction which satisfies the three above-mentioned conditions may occur in the gas; suppose for example, that we have electrolytic gas in place of atmospheric air. A local elevation of temperature will then produce a wave of the kind described, but with the difference that the temperature, especially at first, will sink less rapidly during its propagation, because the chemical change produced by the elevation of temperature evolves heat. The value of $\triangle T$ will thus be diminished, and the graphical representation of the temperature of the hot wave will be given by the curve $T_1A'_1$ (fig. 32).

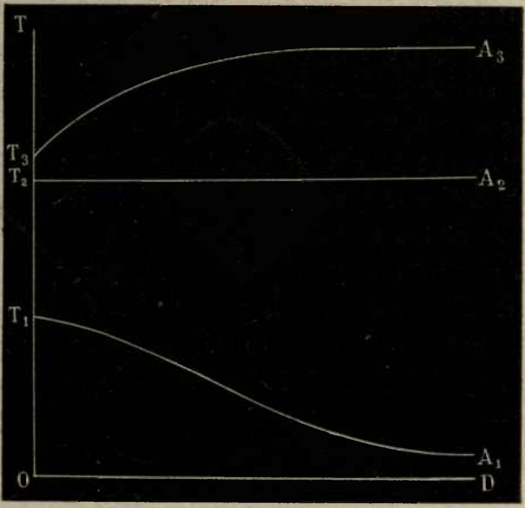


Fig. 32.

We will now consider the effect of a greater initial elevation of the temperature in the two cases. The matter is simple, so far as the substance which does not undergo chemical change is concerned; the temperature of the hot wave will fall more rapidly than before, owing to the greater difference of temperature between it and the medium through which it is propagated; this is represented by the curve T_2A_2 in fig. 31. When a chemical change occurs, however, as with electrolytic gas, we have in addition to this influence, which increases $\triangle$ T, another which diminishes it, for the chemical change, accelerated by the higher temperature, will now produce a greater quantity of heat. If the action which tends to diminish $\triangle$ T exceed that which tends to increase it, it is evident that the value of $\triangle$ T will diminish as the initial temperature rises.

This being the case, we perceive the possible existence of a temperature, T_2, at which the value of $\triangle$ T will be zero, in other words, of a temperature at which the wave will preserve its initial temperature unchanged; this is represented by the line T_2A_2 (fig. 32).

A still higher initial temperature, T_3, would give rise to a hot wave the temperature of which, instead of falling, would rise until it reached the temperature which the total transformation of the substance is capable of producing. (T_3A_3, fig. 32.)

It is obvious that those waves the temperature of which falls can only give rise to a very minute quantity of change, while those of which the temperature rises lead to the transformation of the whole of the substance. The temperature T_2, therefore, which gives rise to a wave of constant temperature, corresponds in every particular to the ignition temperature.

It would not be difficult to translate the preceding into mathematical symbols, but it is preferable to express it in words as follows: —

The ignition temperature is the temperature at which the initial loss of heat, due to conduction etc., is equal to the heat evolved in the same time by the chemical reaction.

It must, however, be remarked that certain facts are not accounted for by the foregoing considerations. It is known that, at a given temperature, phosphorus is no longer luminous in oxygen gas the pressure of which exceeds a certain limit; in other words there is a definite pressure at which the velocity of the reaction suddenly assumes a finite value.

Joubert[1] found that the luminosity first became visible at the different temperatures given in the following table, when the pressure of the oxygen was diminished to the corresponding value which is given.

Temp.	Pressure of oxygen.	Temp.	Pressure of oxygen.
1.4°	355 mm.	9.3	538 mm.
3.0	387	11.5	580
4.4	408	14.2	650
5.0	428	18.0	730
6.0	460	19.2	760
8.9	519		

Representing these numbers by means of a curve, the abscissae of which are the temperatures, and the ordinates the pressures, we obtain the approximately straight line shown in fig. 33.

Suppose, now, that the pressure of the oxygen is maintained

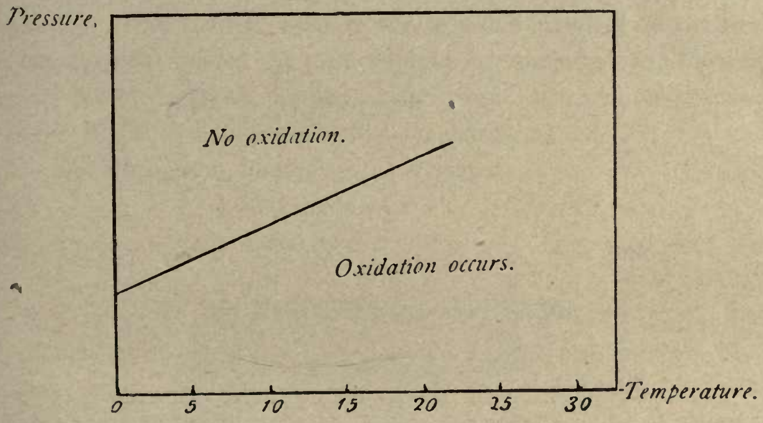


Fig. 33.

constant and the temperature raised, then, passing from left to right across the figure, as soon as we cross the line oxidation suddenly begins, in other words, we find, on raising the temperature, a *per saltum* transition from conditions under which no oxidation occurs to conditions under which it does occur.

---

[1] Thèse, p. p. 29, 30. See also p. 52 ante.

Mathematically considered the phenomenon perhaps indicates that the equation

$$\frac{d \log k}{dT} = \frac{A}{T^2},$$

should have another term containing (T—t), where t would represent the temperature at which the discontinuity occurs.

CHEMICAL EQUILIBRIUM.

FIRST PART.

THE THREE FORMS OF CHEMICAL EQUILIBRIUM.

The study of chemical equilibrium yields results which form a very important addition to our knowledge of chemical change. This will be obvious if, with PFAUNDLER, we regard equilibrium as the result of two changes taking place in opposite directions with equal velocity.

Since, according to HORSTMANN, the principles of thermodynamics may be applied to chemical equilibrium, and since the experimental difficulties which are encountered in its study are frequently much smaller than is the case in dynamical researches, the experience gained in the domain of chemical equilibrium may advantageously be applied in the study of chemical change.

Three kinds of equilibrium may be distinguished: —

1. Equilibrium in homogeneous systems.
2. ,, ,, heterogeneous ,,
3. ,, ,, condensed ,,

I. HOMOGENEOUS SYSTEMS.

a. *At constant temperature.*

In cases of equilibrium in homogeneous systems the bodies forming the system may be gaseous, liquid, or solid. [1]

An example of the first of these is found in the case, which has already been mentioned, of the dissociation of nitrogen peroxide

---

[1] This latter form of equilibrium will not occupy us further; the so called "solid solutions", and also many diffusion phenomena in solid bodies show, however, that it is probably justifiable to speak of equilibrium in a homogeneous solid system.

$$N_2O_4 \rightleftarrows 2\ NO_2.$$

The following is an example of a homogeneous equilibrium in a liquid system,

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

As we have already observed, the equilibrium is to be regarded as the result of two changes taking place with the same velocity in opposite directions, so that, in the case of a homogeneous equilibrium, the study of the velocities of the opposing reactions permits us to calculate the ratio between the concentrations of the two systems when the state of equilibrium is attained.

In the example chosen[1],

$$N_2O_4 \rightleftarrows 2\ NO_2,$$

the velocities of the two reactions are given by the equations,

$$-\frac{dC_1}{dt} = k_1C_1, \text{ and } -\frac{dC_2}{dt} = k_2C_2^2.$$

C_1 and C_2 are the concentrations of the systems N_2O_4 and NO_2 respectively, in the units which have already[2] been employed (92 kgrms. per cubic metre).

Equilibrium having been attained, the velocities of the reactions $\left(-\frac{dC_1}{dt} \text{ and } -\frac{dC_2}{dt}\right)$ are equal, and therefore

$$k_1C_1 = k_2C_2^2,$$

or in general,

$$k_1\ C_1^{n_1} = k_2\ C_2^{n_2},$$

---

[1] Henceforward the system written to the left of the $\rightleftarrows$ sign will be called the "first system", that to the right the "second system", the letters C_1 and k_1 will be used with reference to the first, C_2 and k_2 to the second. This choice is of course purely arbitrary, since the part taken by the two systems in producing equilibrium is the same.

[2] Page 4.

where n_1 and n_2 are the numbers of molecules in each of the systems which take part in the reaction.

An equation of this form has already been given by GULDBERG and WAAGE, by PFAUNDLER, and also by HORSTMANN.

It is to be noticed, however, that we have deduced it from the equation

$$-\frac{dC}{dt} = kC^n,$$

which is exactly true only for great dilution. The derived equation also is therefore subject to the same restriction, and where this restriction is observed the experimental results are found to be in agreement with those obtained from the equation.[1]

Just as the determination of the velocity constants may be used in order to calculate the ratio between the concentrations of the opposing systems in the state of equilibrium, so this ratio may be employed to obtain a knowledge of the velocity constants. The investigation of the equilibrium gives the values of the concentrations of the systems taking part in it, and, therefore, that of the ratio between the velocity constants k_1 and k_2 which henceforth will be denoted by the letter K and called the *equilibrium constant*.

We have thus,

$$\frac{C_2^{n_2}}{C_1^{n_1}} = \frac{k_1}{k_2} = K.$$

If, for example, k_1 had been determined by the study of the velocity of one of the two opposing changes, the value of the velocity constant of the other change would be obtained from a study of the equilibrium.

BERTHELOT and PÉAN DE SAINT GILLES[2] have determined, under conditions which were varied as much as possible, what part of an acid is convertible into ester by treating it with a given quantity of an alcohol.

---

[1] Journ. prakt. Chem. (2), 19, 69 et seq. 1879.

[2] Ann. Chim. Phys. (3), 65, 385, 1862; (3), 66, 5, 1862; (3), 68, 225, 1863 Also VAN 'T HOFF, Berichte, 10, 669, 1877.

The reaction takes place as follows,

$$\text{Acid} + \text{alcohol} \rightleftarrows \text{Ester} + \text{water}.$$

If we bring together 1 gram-molecule of acid, w gram-molecules of water, and a gram-molecules of alcohol, we have in the condition of equilibrium when e gram-molecules of ester have been formed,

$$k_1 \frac{(1 - e)(a - e)}{V} = k_2 \frac{e(w + e)}{V},$$

where V is the volume of the mixture, and k_1 and k_2 are the velocity constants.

Or,

$$k_1 (1 - e)(a - e) = k_2 e (e + w) \quad . \; . \; . \; . \quad (I)$$

When k_1 and k_2 are known, this equation allows the quantities of the different substances which will exist side by side in equilibrium (their "limiting values") to be calculated, and the equation may therefore be called the *limiting equation.*

The experiments of BERTHELOT and PÉAN DE SAINT GILLES show that when acid and alcohol are mixed together in molecular proportions, $^2/_3$ of the mixture is converted into ester. That is, experiment gives $e = {}^2/_3$, for $a = 1$, and $w = 0$.

Putting these values into the limiting equation we get,

$$k_1 (1 - {}^2/_3)(1 - {}^2/_3) = k_2 \, {}^2/_3 \cdot {}^2/_3,$$

or

$$\frac{k_1}{k_2} = K = 4.$$

Introducing this value into the limiting equation, and solving it for e, we obtain

$$e = \frac{1}{6}\left[4(a + 1) + w - \sqrt{16(a^2 - a + 1) + 8w(a + 1) + w^2}\right]$$

Since the experiments of BERTHELOT and PÉAN DE SAINT GILLES were made with mixtures of acid and alcohol without the addition of water, we must put $w = 0$ in the last equation, and find

$$e = {}^2/_3 \left(a + 1 - \sqrt{a^2 - a + 1}\right)$$

The following table contains, under a the number of molecules of alcohol used to one molecule of acid, under e the number of molecules of ester formed.[1]

a	e observed.	e calculated.
0.05	0.05	0.049
0.08	0.078	0.078
0.18	0.171	0.171
0.28	0.226	0.232
0.33	0.293	0.311
0.50	0.414	0.423
0.67	0.519	0.528
1.00	0.665	0.667
2.00	0.858	0.845
8.00	0.966	0.945

It may also to be pointed out that the further conclusions deducible from equation (I) on page 146, $\frac{k_1}{k_2}$ being taken as equal to 4, are in agreement with the results of experiment.

1. If we write the equation in the form

$$4\,(1 - e)\left(1 - \frac{e}{a}\right) = \frac{e\,(e + w)}{a}$$

we find $e = 1$ when $a = \infty$, that is if a given quantity of an acid be mixed with a very large quantity of an alcohol, the whole of the acid will be converted into ester.

From the form of the original equation (1) it is easily seen that the same is true for the alcohol if it be mixed with a large quantity of acid.

2. The transformed limiting equation gives $e = o$ when $a = o$, that is, no ester is formed from acid without addition of alcohol and *vice versa*.

---

[1] See also VAN 'T HOFF's original memoir, Berichte, 10, 669, 1877.

3. If the equation be written

$$e = \frac{4\ (1 - e)\ (a - e)}{w + e}$$

we find for $w = \infty$ $e = o$, that is, formation of ester is prevented by a very large addition of water. The same is true for addition of a very large quantity of ester.

b. *The temperature is variable.*

Application of Thermodynamics.

The influence of the temperature on the equilibrium constant is expressed by the following equation[1],

$$\frac{d \log K}{dT} = \frac{q}{2\,T^2},$$

where T is the absolute temperature, q the quantity of heat evolved when unit quantity (in kgrm. molecules) of the second system is transformed into the first at constant volume.

This equation, which is true both for homogeneous and for heterogeneous equilibrium in gases and in dilute solutions, may be obtained in the following way: —

Let us suppose that equilibrium exists between (1 — x) kgrm-molecules of the first and x kgrm.-molecules of the second system, that the volume of the whole is V, and the temperature T. A reversible cycle of operations may be carried out with the system for which we shall have, (from thermodynamics),

$$\frac{1}{J}\left(\frac{dP}{dT}\right)_V = \frac{1}{T}\left(\frac{dQ}{dV}\right)_T,$$

where P is the pressure acting on the system.

$\left(\frac{dQ}{dV}\right)_T$ is the quantity of heat which is absorbed when the volume of an indefinitely large quantity of the system is increased by unity at the temperature T. Call q the quantity of heat which is absorbed when unit quantity of the first system is converted into the second without any external work being performed. When the volume of the system changes at constant temperature a certain quantity of the second system is formed (viz. $\left(\frac{dx}{dV}\right)_T$), the quantity of heat absorbed by this, (viz. $q\left(\frac{dx}{dV}\right)_T$) may also be obtained by subtracting the quantity of heat equivalent to the external work done by the system during the expansion, viz. $\frac{P}{J}$ cals, from the total amount of heat absorbed, $\left(\frac{dQ}{dV}\right)_T$; so that we obtain

---

[1] J. H. van 't Hoff, Lois de l'équilibre chimique dans l'état dilué, gazeux ou dissous. Kongl. Svenska Vet. Akad. Handlingar, 21, 1885; Archiv. Néerland. 20, 239, 1885.

$$q\left(\frac{dx}{dV}\right)_T = \left(\frac{dQ}{dV}\right)_T - \frac{P}{J} = \frac{1}{J}\left\{T\left(\frac{dP}{dT}\right)_V - P\right\} = \frac{T^2}{J}\left\{\frac{d\frac{P}{T}}{dT}\right\}_V \ldots . (1)$$

If n_1 molecules of the first and n_2 molecules of the second system take part in the reaction, we have

$$PV = [\,n_1(1 - x) + n_2 x\,]\,RT. \quad . \quad . \quad . \ (2)$$

Therefore

$$\frac{P}{T} = [\,n_1 + (n_2 - n_1)\,x\,]\,\frac{R}{V}$$

and

$$\left(\frac{d\frac{P}{T}}{dT}\right)_V = (n_2 - n_1)\left(\frac{dx}{dT}\right)_V \frac{R}{V}$$

Substituting this in equation (1), we obtain

$$q\left(\frac{dx}{dV}\right)_T = \frac{T^2R}{JV}\,(n_2 - n_1)\left(\frac{dx}{dT}\right)_V \quad . \quad . \quad . \quad . \ (3)$$

At constant temperature, we have the relationship

$$\frac{C_2^{n_2}}{C_1^{n_1}} = K, \text{ or } \frac{\left(\frac{x}{V}\right)^{n_2}}{\left(\frac{1 - x}{V}\right)^{n_1}} = K, \quad . \quad . \quad . \quad . \ (4)$$

and therefore,

$$\log K + (n_2 - n_1)\log V = n_2 \log x - n_1 \log(1 - x).$$

By partial differentiation with respect to V, this yields

$$\left(\frac{dx}{dV}\right)_T = \frac{n_2 - n_1}{V\left(\frac{n_2}{x} + \frac{n_1}{1-x}\right)}.$$

Similarly differentiating with respect to T, we obtain

$$\left(\frac{dx}{dT}\right)_V = \frac{\frac{d \log K}{dT}}{\left(\frac{n_2}{x} + \frac{n_1}{1-x}\right)}.$$

Introducing these values into equation (3), it becomes

$$\frac{d \log K}{dT} = \frac{Jq}{RT^2} = \frac{q}{2\ T^2}.$$ [1]

This equation applies likewise to the case of heterogeneous equilibrium, for equations (2) and (4) apply equally well in this case when n_1 and n_2 are taken to mean the numbers of molecules of the gaseous or dissolved substances which take part in the reaction. Since the values of n_1 and n_2 do not appear in the equation $\frac{d \log K}{dT} = \frac{q}{2\ T^2}$, this alteration in their signification makes no difference.

Applications.

In applying the equation to homogeneous chemical equilibrium we have to distinguish two cases: —

a. The value of q is zero.
b. The value of q is $\gtrless$ zero.

a. *The value of q is zero.*

In this case we have equilibrium between two systems which may change into each other, at constant volume, without evolution or absorption of heat, consequently

---

[1] This formula has also been deduced from the principle of the increase of the entropy by VAN DEVENTER, Zeit. Phys. Chem. 2, 92, 1888.

$$\frac{d \log K}{dT} = 0,$$

which indicates that K is independent of the temperature.

An equilibrium of this kind is therefore not displaced by elevation or depression of the temperature at constant volume. We therefore obtain the rule: *If a displacement of the equilibrium has no effect on the temperature, a change of temperature will not displace the equilibrium.*

As examples of equilibria which are unaffected by changes of temperature the following may be mentioned:

1. *The equilibrium of etherification.*

$$CH_3COOH + C_2H_5OH \rightleftarrows C_2H_3O_2C_2H_5 + H_2O.$$

The opposing changes are here accompanied by an insignificant evolution of heat,[1] and the equilibrium is found to be practically unaffected by a change of temperature. At 10° the limit of etherification is reached when 65.2 per cent has undergone change, at 220° the limit is found at 66.5 per cent.[2]

2. *Equilibrium between optical isomers.*[3]

The mutual transformation of optical isomers developes no heat, and it is found that the equilibrium between them is unaffected by the temperature; a mixture of them which is inactive at the ordinary temperature remains inactive when it is heated.

3. The following case is also of interest,

$$H_2O + CO \rightleftarrows H_2 + CO_2.$$

At moderate temperatures this change is accompanied by an evolution of heat, which diminishes as the temperature rises in consequence of the difference between the specific heats of the two systems; its value should be zero at 1700°.[4] Horstmann[5] has found that the equilibrium ceases to be displaced at a temperature which he estimates to be 2250°. The difference between 1700° and 2250° may well be due to the difficulty of determining such high temperatures.

---

[1] Bull. Soc. Chim. 31, 352, 1879.

[2] Berthelot, Essai de Mécanique Chimique, II, 73.

[3] Van 't Hoff, Die Lagerung der Atome im Raume, 1894, p. 33.

[4] Compt. Rend. 93, 104, 1881.

[5] Ueber Verbrennungserscheinungen bei Gasen. II. Verhandlungen des naturhistorischen med. Vereins zu Heidelberg.

b. *The value of q is $\gtrless$ zero.*

In this case K will vary with the temperature, and by means of the equation

$$\frac{d \log K}{dT} = \frac{q}{2T^2}$$

it will be possible to calculate the value of q from observations of the equilibrium, and to compare the value so obtained with that directly determined by experiment.

As an example of this we shall consider the equilibrium

$$N_2O_4 \rightleftarrows 2NO_2.$$

The quantities which occur in the equations

$$\frac{d \log K}{dT} = \frac{q}{2T^2} \text{ and } K = \frac{C_2^{n_2}}{C_1^{n_1}},$$

have the following signification in this special case: —

C_1 and C_2 are the concentrations of the first and second systems respectively, that is the quantities of N_2O_4 and $2NO_2$ per cubic metre, unit quantity being, in both cases, 92 kgrms; n_1 and n_2 are the numbers of molecules forming the first and second systems, in this case, their respective values are 1 and 2; q is the heat, in calories, which is evolved when 92 kgrms. of the second system are converted into the first at constant volume.

The dissociation of nitrogen peroxide has been studied by Deville and Troost,[1] whose observations will be used in order to calculate q. They determined the vapour density of nitrogen peroxide, at atmospheric pressure, at different temperatures.[2].

---

[1] Compt. Rend. 64, 237, 1867.

[2] See also A. J. Swart, Inaugural Dissertation, Amsterdam, 1890. Zeit. phys. Chem. 7, 120, 1891.

The fraction x of the peroxide which exists as $2NO_2$ is obtained from the expression

$$x = \frac{3.179}{D} - 1,$$

where 3.179 is the vapour density of N_2O_4 compared with air, and D is that of the dissociated mixture.

In order to calculate q, the equation

$$\frac{d \log K}{dT} = \frac{q}{2T^2}$$

must be integrated, whence we obtain

$$\log \frac{K_2}{K_1} = \frac{q}{2} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \ldots . \, (1)$$

K_1 and K_2 are here the equilibrium constants at the absolute temperatures T_1 and T_2.

Further since

$$K = \frac{C_2^2}{C_1}$$

we obtain

$$K_2 : K_1 \; \frac{x_2^2}{T_2\,(1 - x_2^2)} : \frac{x_1^2}{T_1\,(1 - x_1^2)},$$

where x_1 and x_2 are the fractions of the dissociated mixture existing in the form $2\ NO_2$ at the temperatures T_1 and T_2.

Substituting this value of the ratio $K_2 : K_1$ in equation (1), we obtain

$$\log \frac{x_2^2}{T_2\,(1 - x_2^2)} - \log \frac{x_1^2}{T_1\,(1 - x_1^2)} = \frac{q}{2} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

The following table contains the experimental data, and the results of the calculation.

T.	D.	x.	q.
273 + 26.7	2.65	0.1996	12900
273 + 111.3	1.65	0.9267	

On the other hand the value of q may be calculated approximately from the calorimetric researches of Berthelot and Ogier[1], who determined the specific heat of nitrogen peroxide at atmospheric pressure between 27° and 150°; in this interval 92 kgrms. of the gas absorb 12620 cals. This heat has served to produce three changes, corresponding to three quantities of heat a, b, and c.

1. The temperature has been raised from t_1 to t_2 at constant pressure. The quantity of heat required for this purpose (a) may be calculated from the heat capacity of nitrogen peroxide at higher temperatures, where the change of dissociation may be neglected, this is 16.86 cals. for 92 kgrms., so that

$$a = 16.86\ (t_2 - t_1).$$

2. A certain amount of external work is performed when N_2O_4 is converted into $2NO_2$ at constant pressure, for 92 kgrms, it is 2T cals., so that since the part of the gas existing as $2NO_2$ increases from x_1 at t_1 to x_2 at t_2 the heat equivalent to this work will be

$$b = 2\,T\ (x_2 - x_1).$$

3. A quantity of heat (c) is absorbed by the conversion of N_2O_4 into NO_2, for 92 kgrms. this is q cals., so that

$$c = q\ (x_2 - x_1).$$

The following table contains the results of the calculation.

---

[1] Bull. Soc. Chim. 37, 435, 1882.

REESE LIBRARY OF THE UNIVERSITY OF CALIFORNIA

t	a+b+c	a = $16.86(t_2-t_1)$	x = $\frac{3.179}{D}-1$	b = $2T(x_2-x_1)$	q = $\frac{c}{x_2-x_1}$
27°	12620	2074	0.2015	577	12500
150°			1		

The values of q obtained from the study of the equilibrium (12900), and calculated from the calorimetric determinations (12500) are, therefore, in very satisfactory agreement with each other.

II. EQUILIBRIUM IN HETEROGENEOUS SYSTEMS.

Heterogeneous equilibrium is characterised by the existence in presence of each other of gaseous or dissolved bodies and liquid or solid (undissolved) bodies. The following cases may serve as examples: —

$$NH_5S \rightleftarrows NH_3 + H_2S,$$

where the ammonia and sulphuretted hydrogen are in the gaesous, the ammonium sulphide in the solid condition;

$$C_2O_4Ca + HCl \rightleftarrows C_2O_4H_2 + CaCl_2,$$

where all the substances, except the calcium oxalate, are in the dissolved state.

An equilibrium of this kind may be regarded as a special case of homogeneous equilibrium, for it may be produced from the latter by diminishing the volume, or by removing solvent, until the maximum vapour pressure, or the maximum solubility, of one of the bodies taking part in the equilibrium has been attained, after which this body will undergo partial condensation or precipitation.

We must therefore assume that, in the examples chosen, a certain, perhaps very small, quantity of the NH_5S or CaC_2O_4 exists in the gaseous and dissolved conditions respectively, and that this gaseous or dissolved part is in equilibrium, on the one hand, with its products of decomposition, which likewise exist in the gaseous or dissolved state, on the other hand with the solid substances, so that the NH_5S or CaC_2O_4 existing as gas or in solution remain constantly in the condition of saturated vapour, or of saturated solution, at the given temperature.

The equilibrium which exists here between the condensed, or precipitated and the gaseous, or dissolved parts of the same substance belongs to the class of physical equilibria.

The law by which this latter class of equilibria is governed requires that the concentration of the gaseous or dissolved part, which is proportional to the vapour pressure or solubility of the substance, shall depend only on the temperature and not on the volume of the system.

It has already been pointed out on page 150 that the formulae

$$K = \frac{C_2^{n_2}}{C_1^{n_1}}, \text{ and } \frac{d \log K}{dT} = \frac{q}{2T^2}$$

hold good in the case of heterogeneous equilibrium, n_1 and n_2 referring, however, only to those substances which exist in the gaseous or dissolved condition.

We must, therefore, conclude that a heterogenous equilibrium *is not displaced by a change of temperature when* $q = 0$; and that the value of q may be calculated, in the same way as formerly, from determinations of the equilibrium, and compared with the value obtained from calorimetric determinations.

Cases investigated.

As an example of a calculation of this kind, we will take the dissociation of ammonium sulphide,

$$NH_5S \rightleftarrows NH_3 + H_2S,$$

which was investigated by Isambert.[1]

The value of q will first be calculated by means of the equation

$$\log \frac{K_2}{K_1} = \frac{q}{2}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

---

[1] Compt. Rend. 92, 919, 1881.

For this purpose, we put

$$n_1 = 0, \text{ and } n_2 = 2,$$

and, therefore, $K = C_2^2$.

We have, further, the following connexion between the maximum vapour pressure p of the mixture of ammonia and sulphuretted hydrogen, which was determined experimentally by Isambert, and its concentration C_2: —

$$(C_2)_1 : (C_2)_2 = \frac{p_1}{T_1} : \frac{p_2}{T_2}$$

where $(C_2)_1$ and $(C_2)_2$ are the concentrations at the absolute temperatures T_1 and T_2, and p_1 and p_2 are the corresponding pressures.

Substituting this for $\log \frac{K_2}{K_1}$, we obtain

$$\log \frac{p_2}{T_2} - \log \frac{p_1}{T_1} = \frac{q}{4}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

from which q may be calculated.

The experimental data are the following: —

T.	p.	q (calculated.)
273 + 9.5	175 mm.	21550
273 + 25.1	501 mm.	

Again, the heat evolved by the formation of 51 kgrms. of NH_5S at constant volume, according to the equation $NH_3 + H_2S = NH_5S$, which we have called q, may be obtained from thermochemical data.

Calculated from the numbers given by different observers, the amount of heat evolved by the change, under constant pressure, varies from 22620 to 22990 cals[1]. Subtracting from this the quantity of heat which is equivalent to the external work performed during the change, viz. 4 T = 1160 cals, we obtain q = 21460 to 21830 cals.

[1] Berichte, 14, 1243, 1881.

The value calculated (21550) is, therefore, in good agreement with that found by direct experiment (21460—21830).

b. The dissociation of salts containing water of crystallisation, which has been studied by Frowein[1] and others with special reference to the thermodynamical equation, may suitably be considered here.

Taking, for example, the equilibrium

$$CuSO_4 . 5H_2O \rightleftarrows CuSO_4 . 4H_2O + H_2O,$$

we may apply the equations

$$K = \frac{C_2^{n_2}}{C_1^{n_1}}, \text{ and } \frac{d \log K}{dT} = \frac{q}{2\,T^2},$$

when n_1 and n_2 refer only to the uncondensed substances, in this case, therefore, to the aqueous vapour, so that $n_1 = 0$, $n_2 = 1$, and, therefore, $K = C_2$.

That is, K is equal to the concentration of the aqueous vapour which is in equilibrium with the salt. Call this concentration C_S.

q is here the quantity of heat which is evolved when 18 kgrms. of aqueous vapour combine with the salt $CuSO_4 . 4H_2O$ to form $CuSO_4 . 5H_2O$; calling this q_S, our equation becomes

$$\frac{d \log C_S}{dT} = \frac{q_S}{2\,T^2} \quad . \quad . \quad . \quad . \quad (1)$$

This expression may, however, be transformed so that q_S is replaced by the quantity of heat determined calorimetrically, that is, the quantity of heat which is evolved by the combination of 18 kgrms. of *liquid* water with the dehydrated salt.

Since the general equation, $\frac{d \log K}{dT} = \frac{q}{2T^2}$, applies to physical as well as to chemical equilibrium[2], we may write

$$\frac{d \log C_W}{dT} = \frac{q_W}{2\,T^2}, \quad . \quad . \quad . \quad . \quad (2)$$

---

[1] Zeit. phys. Chem. 1, 1, 1887.

[2] See page 205.

where C_W is the concentration of saturated steam, and q_W the heat which is evolved by the condensation of 18 kgrms. of saturated steam at the temperature T.

The quantity of heat which is determined calorimetrically, q_K, is the difference between q_S and q_W.

By subtracting equation (2) from (1), we obtain

$$\frac{d \log \frac{C_S}{C_W}}{dT} = \frac{q_S - q_W}{2T^2} = \frac{q_K}{2T^2}.$$

$\frac{C_S}{C_W}$ is the ratio between the dissociation pressure of the salt and the vapour pressure of water, both at T. Calling this F, we obtain

$$\frac{d \log F}{dT} = \frac{q_K}{2\,T^2},$$

where q_K is the heat evolved by the combination of 18 kgrms. of liquid water with the partially dehydrated salt.

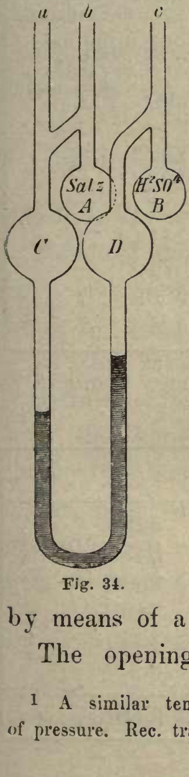


Fig. 34.

Assuming that q_K is constant for small intervals of temperature, we obtain by integration of the above equation

$$q_K = \frac{2T_1T_2}{T_1 - T_2} \log \frac{F_1}{F_2},$$

from which q_K may be calculated when F_1 and F_2 are known at the temperatures T_1 and T_2.

The apparatus, a tensimeter, which was employed in determining the vapour pressures of salts containing water of crystallisation is shown in fig. 34.

Two bulbs, A and B,[1] contain the finely powdered and dry salt, and strong sulphuric acid respectively; they are connected together by means of a U-tube half filled with olive oil.

The openings at *a* and *b* having been closed before the blowpipe, the apparatus is placed in a horizontal position, the oil collecting in the bulbs C and D, connected to the air-pump at *c*, and evacuated, the last trace of air being removed by warming the whole apparatus with the flame of a spirit-lamp; it is finally sealed at *c*. The apparatus having been left to itself for 24 hours in a vertical position, in order that the water of crystallisation may be equally distributed throughout the salt, the measurements of pressure are begun. These are made by means of a cathetometer, the tensimeter being immersed in a HERWIG'S water bath the temperature of which is maintained constant by continual stirring. Two separate tensimeters were used simultaneously in each experiment. After the completion of the observations, the bulbs containing the salt were detached and the water of crystallisation determined.

---

[1] A similar tensimeter was used by BREMER for the determination of differences of pressure. Rec. trav. chim. des Pays-Bas, 6, 121, 1887.

The following table contains the results of the experiments with copper sulphate.

Temperature.	Maximum pressure of the aqueous vapour over the crystals in mm. of Hg.	Ratio of the maximum pressures of aqueous vapour over crystals and water. F.
13°.95	2.993	0.2522
20 .46	5.056	0.2828
26 .30	8.074	0.3174
30 .20	10.897	0.3414
34 .75	15.307	0.3710
39 .55	21.452	0.3999
39 .70	21.726	0.4019

The heat of combination q_K calculated from these numbers is given in the next table.

Temperatures.	q_K
13°.95—26°.30	3220
20 .46—26 .30	3475
26 .30—30 .20	3390
26 .30—34 .75	3400
26 .30—39 .55	3250
26 .30—39 .70	3300
Mean	3340

Thomsen's[1] direct determination gives $q_K = 3410$ cals. The agreement is thus satisfactory.

The whole of Frowein's results are given in the following table, from which it may be seen that there is a good agreement between the values of q_K obtained directly and indirectly.

Salt examined.	q_K.	
	Determined by the calorimeter.	Calculated from the vapour pressures.
$CuSO_4 . 5H_2O$	3410	3340
$BaCl_2 . 2H_2O$	3830	3815
$MgSO_4 . 7H_2O$	3700	3990
$ZnSO_4 . 7H_2O$	3417	3440
$ZnSO_4 . 6H_2O$	2178	2280
$Na_2HPO_4 . 12H_2O$	2244[2]	2242

c. The decomposition of copper bi-potassium chloride, which takes place at 92° according to the equation

$$CuCl_2 . 2\,KCl . 2\,H_2O \rightleftarrows CuCl_2 . KCl + KCl + 2\,H_2O,$$

has been investigated by J. G. C. Vriens.[3]

The heat evolved by the combination of the water of crystallisation may be calculated, as before, from the pressure of dissociation by means of the formula on page 159, and, inversely, when the value of the dissociation pressure is known at one temperature its value at other temperatures may be calculated from the known value of q_K, and compared with the numbers obtained by experiment.

The heat of combination for 18 kgrms. of the water of crystallisation contained in the salt $CuCl_2\ 2KCl\ 2H_2O$ was determined, by means of the calorimeter, as the difference between the heats of solution of $CuCl_2$ KCl + KCl and $CuCl_2$ 2KCl $2H_2O$; the mean of two experiments gave 3063 calories.

---

[1] Thermochemische Untersuchungen III, p. 141.

[2] This number is given by Thomsen, Thermochem. Unters. III, while Pfaundler, Berichte, 4, 773, 1871, gives 2234.

[3] Inaugural Dissertation. Amsterdam, 1890; Zeit. phys. Chem. 7, 194, 1891.

The apparatus used in measuring the pressures was the same in principle as that employed by Frowein but somewhat different in detail.

The pressure of the aqueous vapour evolved by a mixture of $CuCl_2$ 2KCl. $2H_2O$, $CuCl_2$ KCl, and KCl was: —

Temperature.	Pressure found.	Pressure calculated.
42°.3	18.9 mm.	18 mm.
46 .6	24 ,,	24 ,,
51 .5	30.9 ,,	33 ,,
56 .1	42 ,,	44.1 ,,
59 .1	50.7 ,,	53 ,,
64 .5	73.2 ,,	73.4 ,,
74 6	131 ,,	129.5 ,,
89 .2	278.5 ,,	277.6 ,,
91 .1	308 ,,	305.1 ,,
92	319 ,,	318.9 ,,
92 .6	327 ,,	328.4 ,,

The numbers in the column headed "calculated" are the pressures, in mm. of mercury, which have been calculated by means of the equation given on page 159, q_K being taken as 3063 cals., and the pressure observed at 46°.6 being used as starting point.

The agreement between the values calculated and observed[1] shows that the loss of water of crystallisation is really accompanied by a decomposition of the double salt, this being the assumption made in determining q_K.

d. The decomposition of Rochelle salt into its components, which occurs at temperatures higher than 55° according to the equation

---

[1] With respect to the deviations which occur it is to be remembered that the pressures are determined at temperatures ranging from 40° to 100°, while q_K is determined at 16°, and doubtless is only to be regarded as independent of the temperature over a very small range.

$$2(C_4H_4O_6\ NaK.\ 4H_2O) \rightleftarrows C_4H_4O_6K_2.\ \tfrac{1}{2}\ H_2O + C_4H_4O_6Na_2.\ 2H_2O + 5^1/_2\ H_2O,$$

has been studied by J. Docters van Leeuwen.[1]

At temperatures lower than 55° the double salt is reformed from its components.

Here, again, q_K may be calculated from the dissociation pressure of the crystals.

The pressures were determined by means of a tensimeter (fig. 36) containing finely powdered and partially dehydrated Rochelle salt in the bulb *d*, and concentrated sulphuric acid in the bulb *e*.

Temperature.	Dissociation pressure.
18°.8	6.20 mm.
20 .95	7.18
25 .70	10.25
31 .05	14.33

From these figures q_K is calculated as follows: —

Temperatures.	q_K
20°.95—25.70	2530
25 .70—31.05	2505
18 .80—31.05	2247

while Berthelot[2] found $q_K = 2370$ cals.

III. CONDENSED SYSTEMS.

A simple example of the class of phenomena referred to in this section will first be given.

---

[1] The experimental data, which will shortly be published, have been kindly placed at my disposal by the author. (Cohen).

[2] Essai de mécanique chimique. I. 539.

In the course of an investigation on ammonium nitrate LEHMANN[1] made the following observations: —

"When fused ammonium nitrate is allowed to solidify, skeleton crystals belonging to the regular system are formed. The behaviour of these crystals in polarised light shows them to be completely isotropic. On further cooling a sudden change occurs at about 127°, the crystals becoming doubly-refractive. On still further cooling needle shaped rhombic crystals are formed at about 87°, these can also be obtained from a hot alcoholic solution. These crystals generally change while still in contact with the solution, and invariably on removing them from it, into a fourth modification which also belongs to the rhombic system and which may be obtained in fairly good crystals from aqueous solutions at the ordinary temperature. On heating this fourth modification gradually, it passes through all the changes described, but in inverse order, at about 36° the other rhombic modification is formed, at about 87° the rhombohedric, and at 120 the regular".

We are therefore dealing here, not with an equilibrium such as is found in homogeneous and in heterogeneous systems which is continuously displaced by a continuous change of temperature, but rather with *per saltum* displacements of the equilibrium at 36°, 87°, and 120°.

At the latter temperature an equilibrium exists which may be represented thus,

$$NH_4NO_3 \text{ rhombohedric} \rightleftarrows NH_4NO_3 \text{ regular.}$$

The characteristic part of the phenomenon is that, on cooling the system below 120° the equilibrium is displaced totally towards the left-hand side of the equation, on raising the temperature above 120° it is displaced completely towards the right. A temperature possessing properties of this kind will be called a *transition point*,[2] for the system concerned.

The kind of equilibrium just described may be expected to occur when none of the substances are in the gaseous or liquid condition; viz. in so called condensed systems.

---

[1] GROTH's Zeitschrift für Krystallographie, 1, 106, 1877.

[1] When the expression "transition point", or "transition temperature" is used, the transition temperature under the pressure of one atmosphere is always meant. The influence of pressure is considered later.

The necessity of the existence of a point of transition in such cases may be proved, quite generally, from the known laws of equilibrium.[1]

Consider an equilibrium between dissolved substances, for example two salts which have undergone a partial double decomposition, then in order to find what the condition of equilibrium will be in the absence of the solvent we may remove it gradually, at constant temperature, by evaporation.

During the evaporation all the dissolved substances will separate out except one, in the special case considered three of the salts separate; the remaining substance (the fourth salt) cannot separate out owing to the laws governing solubility and chemical equilibrium. The laws of solubility require that each substance which separates out shall have a certain concentration in the solution corresponding to saturation, while those of chemical equilibrium require that these shall be a certain definite relationship between the concentrations of all the dissolved bodies.

Owing to these two conditions the concentration of the last substance is, after all the others have partially separated out, definitely fixed; further evaporation cannot increase it, and it must, therefore, remain equally far removed from the concentration corresponding to saturation even when the solution is evaporated to dryness. This last substance can thus never separate in the solid state.

From this it follows, that in case the substances are present in equivalent quantities, the whole system to which the last body belongs must be absent in the condensed condition, while if equivalent quantities are not used, only the excess of the substances belonging to this system can separate out. Both systems, therefore, cannot exist together in the solid condition. This may be called *the law of the incompatibility of condensed systems.*

The coexistence of both systems in the condensed condition is, however, possible under certain exceptional circumstances.

Consider again the condition of affairs described above; by evaporating a solution containing a number of substances in chemical equilibrium with each other all of them had been caused to separate out partially, except one, the concentration of which remains constant, and less than the concentration corresponding to saturation, so long as the temperature does not change.

---

[1] Van 't Hoff and van Deventer, Zeit. phys. Chem. I 164, 1887.

Since the concentration of a saturated solution generally changes with the temperature, and since this is also the case with the condition of equilibrium of substances in solution, it will be possible, by raising or lowering the temperature, to cause the concentration of the substance which has not separated out to approach the saturation point, and it is, therefore, conceivable that there is a temperature at which this will be reached. At this temperature, and at it only, is the separation of all the substances, and, therefore, the coexistence of both systems in the condensed condition, possible. It must now be shown that above and below the temperature at which the two systems can coexist either the one or the other of them is in stable equilibrium, and that the name "transition temperature" is therefore justified.

In order to do this we may write the equation for a chemical equilibrium in the form

$$\frac{F\ (C_2 \ldots\ldots)}{F\ (C_1 \ldots\ldots)} = K \ldots\ldots (1)$$

where $F\ (C_2 \ldots)$ is the product of certain powers of the concentrations of the constituents of the second system, and $F\ (C_1 \ldots)$ is the same for the first system.

Calling c_2 and c_1 the concentrations corresponding to saturation, and substituting them in the above equation, we obtain a value of K which we may call M.

$$\frac{F\ (c_2 \ldots\ldots)}{F\ (c_1 \ldots\ldots)} = M \ldots\ldots (2)$$

In general K and M will vary in different ways with the temperature, and may therefore be represented by curves which will cut each other at some temperature T; at this point K and M are equal to each other, at temperature above or below it they differ. The temperature T is thus the temperature at which equation (1) is satisfied when the solution is just saturated for all the substances which are in equilibrium, at this temperature all the substances will separate out of the solution on evaporation, and consequently the two systems can coexist.

When we have $K > M$, the second system only can separate out; for $K < M$, the first only A partial separation of all the substances except one having occurred, we may replace the values of $C_2 \ldots$, and $C_1 \ldots$, in equation (1), all except one, by $c_2 \ldots$, and $c_1 \ldots$; for $K > M$ this unreplaced concentration, which must be smaller than the concentration corresponding to saturation, must occur in the denominator, that is the first system cannot separate out; for $K < M$ the second system must be absent in the solid condition for similar reasons. There is thus, as the name "transition temperature" clearly indicates, a complete transformation of the one system into the other on passing through this point.

Cases investigated.

The examples of the phenomenon which have been investigated may be grouped under the following headings: —

a. The transition temperature of polymorphous bodies.

b. The transition temperature of salts containing water of crystallisation.

c. The transition temperature in the case of the formation and decomposition of double salts.

d. The transition temperature in the case of double decomposition.

e. The transition temperature of isomeric bodies.

The very close relationship which exists between these phenomena and that of ordinary fusion, or solidification, may be pointed out here.[1]

a. *The transition temperature of polymorphous bodies.*[2]

An exceedingly simple case of this kind has been investigated by Reicher[1] by a method which will be described later. The equilibrium referred to is that between rhombic and monosymmetric sulphur. The transition temperature was found to be 95°.4, that is, under atmospheric pressure rhombic and monosymmetric sulphur can exist side by side at 95°.4, while above this temperature only the monosymmetric modification is in stable equilibrium, and below it only the rhombic modification; on passing through the point of transition a complete transformation of the one into the other occurs.

---

[1] It is considered in more detail later

[2] The literature of the subject is given pretty fully by W. SCHWARZ, Beiträge zur Kenntniss der umkehrbaren Umwandlungen polymorpher Körper, Göttingen 1892. See also SILVIO LUSSANA, Nuovo Cimento, (4), vol 1, 97, 1895.

Lehmann's observations on the changes of the different crystalline modifications of ammonium nitrate into each other have already been mentioned.

b. *The transition temperature of salts containing water of crystallisation.*

The apparent melting of salts containing water of crystallisation is often due to a chemical change which occurs above a certain temperature and which is reversed at lower temperatures, as is shown by the fact that a salt containing less water than the original substance oftenseparates out during the fusion.

Phenomena of this kind are observed not only in the case of salts containing water of crystallisation, but also with many other hydrates, such as those of carbon bisulphide[2], phosphorus hydride[3], sulphuretted and seleniuretted hydrogen, methyl chloride[4], chloroform[5], sulphur dioxide, bromine, chlorine, and hydrobromic acid[6].

It is well known that Glauber's salt "melts" at a definite temperature in its own water of crystallisation (Loewel[7], Mulder[8]); the apparent melting-point is however nothing but the transition point in the equilibrium

---

[1] Groth's Zeitschrift für Krystallographie 8, 593, 1884. Inaugural Dissertation, Amsterdam, 1883.

[2] Duclaux, Compt. Rend. 64, 1099, 1867.

[3] Cailletet and Bordet, Compt. Rend. 95, 58, 1882.

[4] De Forcrand, Compt. Rend. 94, 967, 1882.

[5] Chancel and Parmentier, Compt. Rend. 100, 27, 1885.

[6] Bakhuis Roozeboom, Rec. des Trav. Chim. des Pays-Bas, 3 and 4, 1885-86.

[7] Ann. Chim. Phys. (3), 29, 62, 1850; (3), 37. 157, 1853; (3), 49, 32, 1857.

[8] Geschiedenis van het scheikundig gebonden water. Rotterdam, 1864.

$$Na_2SO_4.\ 10H_2O \rightleftarrows Na_2SO_4 + 10H_2O,$$

which van 't Hoff and van Deventer, Cohen and Bredig, and Verschaffelt have found, by different methods, to be about 33°.

Similar changes have been investigated in the cases of $CdCl_2.2H_2O$ [1], which loses a molecule of water of crystallisation at about 34°, of $ZnSO_4.7H_2O$ [2], where the same thing occurs at about 40°, and of $Na_2HPO_4.12H_2O$, [3] which is converted into the salt containing seven molecules of water of crystallisation at about 37°.

c. *The transition temperature in the formation and decomposition of double salts.*

A few characteristic cases will be fully described.

1. The formation of astrakanite.

The equilibrium is represented by the following equation.

$$Na_2SO_4.10H_2O + MgSO_4.7H_2O \rightleftarrows Na_2Mg(SO_4)_2.4H_2O + 13H_2O,$$

and the transition temperature is about 21°.5. [4] The double salt is known mineralogically as astrakanite, simonyite, or bloedite.

If finely powdered astrakanite be mixed with water in the proportion represented by the above equation, at temperatures below 21°.5, the thin paste which is at first formed solidifies after a short time to a dry, solid mixture of the sulphates of sodium and magnesium; at temperatures higher than 21°.5 this does not take place. A finely powdered mixture of the hydrated sulphates of sodium and magnesium remains completely unchanged at temperatures below 21°.5, if it be preserved in closed flasks in order to prevent loss of water; on warming the mixture, however, above 21°.5 astrakanite is formed sooner or later, partial fusion being apparently produced by the water liberated.

---

[1] E. Cohen and D. M. Kooij, Zeit. phys. Chem. 14, 71, 1894.

[2] E. Wiedemann, Wied. Ann. 17, 561, 1882, investigated several sulphates. Cf. E. Cohen loc. cit.

[3] A. E. Baur, Zeit. phys. Chem. 18, 180, 1895. See p. 203.

[4] Van 't Hoff and van Deventer, Zeit. phys. Chem. 1, 170, 1887.

The last-mentioned change is accelerated, and takes place more readily, if astrakanite be added to begin with, but even without this it occurs after some time.

2. The formation of sodium ammonium, and of sodium potassium racemate.

In the case of astrakanite we were dealing with the combination of two sulphates to form a double salt, while here we have to do with the combination of sodium ammonium dextro- and lævo-tartrates, $NaNH_4C_4H_4O_6.4H_2O$, to form the racemate $(NaNH_4C_4H_4O_6.H_2O)_2$, which was first prepared by Scacchi.[1]

$$2(NaNH_4C_4H_4O_6.4H_2O) \rightleftarrows (NaNH_4C_4H_4O_6.H_2O)_2 + 6H_2O.$$

The transition temperature is about 27°, according to van 't Hoff and van Deventer,[2] who found that if finely powdered sodium ammonium racemate be mixed with water in the proportion given in the above equation, at temperatures below 27°, the thin paste which is at first obtained solidifies after some time to a completely dry, solid mixture of the two tartrates, and that at temperatures above 27° this does not occur.

Further, the finely powdered mixture of equal quantities of the two tartrates may be preserved without change in closed vessels at temperatures below 27°, whereas on warming it above 27° the formation of racemate occurs after a more or less prolonged period, the water set free giving rise to partial liquefaction.

The formation of potassium sodium racemate, a salt which was first prepared by Wyrouboff,[3] has been investigated by van 't Hoff and Goldschmidt,[4] who found it to be completely analogous to that of the sodium ammonium salt. The transition temperature in the equilibrium

---

[1] Rendi conti di Napoli, 1865, p. 250. See also van 't Hoff, Die Lagerung der atome im Raume, zweite Aufl. 1894, p. 34.

[2] Zeit. phys Chem. 1, 170, 1887. See also Zeit. phys. Chem. 17, 47, 1895.

[3] Ann. Chim. Phys. (6) 9, 224, 1886.

[4] Zeit. phys. Chem. 17, 505, 1895.

$$2\,(C_4H_6O_6\,K\,Na.\,4H_2O) \rightleftarrows (C_4H_4O_6\,K\,Na.\,3H_2O)_2 + 2\,H_2O,$$

is about —6°.

3. The decomposition of sodium ammonium, and of sodium potassium racemate.

Sodium ammonium racemate, which is formed from the dextro- and lævo-tartrates at 27°, decomposes again according to VAN 'T HOFF, GOLDSCHMIDT, and JORISSEN[1] at 35° into sodium and ammonium racemates.

$$2\,(Na\,NH_4\,C_4H_4O_6.\,H_2O)_2 \rightleftarrows (Na_2\,C_4H_4O_6)_2 + [(NH_4)_2\,C_4H_4O_6]_2 + 4H_2O.$$

The change in the case of potassium sodium racemate is, according to VAN 'T HOFF and GOLDSCHMIDT[2], quite similar.

$$2\,(K\,Na\,C_4H_4O_6.\,3\,H_2O)_2 \rightleftarrows (Na_2\,C_4H_4O_6)_2 + (K_2\,C_4H_4O_6\,2\,H_2O)_2 + 8\,H_2O.$$

The transition temperature is about 41°.

A similar change occurs in the case of a mixture of sodium ammonium lævo- and dextro-tartrates which changes into a mixture of sodium and ammonium racemates at 30°, and also in the case of the analogous mixture of the potassium sodium salts, with which the change occurs at 33°.

$$4(NaNH_4\,C_4H_4O_6.\,4H_2O) \rightleftarrows (Na_2C_4H_4O_6)_2 + [(NH_4)_2\,C_4H_4O_6)]_2 + 16H_2O.$$

$$4(K\,Na\,C_4H_4O_6.\,4H_2O) \rightleftarrows (K_2\,C_4H_4O_6.\,2H_2O)_2 + (Na_2\,C_4H_4O_6)_2 + 12H_2O.$$

4. The decomposition of copper calcium acetate.

It has been observed by H. KOPP that from solutions containing the acetates of copper and calcium in equal molecular quantities the salts sometimes crystallise out separately, sometimes in the form of the double salt; he thought it probable that the temperature might be the determining factor.

REICHER[3] showed that this is the case, an equilibrium ocurring which may be represented as follows,[4]

---

[1] Zeit. phys. Chem. 17, 47, 1895.

[2] Zeit. phys. Chem. 17, 505, 1895.

[3] Zeit. phys. Chem. 1, 221, 1887.

[4] The composition of copper calcium acetate is often erroneously given as $CuCa(C_2H_3O_2)_4.8H_2O$ on the authority of ETTLING (LIEB. Ann. 1, 286. 1832). It has been more fully investigated by RÜDORFF (Berichte, 21, 279, 1888) who found that the formula is $CuCa(C_2H_3O_2)_4.6H_2O$.

$$Cu\,Ca\,(C_2H_3O_2)_4.\ 6\ H_2O \rightleftarrows Cu\,(C_2H_3O_2)_2.\ H_2O + Ca\,(C_2H_3O_2)_2.\ H_2O + 4\ H_2O,$$

the transition point lying between 76°.2 and 78°.

The formation of astrakanite and of the double racemates, which we have already considered, occurs on raising the temperature, while in this case the double salt is the stable system at temperatures lower than about 77°, while above this temperature decomposition into its components takes place. The transition from one system to the other is accompanied by a change of colour from blue to green which is due to the facts that the tetragonal double salt is blue, while the monosymmetric copper acetate is green, and the small needle-shaped crystals of calcium acetate are colourless.

5. The decomposition of copper bi-potassium choride and of schönite.

The first-named salt was studied by W. Meyerhoffer[1] and J. Vriens[2] by different methods. It was found that the salt, $CuCl_2.\ 2KCl.\ 2H_2O$, which crystallises in blue tabular crystals, decomposes into copper potassium chloride, $CuCl_2.\ KCl$, potassium chloride, and water at about 92°, while below that temperature it is formed from its constituents.

$$CuCl_2.\ 2KCl.\ 2H_2O \rightleftarrows CuCl_2.\ KCl + KCl + 2H_2O.$$

This case is quite analogous to that of copper calcium acetate. If a molecule of copper chloride, $CuCl_2\ 2H_2O$, be added to the double salt to begin with, the transition temperature is depressed[3] to about 56°, which is to be regarded as the transition temperature in the equilibrium

$$CuCl_2.\ 2\ KCl.\ 2\ H_2O + CuCl_2.\ 2\ H_2O \rightleftarrows 2\ CuCl_2.\ KCl + 4\ H_2O.$$

The researches of J. van der Heide[4] show that the double salts which may be formed from K_2SO_4 and $MgSO_4$, i. e. schoenite,

---

[1] Zeit. phys. Chem. 3, 336, 1889; 5, 97, 1890.

[2] Zeit. phys. Chem. 7, 194, 1891; Inaugural Dissertation, Amsterdam, 1890.

[3] This depression of the transition temperature is quite analogous to the depression of the freezing-point of a solvent by the addition of a foreign substance.

[4] Inaugural Dissertation, Amsterdam, 1893. Zeit. phys. Chem. 12, 416, 1893.

$K_2Mg(SO_4)_2.6H_2O$, and potassium astrakanite, $K_2Mg(SO_4)_2.4H_2O$, undergo decompositions which are quite analogous to that which has just been considered.

d. The transition temperature in cases of double decomposition.

Schiff[1] observed that on grinding together potassium chloride and Glauber's salt, the mixture liquefied, which he supposed to be due to a double decomposition accompanied by the formation of water. Van 't Hoff and Reicher[2] subsequently showed that this supposition is correct, and that the double decomposition which occurs is represented by the equation

$$Na_2SO_4.10H_2O + 2KCl \rightleftarrows K_2SO_4 + 2NaCl + 10H_2O,$$

the transition temperature being 3°.7.

If the potassium chloride be replaced by ammonium chloride an analogous double decomposition occurs, the transition temperature of which is 10°.8.

e. *The transition temperature of isomeric compounds.*

According to Troost and Hautefeuille[3] the vapour of cyanic acid condenses in the form of cyanuric acid or of cyamelide according as the temperature at which the condensation occurs is above or below 150°. Weltzien[4] succeeded in converting cyamelide into cyanuric acid by heating it with concentrated sulphuric acid until decomposition began; after some days crystals of cyanuric acid separated out. From these facts it would appear that a point of transition exists for the change

$$\text{cyamelide} \rightleftarrows \text{cyanuric acid}.$$

These observations have been confirmed by van Deventer[5], who found that the vapour of cyanic acid when maintained at a temperature of 125° for six hours, under a pressure of two atmospheres, condensed in the form of a finely divided film, which was insoluble in water and under the microscope appeared to be mainly amorphous, isolated crystalline fragments being visible in several places. When the condensation is allowed to take place at 175°, the product is completely soluble in water and consists of well formed doubly-refracting crystals.

---

[1] Lieb. Ann. 114, 68, 1860.

[2] Zeit. phys. Chem. 3, 482, 1889.

[3] Compt. Rend. 67, 1345, 1868.

[4] Lieb. Ann. 132, 222, 1864.

[5] By experiments which have not yet been published, kindly placed at my disposal by the author. (E. Cohen.)

In order to convert cyamelide into cyanuric acid directly, van Deventer heated small tubes containing cyamelide, subsequently determining the quantity of cyanuric acid contained in the mixture produced. The determinations were made by titration with baryta solution, it having been found that phenol phthaleïn is reddened when sufficient baryta has been added to convert the cyanuric acid into the di-hydrogen salt. It was found in this way that the change of cyamelide into cyanuric acid occurs at temperatures higher than 135° (uncorr.), and that it is considerably facilitated by the addition of ready formed cyanuric acid. No increase in the quantity of cyanuric acid could be detected after heating to 135° for 40 hours.

The reversal of the change at temperatures below 135° could not be produced; perhaps a better result might be obtained by the use of a solvent.[1]

3. Solubility and vapour pressure at the transition temperature.

The transition temperature has been defined as the temperature at which all the substances belonging to two systems in equilibrium can separate out of a solution containing them when it is evaporated, so that at this temperature a solution may exist which is saturated for both systems. The curves of solubility of the two systems therefore intersect at the transition point; at temperatures above or below it, only the first or the second system can separate out in the solid state, because, as has already been proved, a solution which is saturated for one system is unsaturated for the constituents of the other.

---

[1] Compare page 87.

REESE LIBRARY OF THE UNIVERSITY OF CALIFORNIA

Although, at any given temperature, only one of the systems is in a condition of stable equilibrium, the change of the unstable (or meta-stable) system into the stable condition may fail to take place, especially in the absence of the stable system. It is, therefore, generally possible to prepare two different solutions saturated at the same temperature, by bringing together one or other system with the same solvent. These solutions will possess different concentrations, the solution of the system which is stable at the temperature in question being the more dilute, while that of the meta-stable system possesses the characteristics of a supersaturated solution, allowing salt to crystallise out when placed in contact with the constituents of the stable system.

The existence of these supersaturated solutions, which do not deposit the dissolved material spontaneously but only when placed in contact with the substances for which they are supersaturated, is very intimately connected with the existence of a transition point; the two phenomena constantly accompany each other, every transition temperature giving rise to two series of solutions supersaturated with respect to the one system, or the other, according to whether the temperature is above or below the transition point.

It was observed by Loewel[1] that two distinct saturated solutions of sodium sulphate may be obtained by mixing water with pure Glauber's salt, or with the pure anhydride. The quantities of Na_2SO_4 contained in these solutions is given in the following table together with the temperatures at which they are saturated.

Temp.	Saturated for $Na_2SO_4 . 10\, H_2O$.	Saturated for Na_2SO_4.
31°.84	40	50.37
32 .73	50.76	49.71

The above mentioned point of intersection of the curves of solubility therefore exists here at 32°.65, and thus coincides with the so-called melting point (the transition temperature). There are also two different supersaturated solutions, viz., above 32°.65, the saturated solution of Glauber's salt supersaturated with respect to the anhydride, below 32°.65, the saturated solution of the anhydride supersaturated with respect to Glauber's salt; at 32°.65, the solution is saturated for both salts.

---

[1] Ann. Chim. Phys. (3), 29, 62, 1850; (3), 37, 157, 1853; (3), 49, 32, 1857.

Similarly, the following numbers were obtained with astrakanite[1], the numbers giving the percentages of salt in the solution.

Temp.	Astrakanite.			Mixed sulphates.		
	$MgSO_4$.	Na_2SO_4.	Total.	$MgSO_4$.	Na_2SO_4.	Total.
15°.5	20.9	10.2	31.1	17.8	9.7	27.5
24°.5	15	16.4	31.4	19.7	17.1	36.8

Below 21°.5, where the mixed sulphates form the stable system, the solution of them is less concentrated than that of the astrakanite, above 21°.5, the reverse is the case; in other words, below 21°.5 we have a solution of astrakanite supersaturated with respect to the mixed sulphates, above 21°.5 a solution of the mixed sulphates supersaturated with respect to astrakanite.

It is further possible to obtain a relation between the transition temperature and the solubilities of the different salts which take part in the equilibrium.

Taking, for example, the simple case of two salts each consisting of two ions, say the chlorides and bromides of two metals M and m, we will calculate the temperature at which the four salts MCl, MBr, mCl, and mBr are in equilibrium with each other and with their saturated solution.

We shall suppose the salts to be sparingly soluble, so that their saturated solutions are very dilute, and the dissolved salts, therefore, almost entirely dissociated into their ions. The concentrations of each of the ions may then be regarded as the same as those of the salts themselves in their saturated solutions, call the latter C_{MCl}, C_{MBr}, etc.

---

[1] See also BAKHUIS ROOZEBOOM, Rec. des Trav. Chim. des Pays-Bas, 6, 342, 1887; Zeit. phys. Chem. 2, 518, 1888.

In the equilibrium between a salt and its saturated solution the product of the concentrations of the ions is a constant quantity, at constant temperature, so that we obtain,

$$C^2_{MCl} = k_1$$
$$C^2_{MBr} = k_2 \text{ etc.}$$

Again, calling the concentrations of the ions in the solution which is saturated with respect to all the four salts simultaneously C_{Cl}, C_{Br}, etc., we obtain

$$C_M . C_{Cl} = k_1,$$
$$C_M . C_{Br} = k_2, \text{ etc.}$$

and therefore,

$$C_M . C_{Cl} = C^2_{MCl} \qquad C_m . C_{Cl} = C^2_{mCl}$$
$$C_M . C_{Br} = C^2_{MBr} \qquad C_m . C_{Br} = C^2_{mBr}.$$

From which

$$C_{MCl} . C_{mBr} = C_{MBr} . C_{mCl},$$

that is, *the products of the solubilities of the bodies belonging to the opposing systems are equal at the transition point.*

It is also easy to see that above and below this temperature the product of the solubilities of the stable pair of salts is smaller than that of the meta-stable pair.

When the salts dissociate into more than two ions, the above concentrations must be raised to a power equal to the number of ions; if the dissociation into ions be incomplete, each concentration must further be multiplied by the activity coefficient.

At greater concentrations deviations from the rule which has just been established will occur; this detracts, however, but little from its practical utility, since it is still able to give valuable information as to the probable existence, and approximate position of a transition point, which may then be sought and its position accurately determined by experiment.

For example, the equilibrium

$$Na_2\,SO_4 . 10H_2O + 2\,KCl \rightleftarrows K_2SO_4 + 2\,NaCl + 10H_2O$$

was examined with the following results.

Temp.	Na_2SO_4.	KCl.	$C_{Na_2SO_4} \cdot C_{KCl}$.	K_2SO_4.	NaCl.	$C_{K_2SO_4} \cdot C_{NaCl}$.
0°	5	29.5	2.8	8	35.5	5.6
10°	10	32	6	9.5	36	6.7
20°	20	34.5	13	11	36.5	7.9

The table contains, under the formulæ of the different salts, their solubilities, at the given temperature, in parts in 100 of water.

The products of the concentrations of the saturated solutions (in gram equivalents per litre) calculated from these numbers show that the transition temperature probably exists at about 10°, the mixture of Glauber's salt and potassium chloride being the stable system below this temperature, that of potassium sulphate and sodium chloride above it.[1] This has been confirmed[2] by direct experiment, the transition temperature being found at 3°.7.

The curves of solubility are not the only ones which intersect at the transition temperature; the curves representing the vapour pressures of the saturated solutions do so also. That this is necessarily the case is at once obvious when we consider that at a given temperature the vapour pressure of a solution depends only on its concentration.

The experimental proof was obtained by means of the Bremer-Frowein tensimeter described on p. 159, which was used here as a differential instrument.

The two bulbs were filled with moistened astrakanite and with a moistened mixture of the two sulphates respectively, so as to insure the presence of saturated solutions; the difference in the level of the oil, observed at different temperatures, gives the difference between the vapour pressures of the solutions, which corresponds to the difference in their concentrations. The following results were obtained.

---

[1] Cf. Schiff, Lieb. Ann. 114, 68, 1848.

[2] Page 173.

A. With falling temperature.

Temperature.	Astrakanite.	Mixture of sulphates.	Difference.
22°.15	344.5	345.7	— 1.2
21 .43	344.9	344.9	0
20 .75	345.5	344.1	+ 1.4

B. With rising temperature.

Temperature.	Astrakanite.	Mixture of sulphates.	Difference.
21°.15	345.8	344.8	+ 1
22 .95	343.4	347.5	— 4.1

The point of intersection of the curves of vapour pressure is therefore very well marked; below 21°.5, the more concentrated astrakanite solution has the smaller vapour pressure, while above 21°.5 the reverse is true.

4. Relation between the transition temperature of a hydrated salt and the vapour pressures of the salt and of solutions of it.

The transition temperature of a hydrated salt is the temperature at which the vapour pressure of the crystals is exactly equal to that of the saturated solution of the salt; below this temperature, the former is smaller than the latter, above it, it would be greater, if the solid salt continued to exist as such, and did not melt.

The following experiment with Glauber's salt (melting point 33°) shows this in the clearest way. The vapour pressure of the salt is compared with that of its saturated solution; above 33° the salt exhibits a greater vapour pressure than the saturated solution only for a very short time, as owing to the fusion the two become identical. The point of intersection of the vapour pressure curves is therefore in this case, the point at which the vapour pressure of the salt, and of its saturated solution attain the same value, the equality continuing on further elevation of the temperature. The following numbers show this.

Temperature.	Level of the oil.		Difference.
	Moist salt.	Dry salt.	
33°.05	268.2	268.2	0
32 .85	"	"	"
32 .6	"	"	"
32 .5	Difference perceptible.		
31 .79	265.4	271	— 5.6
29	256 3	280.1	— 23.8

At 32°.5—32°.6, therefore, the vapour pressure of Glauber's salt becomes equal to that of its saturated solution, while below this temperature it is smaller. The temperature at which the vapour pressures become equal coincides thus with the melting point, and with the point of intersection of the curves of solubility[1].

5. Methods of determining the transition temperature.

The different methods which, up to the present, have been used for the determination of the transition temperatures of condensed systems are the following: —

a. The dilatometric method.
b. The thermometric method.
c. The crystallisation method.
d. The identity methods.
  α. By determinations of solubility.
  β. By determinations of the vapour pressures
    1. of solutions.
    2. of dissociation.
  γ. By determinations of the solution pressure
    1. of solutions.
    2. of dissociation.

---

[1] See also R. Löwenherz, Zeit. phys. Chem. 13, 490, 1894.

δ. Electrical methods.
   1. Electrical method with both stable and meta-stable phases.
   2. Electrical method with stable and without meta-stable phases.

Each of these will be considered separately and examples of its application given, after which some less general methods will be briefly noticed.

a. THE DILATOMETRIC METHOD.

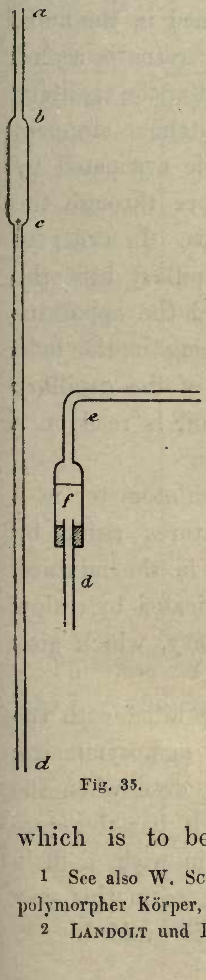


Fig. 35.

This has been most extensively employed by Reicher[1] in his researches on the conversion of rhombic into monosymmetric sulphur.

The method depends on the fact that, in the majority of cases, the substances present before and after the change have different specific volumes, so that the transformation is accompanied by an increase or diminution of volume. The temperature being maintained constant, a change of volume therefore indicates that the reaction has taken place

The specific volume of rhombic sulphur[2], for example is 1/2.07, that of monosymmetric sulphur 1/1.96, so that the conversion of rhombic into monosymmetric sulphur is accompanied by an expansion.

The dilatometer (fig. 27, p. 94), which is used in determining the transition temperature by this method, consists of a cylindrical glass bulb to which a thick-walled capillary tube is fused, the whole having the appearance of a large thermometer.

The bulb is partly filled with the substance which is to be examined, evacuated by means of a water air-pump, and then filled completely with some indifferent liquid, such as oil, petroleum, or mercury, so that the position of the latter can be observed on a paper scale which is glued to the capillary tube.

---

[1] See also W. Schwarz, Beiträge zur Kenntniss der umkehrbaren Umwandlungen polymorpher Körper, Preisschrift, Göttingen, 1892; also Kopp, Pogg. Ann. 80, 175, 1850.

[2] Landolt und Börnstein, Physikalisch-Chemische Tabellen, 2te Aufl. p. 119.

The form of dilatometer shown in fig. 35 may be used in cases in which only a small quantity of substance is available. The reservoir *bc*, which is 12 cm. long and 1 cm. in internal diameter, is prolonged into a narrower tube *ab*, of about 4 mm. diameter, which serves for filling it. The capillary *cd* is about 70 cm. long and 1 mm. wide; at *c* there is a small glass bulb with a narrow stem which fits loosely into the capillary and prevents its stoppage by particles of the substance contained in the bulb.

In order to introduce the petroleum, the apparatus is sealed up before the blowpipe at *a*, inverted, and the end of the capillary *d* connected with the tube *f* by means of a caoutchouc stopper; petroleum is then introduced at *f*, and the whole evacuated by means of the water air-pump. The air escapes through the petroleum, which takes its place in the apparatus, In order to bring the oil to a convenient level in the capillary tube the excess of it remaining at *f* is poured out, and the apparatus again evacuated, the small quantity of air remaining in the bulb expands and forces a quantity of petroleum out of the capillary which is easily regulated. The height of the oil is read on a paper scale glued to the capillary tube.

The observations are made by heating the dilatometer in a thermostat for a considerable time at temperatures rising by successive increments of a degree. The change in the mixture, which gives rise to the change of volume, is indicated by a slow alteration in the height of the oil in the capillary, which goes on for several hours.

Taking sulphur for example, if the bulb be filled with the rhombic modification alone, the change into the monosymmetric modification may be delayed very considerably even when the temperature is higher than the transition point. It has therefore been found advisable in all cases to add, to begin with, a little of the system which is formed by the change, as in this way the delay in the commencement of the reaction is avoided.

By alternately heating the bulb above, and cooling it below the transition point several times, the change is caused to take place much more rapidly, so that dilatometers which have been used several times (with the same contents) allow of much more rapid measurements. The addition of a solvent is also often favourable to the change. Reicher, for example, filled the bulb of a dilatometer with rhombic sulphur and a mixture of 1 volume of carbon bisulphide to 5 volumes of turpentine. About half of the sulphur was converted into the monosymmetric modification by heat, after which the position of the liquid in the capillary was read off at the following temperatures: —

Temperature 95° .1

Time in minutes.	Level of the oil.
5	343.5
30	340.5
55	335.75
65	333

At this temperature monosymmetric sulphur still changes into the rhombic modification.

Temperature 96° .1

Time in minutes.	Level of the oil.
5	342.75
30	354.75
55	360.50
60	361.50

The rise of the oil shows that the change at 96° .1 takes place in the reverse direction.

Temperature 95° .6.

Time in minutes.	Level of the oil.
5	368.75
100	368.
110	368.75

At this temperature the height of the liquid in the capillary tube is practically constant, that is, the two systems are in equilibrium, and the transition temperature is 95° .6.[1]

The dilatometric method may be applied in all cases in which the chemical reaction is accompanied by a change of volume; this is not invariably the case, for example, no change of volume occurs in the conversion of Glauber's salt into anhydrous sodium sulphate and water.[2]

In order to calculate the amount of expansion or contraction which accompanies a change it is necessary to take into account the composition of the systems in the immediate vicinity of the transition point.

For example, in the formation of astrakanite from a dry mixture of hydrated sodium and magnesium sulphates, the substances really formed are astrakanite and a solution saturated with astrakanite, so that the equation which represents the actual change is[3]

$$5.9\,(Na_2SO_4.10\,H_2O) + 7.6(MgSO_4.7\,H_2O) \rightleftarrows 3\,(Na_2Mg(SO_4)_2.4\,H_2O)$$

$$+\ 100\,H_2O \begin{array}{l} \sim 4.6\,MgSO_4 \\ \sim 2.9\,Na_2SO_4. \end{array}$$

b. THE THERMOMETRIC METHOD.

This method is based on the fact that all changes of the kind under consideration are accompanied by an evolution or absorption of heat, that system which is stable at the higher temperature being formed with absorption of heat.

The transition point may be determined by this method by observing the times which are required in order to heat or cool the system through equal intervals of temperature, or by observing the changes of temperature which occur in equal intervals of time. The occurrence of the chemical reaction coincides with the maximum retardation of the change of temperature, in fact the sign of the change of temperature is often reversed.

---

[1] To prevent evaporation the dilatometer was sealed up; the pressure within it was 4 atmos. at 95°.6. T. E.

[2] E. Wiedemann, Wied. Ann. 17, 575, 1882.

[3] Bakhuis Roozeboom. Zeit. phys. chem. 2, 515, 1888. Roozeboom uses the sign $100\,H_2O \begin{array}{l} \sim 4.6\,MgSO_4 \\ \sim 2.9\,Na_2SO_4 \end{array}$ to indicate that 4.6 mols. $MgSO_4$ and 2.9 mols. Na_2SO_4 are dissolved in 100 mols. of water.

The method is practically carried out as follows: —

The substance which is to be investigated is placed in a wide test-tube surrounded by cotton wool, in which a thermometer is placed, it is then heated or cooled and well stirred with the thermometer, and its temperature read from time to time.

The following results were obtained in the decomposition of schoenite represented by the equation[1]

$$K_2Mg(SO_4)_2 . 6 H_2O + H_2O \rightleftarrows K_2SO_4 + MgSO_4 . 7 H_2O.$$

Falling temperature.

Time t.	Temperature T.	$\frac{\Delta T}{\Delta t}$
10 hrs. 43 min.	+ 6°	1.7
,, 46 ,,	+ 1	0.75
,, 50 ,,	— 2	0.13
,, 54 ,,	— 2.5	0.08
11 hrs. 0 min.	— 3	0.5
,, 2 ,,	— 4	0.5
,, 7 ,,	— 6.5	

Rising temperature.

Time t.	Temperature T.	$\frac{\Delta T}{\Delta t}$
12 hrs. 4 min.	— 7°	1
,, 5 ,,	— 6	0.5
9 ,,	— 4	0.33
12 ,,	— 3	0
16 ,,	— 3	0.05
25 ,,	— 2.5	0.14
32 ,,	— 1.5	

A very decided retardation of the change of temperature takes place at — 3°, both on heating and on cooling, from which we may conclude that the decomposition takes place at this temperature.

---

[1] See note 4 on page 172. Compare also W. Schwarz, loc. cit. (note 1, p. 181).

c. THE CRYSTALLISATION METHOD.

This method was employed in the investigation of the equilibrium

$$2\,Na\,NH_4\,C_4H_4O_6 \,.\, 4H_2O \rightleftarrows (Na\,NH_4\,C_4H_4O_6)_2 \,.\, 2\,H_2O + 6\,H_2O.$$

By allowing the salts to crystallise out from solution, Wyrouboff[1] and Scacchi have shown that above 27° sodium ammonium racemate is deposited, while below it a mixture of the dextro- and lævo-tartrates crystallises out.

d. THE IDENTITY METHODS.

W. Meyerhoffer[2] has pointed out that at the transition temperature the solutions of the mutually convertible systems become identical in every respect. We have already seen that the solubilities, and also the vapour pressures of the saturated solutions of the two systems are identical at the transition temperature. Meyerhoffer says further, "There is no doubt that if all the other properties of the solutions such as specific volume, refractive power, viscosity, conductivity, etc. were to be represented graphically as functions of the temperature, the curves would intersect at the transition temperature."

The methods which will now be described all depend on the experimental proof of the identity of the saturated solutions of the mutually convertible systems. According as solubility, vapour pressure, or some other property of the solution be used as the criterion, the methods of determining the transition temperature vary in experimental detail, so that we obtain the different methods mentioned on p. 180, which will now be explained fully.

α. Determination of solubility.

We have already seen that the solubility curves of the two mutually convertible systems intersect at the transition temperature, and have found by interpolation the temperature at which the solubilities of Glauber's salt and anhydrous sodium sulphate become equal from the observations of Loewel (p. 175).

---

[1] Bull. Soc. Chim. 41, 210, 1884; 45, 53, 1886.

[2] Zeit. phys. Chem. 5, 105, 1890.

Bakhuis Roozeboom[1] has determined the transition temperature of astrakanite by means of determinations of solubility, the results of which are given in the following table. The numbers are molecules of the salts to 100 molecules of water in the saturated solutions.

Temperature.	Astrakanite.		Astrakanite + Sodium sulphate.		Astrakanite + Magnesium sulphate	
	Na_2SO_4	$MgSO_4$	Na_2SO_4	$MgSO_4$	Na_2SO_4	$MgSO_4$
18°.5	—	—	—	—	3.41	4.27
22	2.95	4.70	2.95	4.70	2.85	4.63
24 .5	3.45	3.68	3.45	3.62	2.68	4.76

According to these determinations, therefore, the solubilities of the systems astrakanite + sodium sulphate, astrakanite + magnesium sulphate, and magnesium sulphate + sodium sulphate become equal at 22°, that is, 22° is the transition temperature.

β. *Determination of vapour pressure.*

1. Vapour pressures of solutions.

From what has already been said on p. 178 it is clear that a comparison of the vapour pressures of the saturated solutions of the mutually convertible systems leads to a determination of the transition temperature.

Van 't Hoff and van Deventer[2] made use of the differential tensimeter in the investigation of astrakanite in the way described on p. 179. A form of the tensimeter which is to be preferred to that shown in fig. 34 is represented by the accompanying diagram, fig. 36; the porcelain

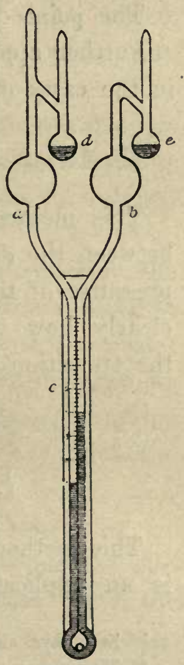


Fig. 36.

---

[1] Zeit. phys. Chem. 2, 513, 1888; Rec. des Trav. Chim. des Pays-Bas, 6, 333, 1887.

[2] Zeit. phys. chem. 1, 169, 1887.

millimetre scale allows the difference of level of the oil to be read without using the cathetometer. The vapour pressures of saturated solutions of Glauber's salt and of anhydrous sodium sulphate have been determined by E. Cohen,[1] the results are contained in the following table.[2]

Temperature.	Vapour pressures of the saturated solutions of Na_2SO_4. 10 H_2O.	Vapour pressures of the saturated solutions of Na_2SO_4.
28°.3	26.20	24.07
30 .1	28.03	26.60
32 .6	30.82	30.82

The point of transition is 32° .6.

Further applications of this method have already been mentioned in the cases of the racemates, copper potassium chloride, etc.

2. Pressure of dissociation.

This method depends on the relation, described on p. 179, between the dissociation pressure of hydrated salts and the vapour pressures of their saturated solutions. The table on p. 180 shows clearly how the tensimeter may be used in order to determine the transition temperature by means of this relationship.

γ. *The solution pressure method.*

1. In the case of solutions.

This method, which has been worked out by J. Verschaffelt,[3] is an application of Nernst's[4] conception of solution pressure.

---

[1] Zeit. phys. chem. 14, 90, 1894.

[2] The vapour pressures are in mm. of mercury at 0°. Compare the values obtained with what is said on p. 174.

[3] Zeit. phys. chem. 15, 437, 1894.

[4] Zeit. phys. chem. 4, 150, 1889. Theoretical chemistry, p. 133.

Just as a liquid possesses a certain power of expanding, in consequence of which it evaporates into any vacant space until the pressure of its vapour reaches a certain maximum value known as the vapour pressure of the liquid, so a liquid, if brought into contact with another liquid, in which it is soluble to a limited extent, will dissolve until the dissolved part has reached a certain maximum osmotic pressure which, on account of the complete analogy between the processes of evaporation and solution, **Nernst** has called the solution tension[1] of the liquid.

If a foreign body be dissolved in the liquid its solution pressure is diminished in the same way as its vapour pressure.

If some liquid in which water is soluble to a limited extent be placed in contact with a hydrated salt which is insoluble in it, the hydrate will give up water to the liquid in the same way as it would effloresce in the air; if a sufficiently large amount of the salt be used a maximum osmotic pressure of the dissolved water will be attained, corresponding to the vapour pressure of dissociation of the salt *in vacuo*, and which may therefore be called the solution pressure of dissociation.[2]

Since at a given temperature the solution pressure only depends on the concentration of the dissolved water, **Verschaffelt** determined the latter only, using amyl alcohol as the solvent and water as the soluble liquid.

In order to determine the concentration of the water in the amyl alcohol solutions, a series of measurements of the solubility of water in amyl alcohol at different temperatures was made; the concentration of any solution could then be obtained by cooling it until it just became turbid, and interpolating the concentration corresponding to the temperature at which the turbidity appeared.

The determinations were made in the following way: —

Exactly weighed quantities of the liquids were brought into the flask of an **Eykman**'s freezing point apparatus[3] and the thermometer placed in position, after bringing the mercury to a suitable position on the scale, and comparing its readings with those of a standard thermometer. The apparatus was then slowly warmed in a water bath, and vigorously shaken until the mixture was homogeneous, after which it was placed in a beaker of water which was allowed to cool by radiation.

---

[1] "Lösungstension" is generally translated "solution pressure", which is perhaps preferable to the more strictly equivalent term "solution tension". T. E.

[2] **Linebarger**, Zeit. phys. Chem. 13, 500, 1894.

[3] The apparatus is described in the Zeitschrift für phys. Chem. 2, 964, 1888, and also in **Ostwald**'s Lehrbuch der allgem. Chem. 1, 766.

The temperature at which the turbidity appeared could be observed with an error of a few tenths of a degree; in the table which follows, the temperatures are given to the nearest whole number so that they may be affected by a maximum error of 0°.5, a degree of accuracy which is sufficient for the present purpose.

The following is an example of the numbers obtained.

Amyl alcohol . . . . . 8.046 grams $= G_a$
Water. . . . . 0.769 ,, $= G_w$

$$\text{Concentration of the water} = 100 \frac{G_w}{G_w + G_a} = 8.72 \text{ per cent.}$$

Temperature at which saturation took place = 6°.

The following are the percentage concentrations of the saturated solutions of water in amyl alcohol at different temperatures.

Temperature.	Concentration.
6°	8.72
15	9.14
25	9.67
32	10.00
36	10.20

The following equation represents the connexion between the concentration c and the temperature t, between 0° and 40°.

$$c = 0.05\ (168 + t).$$

To obtain the concentration of any solution, it is only necessary to introduce the observed temperature at which turbidity appears in it into this equation, and calculate c.

If the temperature at which turbidity appears is inconveniently high or low, a known quantity of amyl alcohol, or water, may be added in order to bring the temperature between suitable limits (20°—40°). From the temperature at which the turbidity now appears the initial concentration of the solution is easily calculated; for example, 8.591 grams of a solution were taken and 0.207 grams of water added to it, the turbidity appeared at 30°, so that the concentration of the new solution was

$$c_1 = 0.05\ (168 + 30) = 9.90 \text{ per cent.}$$

The whole amount of the water is therefore,

$$w_1 = \frac{9.90}{100}\ (8.591 + 0.207) = 0.871 \text{ grams,}$$

and the initial quantity,

$$w = 0.871 - 0.207 = 0.664 \text{ grams.}$$

from which the concentration, which is to be determined, is

$$c = \frac{66.4}{8.591} = 7.72 \text{ per cent.}$$

After these preliminaries, it was possible to determine the transition temperature of Glauber's salt in the following way: — The finely powdered salt was placed in a flask of about 100 cc. capacity, and treated with amyl alcohol which had been saturated with water; the salt takes up water from this forming a saturated aqueous solution.[1] The flask was well closed and maintained at a constant temperature in a thermostat, being well shaken from time to time. In order to obtain a supercooled solution of anhydrous sodium sulphate the flask with its contents was previously heated for some time to a temperature above 33°. Equilibrium having been attained, after about an hour, the salt was allowed to settle and the amyl alcohol filtered, after which the concentration of the water contained in it was determined in the way described.[2]

---

[1] This aqueous solution dissolves a little amyl alcohol, but since the two systems become identical at the transition temperature, they both dissolve the same quantity of amyl alcohol and though the solubility of the salt is changed a little the transition temperature is unaffected.

[2] PFEIFFER, Zeit phys. Chem. 9, 445, 1892, has shown that the addition of foreign bodies to a mixture of two liquids may displace the temperature at which the turbidity appears to a considerable extent. Special experiments on this point showed, however, that sodium sulphate is not sufficiently soluble in moist amyl alcohol to have any appreciable effect.

The following table contains the results of the experiments.

Temperature.	Percentage concentration of the water taken up from a saturated solution of Glauber's salt.	Temperature.	Percentage concentration of the water taken up from a saturated solution of the anhydrous salt.
20°	7.80	40°	6.48
25	7.49	35	6.29
30	6.92	30	6.09
31	6.71	25	5.88
32	6.41		
33	6.11		

The concentrations of the water taken up by the amyl alcohol from the saturated solutions of Glauber's salt at temperatures from 31°—33° lie on the straight line,

$$c = 16.01 - 0.3\ t,$$

those of the water taken up from the solutions of the anhydride are represented by the formula

$$c = 4.88 + 0.04\ t.$$

These two lines intersect at a temperature of 32°.74, which is therefore the transition temperature.

2. Solution pressure of dissociation.

The transition temperature was also determined by means of observations of the solution pressure of dissociation of Glauber's salt in amyl alcohol; in order to make the measurements Glauber's salt may be placed in contact with dry amyl alcohol, or amyl alcohol saturated with water may be brought together with anhydrous sodium sulphate. The salt was ground to fine powder, or when the anhydride was used, Glauber's salt was allowed to effloresce in the air, because the powder formed in this way is so finely divided that it remains suspended in the liquid for a long time. Equilibrium is attained only after some hours.

OF THE UNIVERSITY OF CALIFORNIA

Temperature.	Concentration of the water.[1]
20°	4.41
25	5.09
30	5.81

The concentrations are reproduced by the formula

$$c = 1.60 + 0.14\ t.$$

This curve cuts that of the saturated solutions of Glauber's salt,

$$c = 16.01 - 0.3\ t,$$

at 32°.75.

δ. *Electrical methods.*

1. Electrical method with both stable and meta-stable phases.

This method, which is also one of the identity methods, was devised by E. Cohen.[2]

If two solutions of a salt (say $ZnSO_4$), of different concentrations, be placed in vessels connected together by means of a syphon with limbs of equal length, and an electrode consisting of the same metal as that contained in the salt be placed in each vessel, then, on connecting the electrodes by means of a wire, a current of electricity will flow round the circuit in a direction such that the difference of concentration will tend to disappear. The concentrations having become equal, no further difference of potential will exist; the cause of the current being removed, the current itself ceases. Moser[3] has shown that, in the combination described, the direction of the current is the following:

---

[1] In agreement with Lescoeur's observation that the dissociation pressure is constant, it was found that the solution pressure of dissociation is independent of the quantity of water of crystallisation in the hydrate. At 20° the salt $Na_2SO_4 . 3.88H_2O$ had the same pressure as the salt $Na_2SO_4 . 0.22H_2O$.

[2] Zeit. phys. Chem. 14, 53 and 544, 1894.

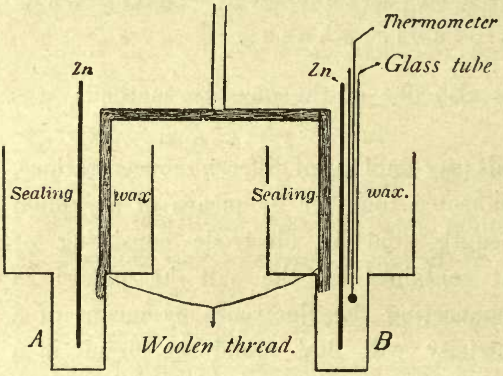
[3] The literature of the subject of concentration currents is given in Ostwald's Lehrbuch, 2te Aufl. II, 824.

Zn, dilute $ZnSO_4$-solution ⟶ concentrated $ZnSO_4$-solution, Zn.

Concentration cells have been constructed by Nernst[2] which differ from those of Moser's type in the fact that, with $ZnSO_4$ for example, SO_4 electrodes are used instead of zinc; with this arrangement the current flows from the more concentrated to the more dilute solution.

We know then, first, that in an equilibrium between condensed substances the solubilities of the two systems, which are different at temperatures above or below the transition point, become equal at that point, and secondly, that when a concentration current flows between two solutions it will disappear when the concentrations of the solutions become indentical.

From these facts it is evident that the disappearance of the concentration current which flows between the saturated solutions of the two mutually convertible systems may be used to determine the temperature at which the solutions have the same concentration, that is, the transition temperature. Just as in the titration of a base with an acid an indicator is used in order to determine the point at which the whole of the base has been neutralised, so here the concentration current is employed as an indicator of the temperature at which the solubilities of the mutually convertible systems become equal, that is, the transition point.



Transition cell.

Fig. 87.

---

[1] Zeit. phys. Chem. 4, 117 and 157, 1889.

As an example, the transition temperature in the reaction

$$ZnSO_4.\ 7\,H_2O = ZnSO_4.\ 6\,H_2O + H_2O$$

will be taken.

The apparatus with which the determinations are made may be called the *transition cell* with meta-stable phase; it is represented in fig. 37, and consists of two vessels, A and B, which are connected by a syphon with limbs of equal length. Zinc sulphate, which has been finely powdered and moistened with a few drops of water, is placed in the narrower parts of the vessels;[1] in this way the solutions, being in contact with a great excess of the solid salt, are maintained in a saturated condition when the apparatus is warmed.

The syphon is filled with cotton wool saturated with a solution of zinc sulphate, and the projecting ends of the wool are pressed into the moist salt in A and B.

Two amalgamated rods of zinc, which are covered with sealing-wax with the exception of about $^1/_2$ cm. of their lower extremities, serve as electrodes. A small thermometer, graduated in $^1/_{10}{}^\circ$, is introduced through the glass tube which is shown in the figure. The wider parts of the vessels A and B are filled with some indifferent substance, such as sealing-wax, in order to prevent any movement of the electrodes during the experiment.[2]

When a salt, such as sodium sulphate, the metal of which cannot be used as an electrode, is under examination an electrode which is unpolarisable with respect to the anion of the salt must be employed; with sodium sulphate, for example, an electrode of mercury, the surface of which is covered with mercurous sulphate, is used. Connexion with the mercury is made by means of a platinum wire fused through a glass capillary tube.[3]

---

[1] Only a few grams of the salt are needed, so that, on warming, the solution very quickly becomes saturated.

[2] Any dissimilarity of the electrodes, which would give rise to a current, is avoided by short-circuiting the cell and allowing it to stand in that condition for some time; the cells when not in use should always be kept in this way. If after a considerable time some inequality still remains, it may be allowed for by applying a correction to the experiments.

[3] The form of transition cell which will be described later may also be used in these experiments.

The transition cell is now to be arranged in the following order:

Unpolarisable electrode.	Saturated solution of the *meta-stable* phase of a salt.	Saturated solution of the *stable* phase of the same salt.	Unpolarisable electrode.

The vessels A and B having been filled with a saturated solution of $ZnSO_4 . 7 H_2O$ in the way described, the contents of B are converted into a saturated solution of $ZnSO_4 . 6H_2O$ by heating B in a beaker of water for an hour to a temperature higher than the transition point.[1] In order to avoid heating A, a screen of of asbestos card is placed between it and the beaker.

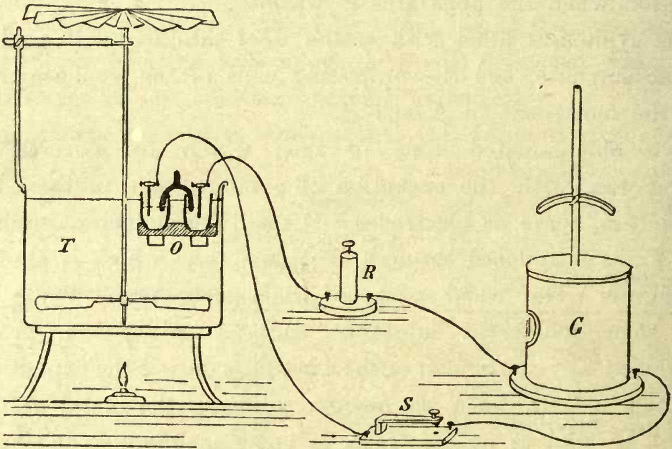


Fig. 38.

The transition cell is then placed in a thermostat (fig. 38) and connected up in circuit with a galvanometer, a key to make or break the circuit, and a variable resistance, such as the Engelmann[2] carbon plate resistance shown in the figure, which makes it possible to bring the spot of light reflected from the galvanometer mirror on to the scale by introducing a suitable resistance into the circuit.

The thermostat is then brought to a temperature from 4 to 5 degrees below the supposed transition point; it is not advisable to depress the temperature much more than this, since the probability of the occurrence of the change of the system $ZnSO_4 . 7 H_2O$ into the system $ZnSO_4$ $6 H_2O$, which is stable at the lower temperature, then becomes too great,

---

[1] The transition point is determined approximately by a preliminary experiment.

[2] Archives Néerlandaises, 22, 1888. Zeit. phys. Chem. 2, 153, 1888.

The temperature of the thermostat is now allowed to rise very slowly so that the solutions remain constantly saturated. Every five minutes the circuit is closed, and the deflection of the galvanometer needle noted ; this becomes smaller and smaller as the temperature rises, a point being finally reached where the deflection is in the opposite direction. The temperature at which the deflection is zero (the transition temperature) is then obtained by interpolation. The explanation of the diminution of the current is to be found in the diminution of the difference between the concentrations of the solutions in A and B with rising temperature; at the transition temperature, where the concentrations are the same, the current is zero, and on further raising the temperature the current is reversed, as is obvious from what is said on p. 174 on the course of the curves of solubility. When the temperature is maintained above the transition point for some time the solutions in A and B again become identical, and the current disappears.

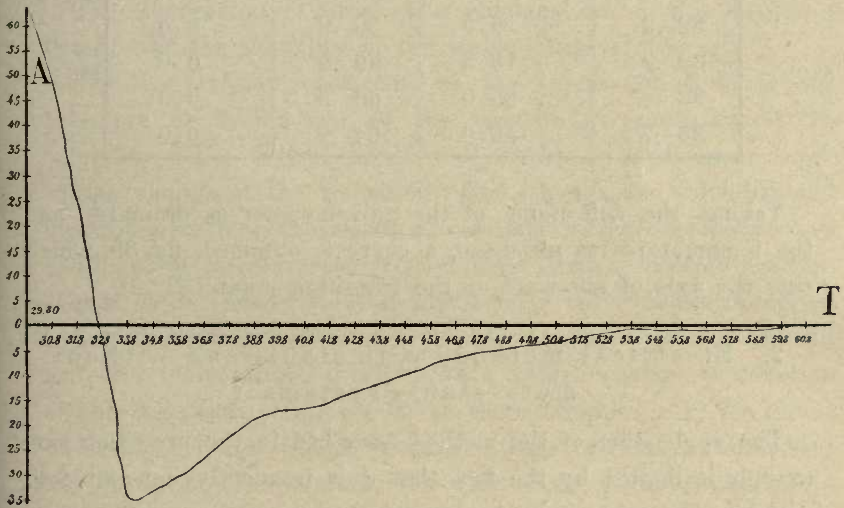


Fig. 39.

The following table contains the results which were obtained with Glauber's salt; the temperature is given under t, the deflection of the galvanometer under α.

t	α	t	α
29°.7	—122.5	34°.1	74.5
30 .3	—104.5	38 .9	43.0
30 .9	— 87.0	42 .5	27.0
31 .6	— 60.5	48 .4	10.5
32 .1	— 38.5	50 .9	7.0
32 .7	— 1.0	53 .9	5.0
32 .9	+ 6.5	56 .9	5.0
33 .2	18.5	59 .9	0.0
33 .4	35.0	60 .9	0.0
33 .7	56.0	61 .9	0.0

Taking the deflections of the galvanometer as ordinates, and the temperatures as abscissae, a curve is obtained, fig. 39, which cuts the axis of abscissae at the transition point (32°.8).[1]

2. Electrical methods with stable and without meta-stable systems.

The application of the method described in the preceding paragraph is limited by the fact that it is frequently impossible to maintain the meta-stable system at the same temperature as the stable system for a considerable period of time, especially when that temperature differs much from the transition temperature. For example, special precautions are necessary in order to supercool anhydrous sodium sulphate, in presence of its saturated solution, several degrees below 32°.6, without its passing over into the more stable hydrate $Na_2SO_4 . 10H_2O$.

An arrangement has been devised by E. Cohen and G. Bredig[2] which permits of the determination of transition temperatures by means of the transition cell without the presence of the meta-stable system. The saturated solution of the meta-stable phase is replaced by an unsaturated solution of known concentration, which remains unchanged (neglecting the small thermal expansion) at all temperatures.

---

[1] Further applications of the method are described in the Zeitschrift für phys. Chem. 14, 53, 1894.

[2] Zeit. phys. Chem. 14, 535, 1894.

The cell is put together as follows:

Unpolarisable electrode.	Solution of the salt of known strength, *without the solid.*	Saturated solution of the salt in presence of the *stable solid* phase.	Unpolarisable electrode.

The electromotive force of a combination of this kind is a function of the solubility of the stable phase of the salt.[1]

The temperature coefficient of the electromotive force will therefore be a function of the temperature coefficient of the solubility. The latter, as is well known,[2] experiences a *per saltum* change at the transition point (though the solubility and electromotive force themselves do not) and therefore *the temperature coefficient of the electromotive force must likewise undergo a sudden change at this temperature.* If therefore, a curve be drawn representing the connexion between the electromotive force of the cell and the temperature, it will have a sudden change of direction at the transition point, similar to those observed with the curves of solubility and vapour pressure. Thus in order to determine the transition temperature, we only need to draw the curves representing the electromotive force of the cell below, and above the transition point, and to determine their point of intersection.

The form of transition cell used is shown in fig. 40. It consists of two tubes *a* and *b*, about 10 cm. long and 3.5 cm. wide, to which capillary tubes are attached; mercury is brought into each of these and its surface covered with mercurous sulphate, electrodes being thus produced which are unpolarisable for SO_4. Over the mercury in the tube *a*, a solution of sodium sulphate of known strength is poured to a depth of 4 or 5 cm., while the tube *b* contains a paste of finely ground Glauber's salt and the same solution. Conducting communication between the two liquids is provided by a ∩-tube about 1 cm. wide filled with cotton wood soaked in the sodium sulphate solution. This tube has a relatively small resistance, which is of importance for the sensitiveness of the method.

---

[1] It is of course assumed that the solution or precipitation of the solid substance in a reversible way occurs simultaneously with the passage of the current. See OSTWALD. Lehrbuch allg. Chem. 2te Aufl. II, 868.

[2] The melting point may be considered as a special case of this; see J. WALKER, Zeit. phys. Chem. 5, 193, 1890; W. L. MILLER, Zeit. phys. Chem. 10, 459, 1892.

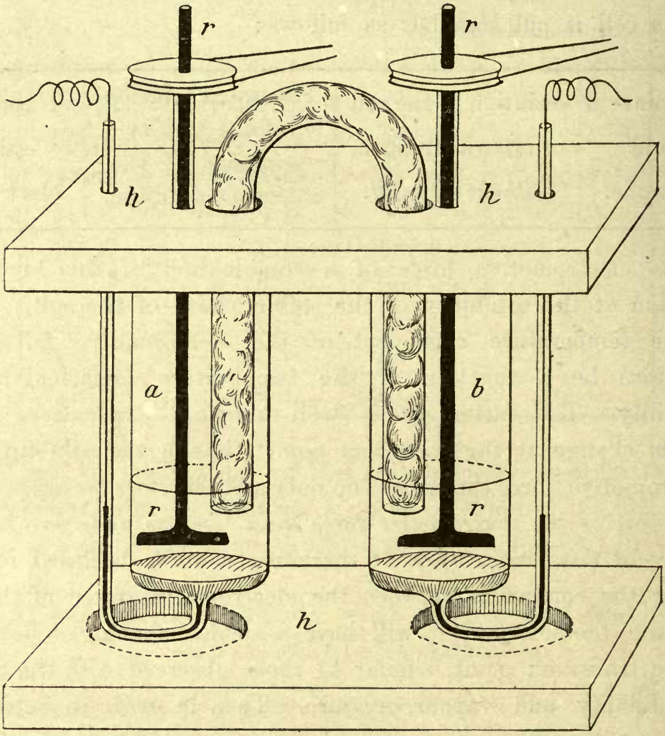


Fig. 40.

Just above the surface of the mercury in *a* and *b*, two ⊥-shaped glass stirrers, *r*, are caused to rotate by means of a small water-motor, so that the pasty mass of crystals and the solution at the electrodes are kept in constant motion, and the solution in *b* remains saturated. The parts of the apparatus are held together by a wooden frame easily taken to pieces, which also serves to support the apparatus in the thermostat.

With Glauber's salt, the solution becomes saturated in about two hours, after which the electromotive force remains constant. The measurements of potential were made by means of the compensation method of Poggendorff and Du Bois Reymond; with the galvanometer used a difference of potential of less than $^1/_{20000}$ volt was appreciable.[1]

Three different cells were investigated, the solutions of constant concentration being N, $N/_2$, and $N/_4$ respectively.

The other solution being a solution of sodium sulphate saturated with respect to the modification which is stable at the temperature given, the following values of the electromotive force E (in millivolts) were obtained.

Cell I. Normal sodium sulphate solution.

t	E_2	t	E_1
20°.1	7. 2	35°	22.2
25 .4	11. 2	40	22.5
30 .2	16. 8	45	25.1

$$E_1 = 25.5 - 0.39\ t + 0.006\ t^2.$$
$$E_2 = 12.8 - 1.097\ t + 0.0407\ t^2.$$

Taking the temperatures as abscissae, and the corresponding values of the electromotive force as ordinates the curves given in fig. 41 result. The point of intersection obtained from the curves, or calculated from the equations given above is 33°.8.

Cell II. $N/_2$ sodium sulphate solution.

t	E_2	t	E_1
20°.1	14.3	35°.1	28.2
25 .2	18.7	40 .0	28.6
30 .1	24.1	45 .0	28.7

---

[1] A Gouy cell was used as standard, a Leclanché as the working cell.

$$E_1 = 16.63 + 0.548\ t + 0.00622\ t^2.$$
$$E_2 = 10.12 - 0.297\ t + 0.0253\ t^2.$$

The transition temperature obtained from these numbers is 33°.0.

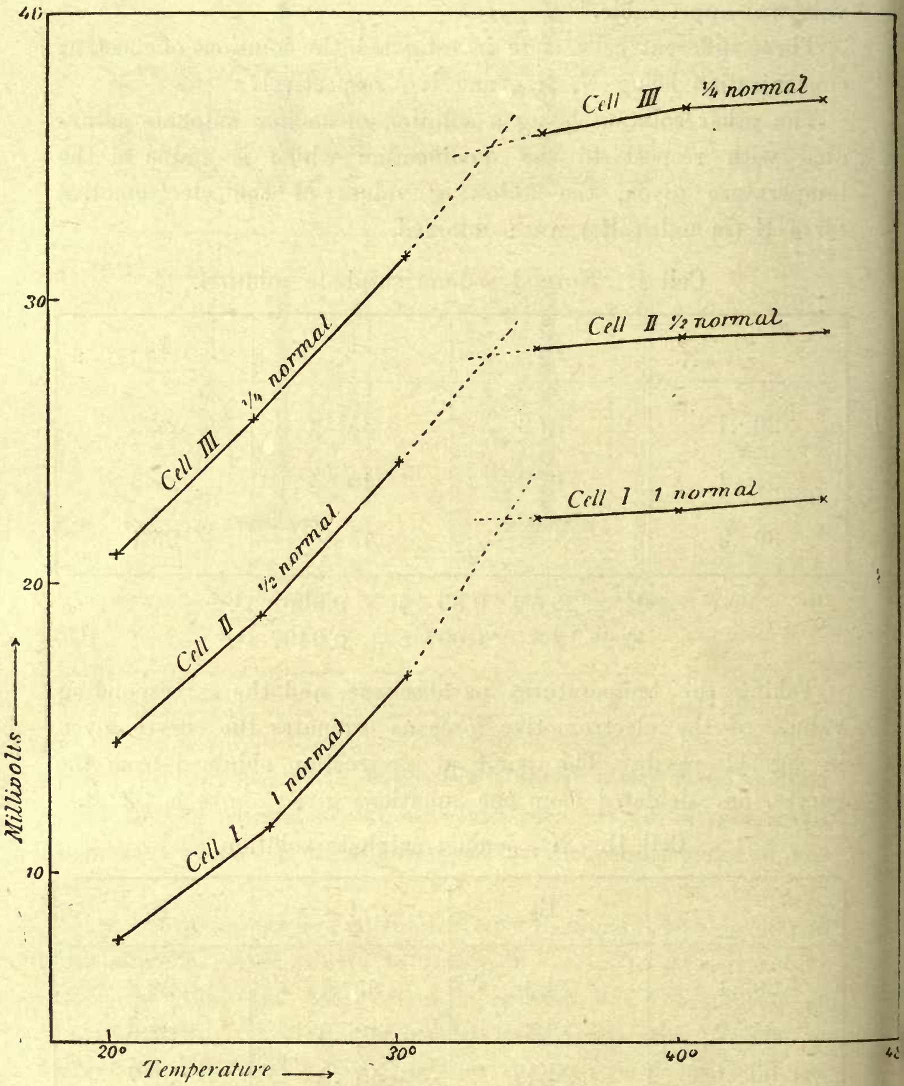


Fig. 41.

Cell III. $N/_4$ sodium sulphate solution.

t	E_2	t	E_1
20°.1	21.1	35°.0	35.8
25 .1	25.7	40°.1	36.7
30 .0	31.4	45 .0	37.1

$$E_1 = 16.32 + 0.889\ t - 0.0095\ t^2.$$
$$E_2 = 15.00 - 0.190\ t + 0.0245\ t^2.$$

The transition temperature is 32°.9.

A. E. Baur [1] has recently employed this method for the determination of the transition point in the reaction

$$Na_2HPO_4.\ 12\,H_2O \rightleftarrows Na_2HPO_4.\ 7\,H_2O + 5\,H_2O,$$

which was found to lie between 36°.5 and 36°.8.

Further methods. [2]

In addition to the methods of determining the transition temperature described under $\alpha - \delta$, there are some others which may be used, according to the nature of the system under investigation. When, as in the case of mercuric iodide, a change of colour accompanies the change, it may be employed to indicate the transition temperature.

The mutual transformation of colourless polymorphous bodies may be recognised by the occurrence of changes in the double refraction, or by its appearance or disappearance. A change in the electrical conductivity may also serve in many cases as an indication of the change.

---

[1] Zeit. phys. Chem. 18, 180, 1895.

[2] See W. Schwarz (cf. p. 181) where the literature is given fully.

EQUILIBRIUM.

SECOND PART.

THE THREE FORMS OF PHYSICAL EQUILIBRIUM.

The occurrence of equilibrium between two different systems, or in general between two different forms of the same kind of matter, is not confined to the domain of chemistry. An analogous physical phenomenon, evaporation, was known long before anything of the kind had been discovered in chemistry.

The equilibrium which, in the evaporation of water for example, exists between water and steam, when the latter has reached its maximum pressure, may be explained by the simultaneous occurrence of two changes in opposite directions, the one being the conversion of water into steam, the other the conversion of steam into water with equal speed.

The symbolic representation which has been used in the case of chemical equilibrium may therefore be employed here also, the special case which we have taken being represented by the symbol:—

$$\text{liquid water} \rightleftarrows \text{water vapour.}$$

There is, as we shall see, a far reaching analogy between chemical and physical equilibria. The latter may be divided into three classes, which are quite similar to those in which the chemical equilibria were arranged, namely

1. Physical equilibrium in homogeneous systems.
2. Physical equilibrium in heterogeneous systems.
3. Physical equilibrium in condensed systems.

I. HOMOGENEOUS SYSTEMS.

The physical analogue of a homogeneous chemical equilibrium such as

$$N_2O_4 \rightleftarrows 2\,NO_2,$$

is a phenomenon which, though not well marked, is of very general occurrence, namely those molecular attractions which cause the deviations from the laws of Boyle and Charles (or Gay Lussac); these attractions do not tend to the formation of any sharply defined product; were there any such tendency we should have a case of chemical equilibrium.

II. HETEROGENEOUS SYSTEMS.

A heterogeneous chemical equilibrium, such as

$$NH_4\,HS \rightleftarrows NH_3 + H_2S,$$

which has already been described, is to be regarded as completely analogous to a physical evaporation, such as

$$\text{Liquid water} \rightleftarrows \text{Steam.}$$

The equations which were used in the first case apply also to the second; we have

$$K = C \text{ and } \frac{d \log K}{d\,T} = \frac{q}{2\,T^2},$$

$$\text{from which } \frac{d \log C}{dT} = \frac{q}{2\,T^2},$$

where C is the concentration of the vapour, q the quantity of heat which is evolved by the condensation of 18 kgrms. of water vapour, without external work being performed.

From the above equation we obtain, by integration,

$$\log \frac{C_2}{C_1} = \frac{q}{2}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where C_1 and C_2 are the concentrations of the saturated steam at the absolute temperatures T_1 and T_2.

From this equation we can calculate the value of q by introducing the vapour pressures p_1 and p_2 at the temperatures T_1 and T_2; we have

$$C_2 : C_1 = \frac{p_2}{T_2} : \frac{p_1}{T_1},$$

and therefore,

$$\log \frac{p_2}{T_2} - \log \frac{p_1}{T_1} = \frac{q}{2}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Introducing the following numerical values,

$$T_1 = 273 \qquad p_1 = 4.54$$
$$T_2 = 273 + 11.54 \quad p_2 = 10.02$$

we find q = 10100.

The heat of evaporation of a kgrm. mol. of water at 5°.77 is 10854 cals. To obtain q from this number, the external work which accompanies the condensation must be subtracted; this is 2 T = 558 cals., and therefore q = 10296 cals., which agrees sufficiently well with the number calculated.

The *solution of solid bodies* is another example of this kind of equilibrium, and may be represented as follows:

Undissolved substance $\rightleftarrows$ dissolved substance.

The equations which apply to chemical equilibrium are also applicable to this case. In employing them to calculate q from the solubility it is, however, necessary to remember that they are only strictly true for very dilute solutions.

As is well known, the law of GULDBERG and WAAGE may be written in the form

$$\frac{C_2^{\Sigma a_2 i_2}}{C_1^{\Sigma a_1 i_1}} = K,$$

for very dilute solutions at constant temperature,[1] where a_1 and a_2 are the numbers of each of the different kinds of molecules which take part in the reaction, i_1 and i_2 depend on the nature of the solvent and of the dissolved substance, and the summations extend to all the bodies belonging to each system.

---

[1] J. H. VAN 'T HOFF. Lois de l'équilibre chimique dans l'état dilué, gazeux ou dissous. Also, Archives Néerlandaises 20, 291, 1885.

Since $\Sigma a_1 i_1$ relates to the dissolved bodies forming part of the first system, we have, in the special case of equilibrium between a solid body and its saturated solution, $\Sigma a_1 i_1 = 0$, and therefore

$$C_1^{\Sigma a_1 i_1} = 1.$$

C_2 is the concentration of the dissolved substance, and $\Sigma a_2 i_2$ is equal to the value of i for this substance, so that at constant temperature

$$C^i = K,$$

that is, at a given temperature the soluble substance has a definite solubility.

Introducing this value of K into the equation which represents the influence of temperature on the equilibrium, we obtain

$$\frac{d \log C^i}{dT} = \frac{q}{2T^2}, \text{ or } \frac{d \log C}{dT} = \frac{q}{2iT^2} \ldots\ldots (1)$$

This equation represents the relation which exists between the change of the solubility C with the temperature T and the heat evolved by the separation of a kgrm. mol. of the substance from the saturated solution, which is its molecular heat of solution with reversed sign. By the molecular heat of solution is meant here the heat of solution of the substance in its own saturated solution. (*Final*, *fictitions or theoretical heat of solution*).[1] This theoretical heat of solution and the heat of solution in a large quantity of water (*integral heat of solution*) may differ very considerably from each other, and even be of opposite sign. Reicher and van Deventer,[2] for example, have shown that copper chloride dissolves in a large quantity of water with evolution of heat, while it dissolves in its own saturated solution with absorption of heat.

It is to be noticed however that with sparingly soluble bodies the difference between the integral and the theoretical heats of solution is negligible, for since there is very little difference between the saturated solution and pure water, they have very nearly the same action on the salt.

[1] C. M. van Deventer and J. van de Stadt, Zeit. phys. Chem. 9, 43, 1892. Bakhuis Roozeboom, Rec. des Trav. Chim. des Pays-Bas, 8, 96, 1888.

[2] Zeit. phys. Chem. 5, 559, 1890.

J. J. van Laar has obtained the following expression for $\frac{d \log C}{dT}$: —

$$\frac{d \log C}{dT} = \frac{q}{2\,T^2}\,\frac{2 - \varkappa}{2}, \quad \ldots\ldots (2)$$

where $\varkappa$ is the so called activity coefficient[1] ($\varkappa = i - 1$). The formula is only applicable to dilute solutions of binary electrolytes. It is to be noticed that when $i = 1$, i. e., with non-electrolytes, and also when $i = 2$, equations (1) and (2) become identical.

Equation (1), p. 207, shows that the sign of the change of solubility with rise of temperature is determined by that of the heat of solution; Le Chatelier[2] obtained this result simultaneously with van 't Hoff.

When the heat of solution is zero the solubility will not change with the temperature. The solubilities of isobutyl-alcohol (Alexejeff[3]), calcium sulphate (Le Chatelier), and of sodium chloride (van Deventer and van de Stadt[4]) in water illustrate the correctness of this result.

If the heat of solution q be positive, that is, heat is absorbed when the substance dissolves, the solubility increases with rising temperature, which is the case with the majority of substances.

Finally if the heat of solution be negative, that is, heat is evolved when the substance is dissolved, the solubility decreases with rising temperature. All the gases, and also ether, carbon bisulphide, bromine, and nicotine (Le Chatelier) belong to this class. Lime and calcium sulphate may likewise be added to the list, the latter having a maximum solubility at about 38° (Marignac).[5]

According to van 't Hoff[6] the equation

$$\frac{d \log C}{dT} = \frac{q}{2\,iT^2},$$

---

[1] The deduction of this relationship is to be found in the Zeit. phys. Chem. 17, 546, 1895.

[2] Compt. rend. 85, 440, 1877, Compt. rend. 100, 50, 1885.

[3] Compt. rend. 100, 442, 1885.

[4] Zeit. phys. Chem. 9, 43, 1892.

[5] Ann. Chim. Phys. (5), 1, 274, 1874. See also Landolt and Börnstein, Phys Chem. Tabellen, 2te Aufl. 238.

[6] Loc. cit. p. 206.

may be employed to calculate the value of q, when the solubilities of a substance at two temperatures, and the value of i are known.

By integration we obtain $\log C = - \frac{q}{2iT} + \text{const.}$,

and therefore, $$\log \frac{C_1}{C_2} = \frac{q}{2i} \left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

or $$q = 2i \frac{T_1 T_2}{T_1 - T_2} \log \frac{C_1}{C^2} \ldots\ldots (3)$$

where C_1 and C_2 are the solubilities at the absolute temperatures T_1 and T_2.

The following table shows that the values of q calculated in this way agree satisfactorily with those which are determined directly.

The substances examined are all rather sparingly soluble; these bodies were chosen because the equation by which q is calculated only applies to dilute solutions.[1]

Substance.	Temperatures.		Solubilities.[2]		i	$\frac{q}{1000}$ Calculated by eq. (3)	$\frac{q}{1000}$ observed.
Oxalic acid	0°	10°	5.2	8.0	1.25	8.2	8.5
Acid potassium oxalate	0	10	2.2	3.1	1.84	9.8	9.6
Succinic acid.....	0	8.5	2.88	4.22	1.00	6.9	6.7
Salicylic acid	12.5	81	0.16	2.44	0.93	8.4	8.5
Benzoic acid	4.5	75	0.182	2.193	0.93	6.3	6.5
Potassium bichromate.......	0	10	4.6	7.4	2.36	17.3	17
Amyl alcohol	0	18	4.23	2.99	0.93	— 3.1	— 2.8
Aniline	16	55	3.11	3.58	0.83	0.6	0.1
Phenol	1	45	7.12	10.2	0.84	1.2	2.1
Baryta...........	0	10	1.5	2.22	2.69	16.3	15.2
Calcium hydroxide	15.6	54.4	0.129	0.103	2.59	— 2.8	— 2.8
Barium nitrate ...	0	10	5.2	7.0	2.19	8.8	9.4
Alum	0	9.38	3.0	4.05	4.45	21.9	20.2
Mannite..........	17.5	23	15.8	18.5	0.97	4.8	4.6
Mercuric chloride.	10	50	6.57	11.84	1.11	3.0	3.0
Potassium chlorate	0	15.4	3.3	6.03	1.78	11.0	10.0
Boric acid	0	12	1.95	2.92	1.11	5.8	5.6
Borax	0	10	2.83	4.65	3.57	27.4	25.8

---

[1] In very dilute solution the theoretical heat of solution and that practically determined are identical, see p. 207.

[2] Phys. chem. Tabellen, LANDOLT und BÖRNSTEIN, 2te aufl. 235. New determinations of the values of q and i are very desirable, those given in the table not being recent. Too much weight is therefore not to be attached to the agreement between the calculated and observed values.

It is noteworthy that van Laar's formula, which applies to binary electrolytes, gives $\frac{q}{1000}$ for $KClO_3 = 10.1$, the observed value being 10.0.

III. CONDENSED SYSTEMS.

The class of chemical equilibria which is characterised by the existence of a transition temperature possesses a complete analogue in the physical changes of fusion and solidification. In the change

$$\text{rhombic sulphur} \rightleftarrows \text{monosymmetric sulphur,}$$

there is a certain temperature above which the one system, below it the other is stable; precisely the same thing is found in physics in the phenomena of fusion and solidification, the change, taking water for example, may be written,

$$\text{water} \rightleftarrows \text{ice.}$$

The far reaching nature of the analogy will become more apparent when we consider the influence of pressure on the transition temperature of condensed systems.

So far, only the fundamental resemblance which exists between chemical and physical phenomena has been pointed out. There is, however, a considerable difference between them in one respect, namely in the surprising variety of the phenomena encountered among chemical equilibria. The reason of this variety is obviously to be found in the fact that, while the number of different conditions of a substance which can take part in a physical equilibrium is limited to three (solid, liquid and gas) no such limitation exists in the case of chemical equilibrium. The parallelism of the two classes will therefore be most evident in those cases of chemical equilibrium in which only two bodies take part.

Again, from what has been said it is evident that physical equilibrium may be regarded as merely the most simple form of chemical equilibrium. Chemical equilibrium in a homogeneous system is found in its most simple form in the physical deviations from the laws of Boyle and Charles. Chemical equilibrium in a heterogeneous system becomes, in its simplest form, evaporation or condensation; equilibrium of incompatible systems corresponds to fusion.

A further difference between physical and chemical equilibrium is found in the velocity with which the condition of equilibrium is reached. While this is very great in physical changes, a certain shuggishness is observed in similar chemical changes. Naumann[1], for example, found that in evaporating naphthalene, or perchlor-ethane, the maximum vapour pressure is much more rapidly attained than with ammonium carbamate. The equilibrium in the dissociation of hydrated salts is generally attained only after the lapse of a considerable time, and the inaccurate results of many measurements of the pressures of dissociation of such salts may be due to this circumstance.[2]

The same difference is also noticeable between the phenomena of fusion and the similar chemical changes in condensed systems; while the former change is complete almost immediately after the change of temperature, the latter takes place very slowly indeed.

It is therefore necessary, in the experimental study of the changes which tend to bring about equilibrium, to take cases of chemical change, for only in such cases is the course of the change sufficiently slow to be susceptible of measurement.

---

[1] Berichte, 4, 646 and 780, 1871.

[2] Frowein, Zeit. phys. Chem. 1, 1, 1887.

EQUILIBRIUM.

THIRD PART.

DIAGRAM OF THE INFLUENCE OF TEMPERATURE ON EQUILIBRIUM. DETERMINATION OF THE TRANSITION POINT OF SULPHUR.

The application of the laws governing equilibrium is greatly facilitated by the diagram which will now be described; this simplifies the expression of the complex phenomena very considerably, and has made it possible to predict the transition temperature of sulphur.

In order to obtain a graphical representation of the equation

$$\frac{d \log K}{dT} = \frac{q}{2T^2},$$

we will take the values of K as ordinates and those of T as abscissae.

The transition temperature of the two crystalline modifications of sulphur may then be calculated in the following way.

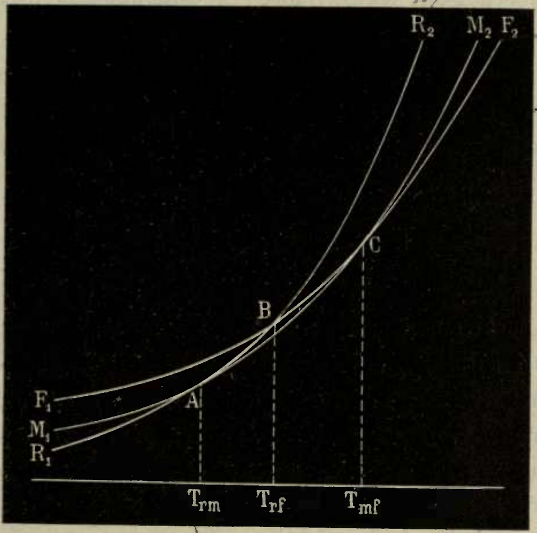
Representing first the physical equilibrium which occurs between solid rhombic sulphur and sulphur vapour, we obtain the curve $R_1 R_2$, the ordinates of which are the concentrations of the sulphur vapour, the abscissae the corresponding absolute temperatures. Since the concentration C_r of the sulphur vapour in equilibrium with rhombic sulphur is equal to K, this curve represents the equation

$$\frac{d \log C_r}{dT} = \frac{q_r}{2 T^2},$$

where q_r is the heat evolved by the condensation of the sulphur vapour in the rhombic form, without the performance of external work.

Monosymmetric sulphur also evaporates until its vapour has reached a certain maximum pressure; the equilibrium may therefore be represented in a similar way by the curve M_1M_2, corresponding to the equation

stable



fused

K

as vapor p.

96

Fig. 42.

$$\frac{d \log C_m}{dT} = \frac{q_m}{2\,T^2},$$

C_m being the concentration of the vapour of monosymmetric sulphur at its maximum pressure, and q_m the heat evolved by the condensation of sulphur vapour in the form of monosymmetric sulphur, without the performance of external work.

The two curves R_1R_2 and M_1M_2 intersect at A, corresponding to the temperature T_{rm}. At this point the concentrations, and therefore the pressures of the vapour given off by the two modifications of sulphur are identical; above it the vapour pressure of the rhombic is greater than that of the monosymmetric modification, from which it follows that at temperatures higher than T_{rm} rhombic sulphur will change into monosymmetric sulphur in consequence of a kind of distillation, since the rhombic emits vapour at a greater pressure than the monosymmetric sulphur.

At temperatures lower than T_{rm} the opposite process will go forward, so that T_{rm} is the transition temperature.

A third curve F_1F_2 may now be added to the two which have been described; this represents the physical equilibrium which exists between fused sulphur and sulphur vapour, it corresponds therefore to the equation

$$\frac{d \log C_f}{dT} = \frac{q_f}{2\,T^2},$$

where C_f is the concentration of the saturated vapour in contact with liquid sulphur, and q_f is the heat evolved by the condensation of sulphur vapour to the liquid condition, no external work being done.

The curve F_1F_2 cuts the curves M_1M_2 and R_1R_2 in the points B and C, which therefore correspond to two transition temperatures. B represents the temperature T_{rf} above which rhombic sulphur passes into the liquid condition and below which the opposite occurs, so that T_{rf} is the melting point of rhombic sulphur on the absolute scale.

Similarly the point of intersection C corresponds to the melting point of monosymmetric sulphur on the absolute scale.

We are now in a position to obtain, by means of the diagram, the relationship which exists between the three transition temperatures T_{rm}, T_{rf}, and T_{mf}, and the quantities of heat which are evolved by the changes occurring at these temperatures. From this relation it is possible to calculate the value of T_{rm}, i. e., the transition temperature of the two crystalline modifications of sulphur.

The triangle A B C may be regarded as bounded by straight lines, since the angles B C A, and B A C are very small. This follows from the fact that the concentrations of the sulphur vapour in the neigbourhood of the transition temperatures (about 100°) viz. AT_{rm}, BT_{rf}, and CT_{mf}, are very small.

We have therefore,

$$AB : BC = \sin BCA : \sin BAC$$

in which $AB : BC = T_{rf} - T_{rm} : T_{mf} - T_{rf}$, approximately.

Again, owing to the small values of $A\,T_{rm}$, $B\,T_{rf}$, and $C\,T_{mf}$, the following relation holds good approximately;

$$\text{Sin } BCA : \sin BAC = \frac{d\,C_m - d\,C_f}{dT} : \frac{d\,C_r - d\,C_m}{dT}$$

$$= \frac{d \log C_m - d \log C_f}{dT} : \frac{d \log C_r - d \log C_m}{dT}$$

From our previous equations we have,

$$\frac{d \log C_m - d \log C_f}{dT} = \frac{q_m - q_f}{2T_{mf}^2} \text{ and } \frac{d \log C_r - d \log C_m}{dT} = \frac{q_r - q_m}{2T_{mr}^2}$$

therefore,

$$\text{Sin } BCA : \sin BAC = \frac{q_m - q_f}{2T_{mf}^2} : \frac{q_r - q_m}{2T_{mr}^2},$$

or

$$T_{rf} - T_{rm} : T_{mf} - T_{rf} = \frac{q_m - q_f}{2T_{mf}^2} : \frac{q_r - q_m}{2T_{mr}^2}$$

In order to calculate the transition temperature T_{rm} the different numerical values must now be introduced.

T_{mf} and T_{rf}, the melting points of monosymmetric and rhombic sulphur respectively, have been determined by Brodie[1] who found

$$T_{mf} = 273 + 120, \qquad T_{rf} = 273 + 114.5.$$

$q_m - q_f$ is the heat evolved by the conversion of fused sulphur into the solid monosymmetric modification, that is its heat of fusion, $q_r - q_f$ is similarly the heat of fusion of the rhombic modification.

According to Berthelot,[2]

$$q_m - q_f : q_r - q_m = 0.15 : 0.04$$

---

[1] Proc. Roy. Soc. 7, 24, 1856.

[2] Essai de Mécanique Chimique 1, 413 and 553.

So that we obtain

$$387.5 - T_{rm} : 5.5 = \frac{0.15}{393^2} : \frac{0.04}{T_{rm}^2},$$

or

$$T_{rm} = 273 + 96.3.$$

The transition temperature of the two crystalline modifications of sulphur is therefore 96°.3. Reicher determined this temperature by direct experiment as 95°.4.

Experiment and calculation are therefore in very satisfactory agreement.

EQUILIBRIUM.

FOURTH PART.

DISPLACEMENT OF EQUILIBRIUM WITH THE TEMPERATURE. PRINCIPLE OF MOBILE EQUILIBRIUM.

The observations which have been made on the different forms of equilibrium lead to a simple general conclusion, which may be expressed in the following way: —

Every equilibrium between two different conditions of matter (systems) is displaced by lowering the temperature, at constant volume, towards that system the formation of which evolves heat.

This principle applies to every possible case, both of chemical and physical equilibrium. It indicates the effect of an elevation, as well as of a depression of the temperature; it expresses, finally, the fact that if no system is present the formation of which evolves heat, a change of temperature will not displace the equilibrium. This principle, which will be called the "*principle of mobile equilibrium*," will now be demonstrated for all cases of equilibrium. The three forms of chemical equilibrium, and the three forms of physical equilibrium will accordingly be considered.

I. THE PRINCIPLE OF MOBILE EQUILIBRIUM APPLIED TO HETEROGENEOUS SYSTEMS.

a. *Physical equilibrium in heterogeneous systems. Evaporation and condensation.*

The two different states of matter with which we have to do in this equilibrium, are, on the one hand, the liquid or solid, on the other hand the gaseous state; the liquid state being that which is formed with evolution of heat from the gaseous one, the principle requires that the quantity of liquid should increase at the expense of the vapour when the temperature is lowered; that is to say, that cooling must favour condensation; nothing further need therefore be said on this point.

b. *Chemical equilibrium in heterogeneous systems.*

As we have already seen, the equations

$$K = \frac{C_2^{n_2}}{C_1^{n_1}}, \text{ and } \frac{d \log K}{dT} = \frac{q}{2\,T^2},$$

hold good here, q being the heat evolved when the system whose concentration is C_1 is formed, and n_1 and n_2 relating to those bodies which are not in the condensed condition. In demonstrating the principle here, it is convenient to distinguish between those cases in which n_1 and n_2 both differ from zero, as in the equilibrium between hydrogen, ferrous oxide, steam and metallic iron,

$$H_2 + FeO \rightleftarrows H_2O + Fe,$$

where n_1 and n_2 are both unity, and those in which n_1 or n_2 is equal to zero, as in the classical equilibrium

$$CaCO_3 \rightleftarrows CaO + CO_2,$$

where $n_1 = 0$, and $n_2 = 1$.

We shall only consider the latter case here, since the former will be explained later together with homogeneous chemical equilibrium. Confining ourselves then to heterogeneous equilibria in which only one of the systems contains substances in the uncondensed condition, and calling the concentration of this system C_2, the equations, after putting $n_1 = 0$, take the following form: —

$$K = C_2^{n_2}, \text{ and } \frac{d \log K}{dT} = \frac{q}{2T^2},$$

and therefore

$$n_2 \frac{d \log C_2}{dT} = \frac{q}{2\,T^2}.$$

From this it is evident that the system whose concentration is C_2 will increase or diminish in quantity, at the expense of the other system, when the temperature rises, according as q is positive or negative, while a fall of temperature will produce the opposite result.

The equilibrium is therefore always displaced by a fall of temperature towards the system which is formed with evolution of heat, as the principle enunciated above requires.

The equilibrium above mentioned,

$$NH_4HS \rightleftarrows H_2S + NH_3,$$

is a good example of the application of the principle; the system NH_4HS, the formation of which from $H_2S + NH_3$ evolves heat, is produced at the expense of the latter when the temperature falls.

II. THE PRINCIPLE OF MOBILE EQUILIBRIUM APPLIED TO CONDENSED SYSTEMS.

a. *Physical equilibrium in condensed systems. Fusion and solidification.*

The solid and liquid states of matter are to be considered here. The principle of mobile equilibrium requires that the solid, the quantity of which suddenly increases at the expense of the liquid when the temperature sinks, shall be formed with evolution of heat; that is, solidification evolves, fusion absorbs heat.

b. *Chemical equilibrium in condensed systems. Incompatible systems.*

In the physical equilibria just considered the truth of the principle is obvious, the phenomena being so well known; we shall see that it is also in complete harmony with the phenomena of chemical equilibrium in condensed systems. These equilibria undergo sudden displacement at a definite temperature; the demonstration of the truth of the principle in this case, depends therefore on showing that the change, which, at the transition point, is brought about by lowering the temperature, will always lead to the production of the system which is formed with evolution of heat.

Taking for example the change of rhombic into monosymmetric sulphur, or that of cyanuric acid into cyamelide, cases in which each system contains only one substance and in which the vapour evolved by both systems is the same, the truth of the principle may be shown as follows.

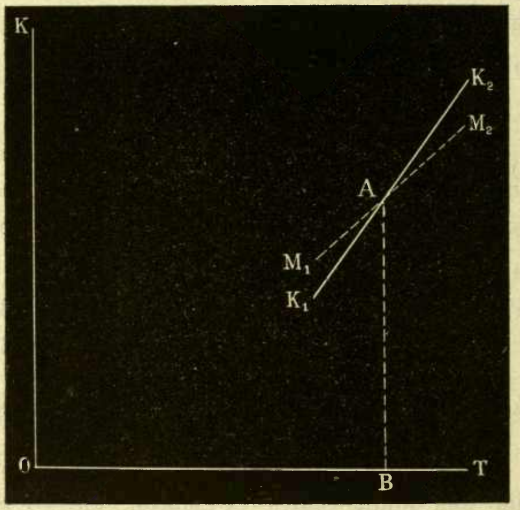


Fig. 43.

The equilibria which subsist between each of the two systems and the vapour which it emits may be represented graphically by taking the concentrations of the vapour, measured at its maximum pressure, as ordinates, and the temperatures as abscissae, fig. 43. Suppose that in the figure the lines $M_1 M_2$ and $K_1 K_2$ represent these quantities for the two allotropic modifications of sulphur.

According to what is said on p. 213 the point of intersection, A, which represents the temperature at which the vapour pressures are equal, is the transition point; above the temperature O B the modification to which the line $M_1 M_2$ refers will exist, below it that referred to by $K_1 K_2$. For sulphur, therefore, $M_1 M_2$ would refer to the monosymmetric, $K_1 K_2$ to the rhombic modification.

It must now be shown that the modification which is stable at the lower temperature is formed with evolution of heat from that which is stable at the higher temperature. The equations, of which the curves $M_1 M_2$ and $K_1 K_2$ are the graphical representations, are

$$\frac{d \log C_r}{dT} = \frac{q_r}{2T^2}, \text{ and } \frac{d \log C_m}{dT} = \frac{q_m}{2T^2},$$

C_r and C_m being the concentrations of the saturated vapour given off by rhombic and monosymmetric sulphur respectively, and q_r and q_m being the quantities of heat evolved by the formation of rhombic and monosymmetric sulphur from sulphur vapour, no external work being performed.

The heat evolved by the conversion of monosymmetric into rhombic sulphur is $q_r - q_m$, and from the figure it is evident that

$$\frac{d \log C_r}{dT} > \frac{d \log C_m}{dT},$$

from which $q_r > q_m$, and therefore $q_r - q_m$, the evolution of heat accompanying the change, is positive, as is required by the principle of mobile equilibrium.

The results of direct experiment are also in agreement with this conclusion. MITSCHERLICH[1] found that heat is evolved when monosymmetric sulphur is transformed into the rhombic modification. TROOST and HAUTEFEUILLE[2] observed that the conversion of cyanuric acid into cyamelide, which takes place when the temperature is depressed, is accompanied by an evolution of heat. LEHMANN[3] found that the different changes which ammonium nitrate undergoes while cooling give rise to liberation of heat. The researches of FROWEIN and of VRIENS (pages 158 and 161) likewise lend support to the principle that the system which is formed at the expense of the other with evolution of heat is produced when the temperature falls.

---

[1] POGG. Ann. 88, 328, 1853.

[2] Compt. rend. 67, 1345, 1868.

[3] GROTH's Zeitschrift für Krystallographie, 1, 106, 1877.

III. THE PRINCIPLE OF MOBILE EQUILIBRIUM APPLIED TO HOMOGENEOUS SYSTEMS.

The physical equilibria which come under this heading may be neglected, since the principle relates to equilibria between two different states of matter, and there is no reason for assuming the existence of two different substances in cases where, for example, deviations from Boyle's law show that some molecular action occurs which, however, is insufficient to give rise to any sharply defined product.

In the case of homogeneous chemical equilibrium, the proof of the truth of the principle depends on the equations

$$K = \frac{C_2^{n_2}}{C_1^{n_1}}, \ldots\ldots \text{(I), and } \frac{d \log K}{dT} = \frac{q}{2T^2}, \ldots\ldots \text{(II)}$$

where q is, as before, the heat evolved by the formation of the system of concentration C_1 at constant volume.

We may distinguish between cases in which q is positive and those in which it is negative. When it is positive, that is, when heat is evolved by the formation of the system of concentration C_1, the constant of equilibrium K will decrease with falling temperature, and therefore C_1 will increase at the expense of C_2, because $C_1 + C_2$ remains constant, the volume being maintained invariable. When q is negative the first system is formed with absorption of heat, and the second, therefore, with evolution of heat; the second system, of concentration C_2, will then be formed at the expense of the first when the temperature falls. A depression of temperature thus always increases the quantity of the system the formation of which evolves heat.

The equilibrium

$$N_2O_4 \rightleftarrows 2\ NO_2$$

may serve as an example of this. According to the principle of of mobile equilibrium the system N_2O_4 will be formed at lower temperatures at the expense of the system $2\,NO_2$, which is well known to be the case.

The application of the principle of mobile equilibrium makes it possible to predict the direction in which any given chemical equilibrium will be displaced at higher or at lower temperatures. Since the equilibrium is displaced, on depressing the temperature, towards those systems which are formed with evolution of heat, these will predominate at lower temperatures, while at higher temperatures they will disappear more and more, giving place to those which are formed with absorption of heat.

In the equilibria

$$N_2O_4 \rightleftarrows 2\,NO_2$$
$$NH_4.HS \rightleftarrows NH_3 + H_2S$$
$$\text{Cyamelide} \rightleftarrows \text{Cyanuric acid}$$

for example, the quantities of the systems on the left hand side will increase more and more at the expense of those on the right as the temperature falls, so that at lower temperatures the fraction of the substance which exists in equilibrium in the form of the system to the left will be very considerable. Since the temperature on the surface of the earth, at which the majority of observations is made, is relatively low, about 273° above absolute zero, it is *a priori* to be expected that under ordinary conditions the majority of chemical equilibria have been displaced towards those systems which are formed with evolution of heat. This view is fully verified in all parts of chemistry; to see this clearly, however, it is necessary to consider more in detail those equilibria which are so completely displaced in one direction that their true character is not at once obvious. Consider for example, the equilibrium

$$2\,H_2O \rightleftarrows 2\,H_2 + O_2,$$

which as is well known, was shown by DEVILLE to occur, owing to the partial decomposition of steam, at about 1000°. According to our principle, the equilibrium must be displaced towards the system which is formed with evolution of heat, that is water, when the temperature is allowed to fall; this is corroborated by experiment. This displacement is such that, at the ordinary temperature, water represents the stable condition of a mixture of oxygen and hydrogen, the latter being converted practically entirely into water under the influence of the most diverse actions.

If, now, chemical equilibria in general are, at the ordinary temperature, displaced towards the systems which are formed with evolution of heat, it is evident that *those chemical changes which occur at the ordinary temperature must in the majority of cases be accompanied by evolution of heat.*

Similar considerations, based on the principle of mobile equilibrium, show that at very high temperatures the opposite must take place, and that the changes which occur under these conditions will in general absorb heat. This conclusion also is fully corroborated by experience.

It is perhaps not superfluous to point out that these conclusions are based on the exact laws of thermodynamics, since the principle of mobile equilibrium itself is deduced from them. The principle may, further, be brought into a form which allows of numerical calculations, the accuracy of which has been shown by numerous applications.

It is also in place here to compare these results with the views which have been expressed by THOMSEN and BERTHELOT on this subject, more especially because the ideas of BERTHELOT, although contradicted by the facts and recently abandoned[1] by the author himself, are still represented in many text books as being in accordance with experience.

In 1853 THOMSEN[2] expressed himself thus: —

"Every simple or complex change of a purely chemical nature is accompanied by an evolution of heat."

BERTHELOT[3] in 1867 put forward his views in the form of the *principle of maximum work*, which states that: "Every chemical change, accomplished without the intervention of external energy tends towards the production of the bodies or of the system which evolves the greatest quantity of heat."

There is a great similarity between these two statements; in both of them the principal idea is that chemical change evolves heat; **Thomsen** confines the application of the statement to purely chemical changes, while **Berthelot** confines it to those which occur "without the intervention of external energy" (une énergie étrangère).

---

[1] Compt. rend. 118, 1378, 1894.

[2] Pogg. Ann. 88, 349, 1853; 90, 261, 1853; 91, 83, 1854; 92, 34, 1854; Berichte, 6, 423, 1873.

[3] Compt. rend. 71, 303, 1870. Ann. Chim. Phys. (4), 18, 103, 1869. Bull. Soc. Chim. 19, 485, 1873.

While **Thomsen**, in his "Thermochemische Untersuchungen", [1] recognises fully the exceptions to his earlier statement which have been discovered, and seeks for a hypothesis which shall be in better accordance with the facts, **Berthelot**, in his "Essai de Mécanique Chimique", [2] upholds his view, attempting to bring the facts into harmony with it, and it is only recently that he has abandoned it.

The principle of mobile equilibrium possesses the advantage that it is entirely free from any hypothesis, being a rigorous deduction from the laws of thermodynamics. It further allows us to predict that under ordinary conditions equilibrium will exist, in a great many cases, when the substances are present almost entirely in the form of the system which is formed with evolution of heat, and therefore that the majority of changes which occur under ordinary conditions will be accompanied by an evolution of heat. The application of the principle shows, also, that at very high temperatures, equilibrium will exist in the majority of cases when the system which is produced with absorption of heat predominates, and therefore that most changes which occur at high temperatures will absorb heat; we might in this case, following the example of **Berthelot**, speak of a *principle of minimum work*. It is also to be noted that the principle of mobile equilibrium places all equilibria, whether physical or chemical, on the same footing, emphasising the great similarity of the two classes of phenomena, and embracing all equilibria between material systems.

Lastly, it is of importance that the principle is capable of quantitative expression, and may therefore be applied to numerical calculations, as has been shown in the examples already considered.

By means of this quantitative expression of the principle it is possible to determine the *conditions under which the principle of*

---

[1] 1883, vol. III, 523.

[2] Vol. I, 421.

maximum work is rigorously true. To do this we have to find the conditions under which any given equilibrium will be displaced completely in the direction of the system which is formed with evolution of heat; we shall see that this only occurs at absolute zero.

In a case of homogeneous equilibrium the quantitative expression of the principle of mobile equilibrium is contained in the equations

$$K = \frac{C_2^{n_2}}{C_1^{n_1}} \ldots\ldots\ldots (I) \text{ and } \frac{d \log K}{dT} = \frac{q}{2\,T^2} \ldots\ldots\ldots (II)$$

Suppose that the system whose concentration is C_1 is formed with evolution of heat, and that q is therefore positive. The problem is to find the conditions under which the concentration of the second system C_2 becomes zero. This is evidently the case when $K = 0$. Integrating equation (II), on the assumption that q is constant, we obtain

$$\log K = -\frac{q}{2\,T} + \text{Const.}$$

This gives $K = 0$ when $T = 0$.

Since q is not quite independent of the temperature (see p. 123) it is better not to employ the integrated equation, since the same result may be obtained from equation (II) which gives $K = 0$, when $T = 0$ and q is positive.

Quite similar considerations apply to heterogeneous equilibria; taking for an example the equilibrium

$$NH_4HS \rightleftarrows NH_3 + H_2S,$$

only the system $NH_4 . HS$, which is formed with evolution of heat, will be present in a condition of equilibrium at absolute zero, in other words its dissociation pressure will have disappeared.

The application of the principle to the third form of equilibrium, viz. that in condensed systems, is of considerable interest, for, at absolute zero physical condensation will have reached its limit, and therefore we might have dispensed with the consideration of homogeneous and heterogeneous equilibria, in which

OF THE UNIVERSITY OF CALIFORNIA

bodies in a condensed condition either do not participate or do so only partially. It is possible to show that in an equilibrium between condensed systems, only that one which is formed with evolution of heat is stable at absolute zero. Suppose that at a given temperature the system whose formation absorbs heat is alone present in the condition of equilibrium, as, for example, is the case with monosymmetric sulphur at about 100° C. in the equilibrium

$$\text{rhombic sulphur} \rightleftarrows \text{monosymmetric sulphur.}$$

We have then to prove that on cooling the system it will pass through a transition point, so that before reaching absolute zero the system which is formed with evolution of heat will have taken the place of the other. As before call C_r the concentration of the vapour of rhombic sulphur at its maximum pressure, q_r the heat evolved by its condensation to rhombic sulphur, and C_m and q_m the corresponding quantities for monosymmetric sulphur, then

$$\frac{d \log C_r}{dT} = \frac{q_r}{2T^2}, \text{ and } \frac{d \log C_m}{dT} = \frac{q_m}{2T^2},$$

and therefore,

$$\frac{d \log \frac{C_r}{C_m}}{dT} = \frac{q_r - q_m}{2\ T^2} = \frac{q_{mr}}{2\ T^2},$$

where q_{mr} is the heat evolved by the transformation of monosymmetric into rhombic sulphur.

The conditions which must be fulfilled in order that the system which is formed with absorption of heat (monosymmetric sulphur) shall exist alone in stable equilibrium are,

$$C_r > C_m \text{ and } q_{mr} > 0.$$

According to the above differential equation $\frac{C_r}{C_m} = 0$ when $T = 0$, and therefore the value of $\frac{C_r}{C_m}$ must be equal to unity at some temperature intermediate between absolute zero and the temperature at which $\frac{C_r}{C_m} > 1$; the temperature at which $\frac{C_r}{C_m} = 1$ is the transition temperature the existence of which was to be proved.

From the preceding, therefore, all chemical equilibria without exception are displaced completely at absolute zero towards those systems which are formed with evolution of heat, and only under these circumstances is the principle of maximum work rigorously true.

AFFINITY.

I. THE COMPARISON OF CHEMICAL AFFINITIES.

This section will be devoted to the determination of the magnitude of chemical affinity in different cases by means of the conceptions already obtained, and without using any special hypotheses.

If affinity be considered as a force, it may be expressed in kilograms or in atmospheres, and the work which it can effect in kilogram-metres or in calories.

Regarding it as the force which produces chemical change we shall arrive, by means of a more detailed consideration of the equilibrium of condensed systems, at a conception which may serve as the starting point of our further studies. Equilibrium in such systems is characterised by the existence of a transition point. For example, in the equilibrium[1]

$$CuCl_2 . 2KCl . 2H_2O \rightleftarrows CuCl_2 . KCl + KCl + 2H_2O,$$

it has been proved experimentally that above 92°.4 the system on the right completely replaces that on the left, while below it the reverse takes place. This temperature, characterised by the fact that at it both systems simultaneously exist in equilibrium, is the transition temperature. The law of the incompatibility of condensed systems makes it possible to predict the existence of a transition temperature in every such equilibrium, for example in the reaction

$$KI + NaCl \rightleftarrows KCl + NaI,$$

the affinity, that is the force which brings about the change, or the difference between the affinities which are at work in the two systems, is zero at the transition temperature; further on passing through the transition temperature the value of the affinity, or of the difference of affinities, changes sign.

---

[1] See p. 172.

In the case of copper bi-potassium chloride, for example, the affinity which brings about the formation of the system to the right is, at 92.°4, equal to that bringing about the formation of the system on the left, or, what is the same thing, the difference between the two affinities is zero at this temperature.

II. MEASUREMENT OF AFFINITY.

The magnitude of the affinity which retains the water of crystallisation in salts.

We will now taken up a question which was attacked by Mitscherlich[1] in 1844, namely: — What is the magnitude of the affinity which binds the water of crystallisation in decahydrated sodium sulphate?

Mitscherlich expresses himself as follows: —

"If a crystal of hydrated sodium sulphate be introduced into the Torricellian vacuum at 9°, the mercury falls 5.45 mm., owing to the water evaporating after having escaped from combination. Under the same circumstances water alone produces a depression of 8.72 mm. and therefore the affinity of the water of crystallisation for the sodium sulphate is equal to a pressure of 3.27 mm., or about $^1/_{84}$ kgrm. per sq. cm."

Although the attraction which sodium sulphate exerts on its water of crystallisation is, as will be shown later, many thousand times greater than Mitscherlich supposed, yet a connexion may be shown to exist between the magnitude of this attraction and the diminution of the vapour pressure.

Consider the attraction which a solution of a salt exerts on pure water, or, as it might be called, the affinity between a solution and water.

This attraction has been measured by Pfeffer[2] by means of a piece of apparatus consisting of a porous cell, in the walls of which a membrane of copper ferrocyanide has been precipitated,

[1] Lehrbuch der Chemie, 4te Aufl. 565.

[2] Osmotische Untersuchungen, Leipzig, 1877, p. 4.

which contains the solution of the salt. The copper ferrocyanide membrane is semi-permeable, that is, it possesses the property of allowing water to pass through it, while the salt is unable to do so.

If now the cell, filled with the solution of the salt, be immersed in pure water, after closing its open end and connecting it to a manometer, the pressure within it will be seen to increase, the water passing in through the membrane in consequence of the attraction of the salt solution. After some time a condition of equilibrium is attained, because the pressure in the porous cell increasingly resists the inflow of water, finally stopping it entirely. The pressure which is then indicated by the manometer, *i. e.* the osmotic pressure of the solution at the temperature of the experiment, is evidently a measure of the affinity between the solution of the salt and pure water.

The following numbers were obtained by Pfeffer[1] with a solution containing one per cent. of sugar.

Temperature.	Osmotic pressure in atmospheres.
6°.8	0.664
13 .7	0.691
14 .2	0.671
15 .5	0.684
22	0.721
32	0.716
36	0.746

By means of this method it is possible to determine the magnitude of the affinity between sodium sulphate and its water of crystallisation. For this purpose it is first necessary to obtain the relation existing between the affinity of a salt for water and the decrease of the vapour pressure of water produced by dissolving a salt in it.[2]

---

[1] Loc. cit. p. 85.

[2] The equations which follow may be obtained from the laws of osmotic pressure, depression of freezing point, etc. which have been discovered since the appearance of the Études de Dynamique Chimique in 1884. The original form has, however, been retained here since it possesses a certain historical interest.

Suppose we have a closed vessel, fig. 44, filled partly with steam E, partly with water. The lower part of the vessel, containing the water, is divided into two compartments A and B by a semi-permeable partition. The aqueous vapour having attained its maximum pressure at the prevailing temperature, and being therefore in equilibrium with the water, an infinitesimal quantity of some salt is dissolved in the water in A. The equilibrium, which is disturbed by the attraction of the salt for the water, will tend to be re-established by the passage of water from B into A by two different paths, first, directly through the semipermeable membrane, secondly, indirectly in the condition of vapour through E.

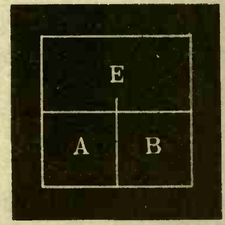


Fig. 44.

The direct passage of the water into A will produce an osmotic pressure which might be measured by means of a manometer as in Pfeffer's experiments; let its value be d D atmospheres.

The pressure which brings about the flow of vapour from E to A may be measured by determining the diminution in the pressure of the vapour at E which would just suffice to prevent condensation in A. This will be the case when the pressure of the vapour in E is equal to the vapour pressure of the solution A. The pressure which causes the flow of vapour from E to A is therefore equal to the diminution in the vapour pressure of water which is produced by dissolving the salt in it; let this be — d S atmospheres.

The attraction of the salt solution for water thus gives rise to two forces, d D and — d S, according as it acts on liquid water or on aqueous vapour. Assuming that the attraction of the solution in A for a molecule of water is independent of the state of aggregation of the water, the ratio between the two forces of attraction will be the same as that between the quantities of water contained in equal volumes of liquid and vapour.

The weight of 1 litre of liquid water may be taken as 1 kgrm., and 1 litre of aqueous vapour under the pressure of S atmospheres weighs

$$S \times 0.000806 \frac{273}{T} = \frac{S}{4.55T} \text{ kgrms.}$$

We may therefore write,

$$- dS : dD = \frac{S}{4.55T} : 1.$$

Integrating this expression we find,

$$- \log S = \frac{D}{4.55T} + \text{const.}$$

If S_w be the vapour pressure of water at T, we have for $S = S_w$, $D = 0$.

The integration constant may be eliminated by means of this, and we obtain

$$D = 4.55\,T \log \frac{S_w}{S_s},$$

or, introducing common logarithms,

$$D = 10.5\,T \operatorname{Log} \frac{S_w}{S_s},$$

where S_s is the vapour pressure of the solution of the salt.

As an example of the application of this equation, the values of D may be calculated for the solutions of sugar the osmotic pressures of which were determined by Pfeffer.

The value of $\frac{S_w}{S_s}$ may be calculated approximately for a given solution from its freezing point by means of thermodynamics.

Guldberg[1] has shown that, the freezing point of an aqueous solution being — t°, the following relation exists between it and $\frac{S_w}{S_s}$: —

$$\frac{S_w}{S_s} = \frac{1}{1 - 0.00954\,t}$$

Introducing this into the equation for D, we obtain

$$D = - 10.5 \operatorname{Log} (1 - 0.00954\,t)$$

---

[1] Compt. rend. 70, 1349, 1870. Ostwald, Lehrbuch der Allgem. Chem. 2te Aufl. I, 757.

Raoult[1] has found that the value of t for a one per cent. solution of sugar is 0.°054.

The following table contains the values of the osmotic pressure of a one per cent. solution of sugar, at the different temperatures given, (1) observed directly by Pfeffer, (2) calculated by means of the above equation.

Temperature.	D observed.	D calculated
6° .8	0.664	0.668
13 .7	0.691	0.684
14 .2	0.671	0.686
15 .5	0.684	0.689
22 .0	0.721	0.704
32 .0	0.716	0.728
36 .0	0.746	0.737

We are now in a position to calculate the magnitude of the force with which a solution, or a hydrated salt, retains the water in it, when the vapour pressure of the solution, or the dissociation pressure of the hydrated salt, is known, and thus to answer the question proposed by Mitscherlich in 1844.

The following table contains the results of the calculation made by means of the equation

$$D = 10.5\ T \operatorname{Log} \frac{S_w}{S_s}.$$

Name of the salt.	Temperature.	$D = 10.5\, T \operatorname{Log} \frac{S_w}{S_s}.$
$CuSO_4.\ 5\,H_2O$	39°.70	1300 atmos.
$BaCl_2.\ 2\,H_2O$	43 .45	1642 ,,
$ZnSO_4.\ 7\,H_2O$	29 .95	532 ,,
$ZnSO_4.\ 6\,H_2O$	29 .95	709 ,,

---

[1] Compt. rend. 94, 1517, 1882.

The values of $\frac{S_w}{S_s}$ have been calculated from the numbers obtained by Frowein (pp. 160 and 161).

The statement that the value of D for $CuSO_4 . 5H_2O$ at 39°.7 is 1300 atmospheres, means that if copper sulphate, from which two molecules, for example, of its water of crystallisation had been removed, were brought, at the temperature mentioned, into Pfeffer's osmometer, a pressure of 1300 atmospheres would be required in order to prevent the water from penetrating the semipermeable membrane and combining with the copper sulphate. The experiment could not of course be actually carried out in the usual way, since we are here dealing with a solid substance.

III. DETERMINATION OF THE WORK WHICH CAN BE DONE BY AFFINITY.

The quantity of work which can be done by affinity of known magnitude will now be calculated.

If a kilogram-molecule of hydrated copper sulphate (249 kgrms. of $CuSO_4 . 5H_2O$) be taken, and a molecule of water (18 kgrms.) be removed from it by means of the air pump, the vapour pressure of the crystals remains, according to the experiments of Pareau[1], completely constant, that is, the salt tends to retain the water which is being removed from it, from beginning to end, with a force of 1300 atmospheres (at 39°.7). If the salt $CuSO_4 . 4H_2O$ were brought into a Pfeffer's cell (under this pressure) the work which would be done by the 18 kgrms, of water on passing into it through the semipermeable membrane, owing to the affinity of the salt for it, would be

$$A = 1300 \times 10333 \times \frac{18}{1000} = 241792 \text{ kgrm.metres, or } 568 \text{ calories.}$$

Generally, the problem may be treated as follows: the magnitude of the affinity is, according to what is said on p. 233,

$$D = 4.55 \ T \log \frac{S_w}{S_s}.$$

---

[1] De Pompbarometer. Inaugural Dissertation. Utrecht, 1875.

The work which this force can do, during the transport of 18 kgrms. of water, is

$$A = \frac{D}{425.7} 10333 \frac{18}{1000} = 2T \log \frac{S_w}{S_s} \text{ calories.}$$

A more complicated case will now be considered. The force will be calculated which comes into play when a salt, say $FeSO_4 . 6H_2O$, takes up water from another hydrated salt, say $MgSO_4 . 7H_2O$, instead of combining with water in the free state. We may say *a priori* that this can only take place when the dissociation pressure of the $FeSO_4 . 7H_2O$ is smaller than that of the $MgSO_4 . 7H_2O$ at the given temperature. The force D which brings about the transference of the water is equal to the difference between the forces with which each of the sulphates retains its water of crystallisation; it is, therefore,

$$D = 4.55\ T \left(\log \frac{S_w}{{}_1S_s} - \log \frac{S_w}{{}_2S_s}\right) = 4.55\ T \log \frac{{}_2S_s}{{}_1S_s},$$

${}_1S_s$ and ${}_2S_s$ being the dissociation pressures of the ferrous and magnesium sulphates respectively.

The work which can be done by this affinity is therefore

$$A = \frac{D}{425.7} 10333 \frac{18}{1000} \text{ kgrm. metres,}$$

$$\text{or, } A = 2\ T \log \frac{{}_2S_s}{{}_1S_s} \text{ calories.}$$

This may now be extended by the introduction of the idea of the transition point. The following table contains some of the measurements of the dissociation pressures of magnesium and ferrous sulphates made by G. WIEDEMANN[1] at different temperatures.

---

[1] Journ. prakt. Chem. (2) 9, 338, 1874. Although the numerical data contained in the table are, according to FROWEIN'S determinations on $MgSO_4 . 7H_2O$, decidedly inaccurate, the truth of the principle which they serve to illustrate is not affected.

Temperature.	$FeSO_4 . 7 H_2O$ ($_1S_s$).	$MgSO_4 . 7 H_2O$ ($_2S_s$).
40°.2	40.1 mm.	46.3 mm.
50°.4	77 „	77 „
60°.0	131.3 „	122.5 „

From these observations it follows that at 40°.2 the dissociation pressure of the magnesium sulphate, at 60°.0 that of the ferrous sulphate is the greater, while at 50°.4 they are equal; consequently, at temperatures lower than 50°.4 water will pass over to the ferrous salt in a mixture of $FeSO_4 . 6H_2O$ and $MgSO_4 . 7H_2O$, producing $FeSO_4 . 7H_2O$ and $MgSO_4 . 6H_2O$, while at temperatures higher than 50°.4 the transference of water will take place in the opposite direction in a mixture of $FeSO_4 . 7H_2O$ and $MgSO_4 . 6H_2O$ forming the original pair of salts, and finally at 50°.4 the two systems will be in equilibrium. There is therefore a transition point at 50°.4 in the equilibrium

$$FeSO_4 . 7 H_2O + MgSO_4 . 6 H_2O \rightleftarrows FeSO_4 . 6 H_2O + MgSO_4 . 7 H_2O.$$

The force D which brings about the transformation of the second system into the first, at different temperatures, may now be calculated by means of the formula

$$D = 4.55 \ T \log \frac{{}_2S_s}{{}_1S_s},$$

while the work A which can be done by this force, during the transport of 18 kgrms. of water, that is, when the second system changes into the first, is

$$A = 10333 \ \frac{18}{1000} \ 4.55 \ T \log \frac{{}_2S_s}{{}_1S_s} \text{ kgrm. metres,}$$

or

$$A = 2 \ T \log \frac{{}_2S_s}{{}_1S_s} \text{ calories.}$$

The following table contains the results of the calculation.

Temperature.	D in atmos.	A in kgrm. metres.	A in cals.
40°.2	+ 205	+ 38130	+ 90
50 .4	0	0	0
60 .0	— 105	— 19530	— 46

As the table shows, the difference between the affinities acting in the two systems, that is, the affinity producing the reaction, changes sign at the transition point (50°.4), passing through zero; the same is true of the work which it can perform.

We shall now obtain a general expression for the work which a change of this kind can do.

As we have seen, the transition point is the temperature at which the pressures of the saturated aqueous vapour in equilibrium with the two systems are equal. The variation of these maximum pressures with the temperature is given by the general equation

$$\frac{d \log C}{dT} = \frac{q}{2T^2},$$

C being the concentration of the aqueous vapour at the pressure which it has when in equilibrium with the salt, and q the quantity of heat evolved by the combination of 18 kgrms. of this vapour with the salt, no external work being performed.

For ferrous sulphate, therefore, we obtain

$$\frac{d \log C_f}{dT} = \frac{q_f}{2T^2},$$

where q_f is the quantity of heat evolved by the reaction

$$FeSO_4.\ 6\,H_2O + H_2O = FeSO_4.\ 7\,H_2O$$

Similarly for magnesium sulphate we obtain,

$$\frac{d \log C_m}{dT} = \frac{q_m}{2\,T^2},$$

q_m being the heat evolved by the reaction

$$MgSO_4.\ 6\,H_2O + H_2O = MgSO_4.\ 7\,H_2O.$$

The heat evolved by the conversion of the second system into the first in the equilibrium

$$FeSO_4.\ 7\,H_2O + MgSO_4.\ 6\,H_2O \rightleftarrows FeSO_4.\ 6\,H_2O + MgSO_4.\ 7\,H_2O$$

being q, we have

$$q = q_f - q_m,$$

and therefore,

$$\frac{d \log \frac{C_m}{C_f}}{dT} = -\frac{q}{2\,T^2}.$$

This equation is easily integrated since q changes but little with the temperature and may be regarded as independent of it; we obtain,

$$\log \frac{C_m}{C_f} = \frac{q}{2\,T} + \text{const.}$$

Since at the transition temperature P, C_f and C_m are equal, we obtain

$$0 = \frac{q}{2P} + \text{const.}$$

and therefore,

$$\log \frac{C_m}{C_f} = \frac{q}{2\,T}\left(\frac{P - T}{P}\right).$$

Since, further, the concentrations are in the same ratio as the vapour pressures, we may write

$$\frac{C_m}{C_f} = \frac{{}_2S_s}{{}_1S_s}.$$

Finally, introducing the value of the work which can be done by the affinity,

EESE LIBRA

$$A = 2T \log \frac{{}_2S_s}{{}_1S_s}.$$

we obtain

$$A = q \left(\frac{P - T}{P}\right) \ldots\ldots \quad (1)$$

or, in words; *the work, expressed in calories, which the affinity in a given chemical reaction can perform, when the reaction takes place at a given temperature, is equal to the quantity of heat evolved by the reaction, divided by the absolute temperature of the transition point, and multiplied by the difference between the temperature of the transition point and the temperature at which the reaction occurs.*

Considering that the maximum quantity of work which affinity can perform is equal to the quantity of work done by the change when it takes place in a reversible way, it will evidently be possible to obtain equation (1) by means of thermodynamics.

Let us take any case in which one condensed system is transformed into another, and let P be the absolute temperature of the transition point, below which the first of the two systems is replaced by the second completely with evolution of q calories. Suppose the following cycle of reversible operations to be performed: The first system is converted into the second at the transition temperature absorbing q calories; the second system, formed in this way, is cooled to the temperature T, at which it is allowed to change into the first. In doing so the work done by affinity will be equivalent to A calories, if the process take place in a reversible way [1], and the heat evolved will therefore be q—A calories. The temperature is finally raised to the transition point in order to bring the system into its initial condition.

The changes which have occurred in this cycle being all reversible, we have, (from the second law of thermodynamics)

$$\frac{q}{q - A} = \frac{P}{T}$$

and therefore,

$$A = q\,\frac{P - T}{P}.$$

---

[1] The practical means by which this may be approximately realised, depend on the nature of the case considered.

In the special case P = T, we have A = 0, that is, the work done by affinity at the transition temperature, (and therefore the force of affinity itself) is zero.

IV. APPLICATIONS.

1. *Work done by affinity at absolute zero. Diagram of the work done.*

The equation

$$A = q \frac{P - T}{P}$$

shows that at absolute zero A = q, that is, the work which may be obtained from the change is equivalent to the whole of the heat which it evolves. At absolute zero the change could thus occur either with evolution of q calories and without doing any work, or evolving no heat and doing a quantity of work equivalent to q calories.

This is in complete agreement with the conclusion arrived at on page 228, where it is pointed out that the "principle of maximum work" is rigorously true at absolute zero, the quantity of heat evolved being then a measure of the work which can be done by affinity, and its sign therefore indicating the direction in which the change will occur. This is no longer the case at higher temperatures. The work which can be done by affinity is then equivalent to a part only of the heat evolved, the two have the same sign, however, until the transition temperature is reached, at this point the work which can be done by affinity is zero and at higher temperatures its sign is reversed, that is to say work must be performed in order to bring about the reaction. The change of sign accompanies the change in the direction of the reaction which occurs at the transition point.

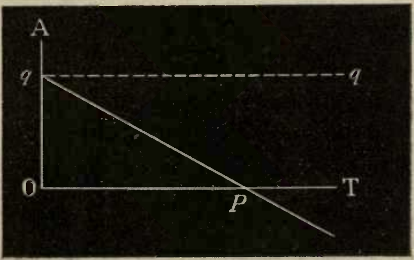


Fig. 45.

Employing the language of the views formerly entertained by

Berthelot, we pass therefore at the transition point from a "*principle of maximum work*" to one of "*minimum work*". This may be represented diagrammatically by taking the quantities of work which can be done by affinity at different temperatures as the ordinates OA and the corresponding temperatures as the abscissae of a curve.

$$\text{For } T = 0,\ A = q, \text{ and for } T = P,\ A = 0.$$

The line q P passing through these points represents the work which can be done by affinity at different temperatures.

Since the heat evolved by the change varies but little with the temperature we may represent it by the straight line qq parallel to OT. It is evident that A and q have the same sign up to the point P, while beyond it they have different signs.

2. *Influence of pressure on the transition point.*

It has already been pointed out on page 210 that there is a close analogy between the transition temperature of condensed systems and the melting point of solid bodies.

The connexion between the latter and the pressure is expressed by the well known equation [1]

$$\frac{dT}{dp} = 10333 \, \frac{T\,(\sigma - \tau)}{425.7\ r}.$$

where $\frac{dT}{dp}$ is the elevation of melting point produced by an increase of one atmosphere in the pressure, T is the absolute temperature, σ the volume of unit weight of the substance in the liquid, and τ that in the solid condition, and r the latent heat of fusion.

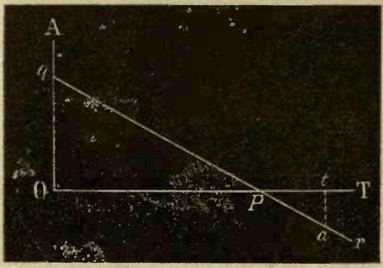


Fig. 46.

It is natural to inquire whether, *mutatis mutandis*, the same equation represents the influence of pressure on the transition temperature. That this is the case is easily shown by means of the diagram (fig. 46), in which the temperatures are taken as abscissæ, and the corresponding quantities of work done by affinity as ordinates.

---

[1] See R. Clausius, Die mech. Wärmetheorie, I, 172, (1887). [1 atmosphere = 10333 kgrms. per square metre, 1 kgrm. degree calorie = 425.7 kgrm.metres].

At temperatures higher than the transition point the work done is represented by the continuation of the line *qP*. The work which can be done by affinity at a temperature *Pt* degrees above *P* is represented by *at*. From the diagram we then obtain

$$\frac{Pt}{OP} = \frac{at}{Oq}.$$

Now Pt is equal to dT, the difference between the transition temperature at atmospheric pressure and that at a pressure d p atmospheres greater, OP = T, the absolute temperature of the transition point, and

$$at = \frac{10333}{425.7} (\sigma - \tau) \text{ dp calories,}$$

$(\sigma - \tau)$ being the increase of volume, in cubic metres, which accopamnies the change of 1 kgrm. of the substance (for example, the change of 1 kgrm. of rhombic into monosymmetric sulphur); Oq = r, the quantity of heat absorbed by the change when it takes place without doing external work.

Making these substitutions we obtain the equation

$$\frac{dT}{dp} = 10333 \frac{T(\sigma - \tau)}{425.7 \, r},$$

which is thus true for a transition point as well as for a melting point when the quantities occurring in it have the meanings given above.

The propriety of applying this equation in such cases has been shown, by quantitative experiments, by Reicher[1], Mallard and le Chatelier[2], and quite recently by Silvio Lussana[3], while Spring and van 't Hoff [1] and Lussana have tested the accuracy of an interesting deduction which may be made from it.

---

[1] Reicher, Inaugural Dissertation, Amsterdam, 1883; Groth's Zeitschrift für Krystallographie, 8, 593, 1884; see also p. 185 ante.

[2] Bull. Soc. Min. de Francc. 7, 478, 1884.

[3] Nuovo Cimento, (4), 1, 97, 1895.

Reicher's experiments refer to the change of rhombic into monosymmetric sulphur. Having found,[2] by means of the dilatometer, that the transition temperature under atmospheric pressure is about 95°.4, he went on to investigate the influence of an increased pressure by means of the apparatus represented in fig. 47. This consists of a dilatometer *D* the capillary of which is connected, on the left, with the apparatus *A B* serving for the production of the pressure, on the right, with the closed manometer *E F*, by means of which the pressure is measured.

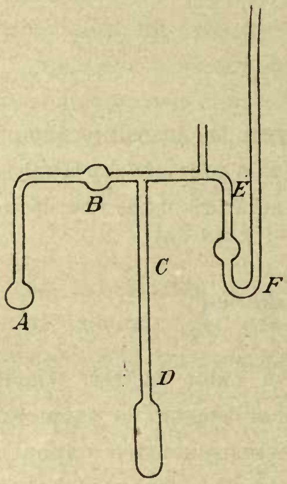


Fig. 47.

The pressure is developed by heating sodium bicarbonate, contained in the bulb *A*, in an oil bath at constant temperature. The small bulb *B* serves to collect the water evolved by the decomposition of the salt. A millimetre scale is attached to the tube of the manometer, which is filled with mercury. At *C* a thread of wool is introduced into the capillary of the dilatometer in order to take up any water which may pass over from *B*; this precaution is necessary since at 95° water decomposes the carbon bisulphide in the mixture of carbon bisulphide and turpentine filling the part of the dilatometer not occupied by sulphur (see p. 183), and by evolving carbon dioxide renders the measurements impossible.

The apparatus being thus arranged is heated to a constant temperature of 95°.6 and the pressure allowed to rise.

---

[1] Zeit. phys. Chem. 1, 227, 1887. See also W. Schwarz, Beiträge zur Kenntniss der umkehrbaren Umwandlungen polymorpher Körper. Göttingen 1892.

[2] See p. 184.

The following table contains the results obtained.

Time.	Level of the liquid in the capillary.	Pressure in atmos.
5 minutes	81.5	9
20 ,,	71.5	14.6
35 ,,	66.5	15.3
50 ,,	64.5	14.1
65 ,,	60.5	15.3
80 ,,	56.25	15.7

The regular fall of the liquid in the capillary shows that monosymmetric sulphur changes into the rhombic form at 95°.6 under a pressure of about 15 atmospheres; the increased pressure therefore causes the change to occur at a temperature at which it would not take place under atmospheric pressure.

It was now attempted, by raising the temperature, to find a point at which the change would not take place under the higher pressure. The following results were obtained at 96°.2.

Time.	Level of the liquid in the capillary.	Pressure in atmos.
5 minutes	59.5	15.7
20 ,,	60.5	15.3
35 ,,	58.5	16
50 ,,	58.75	15.7
65 ,,	58.5	15.7
80 ,,	58	15.9
95 ,,	58	15.3

Since, then, as the table shows, an insignificant change of level was observed at 96°.2 under a mean pressure of 15.8 atmospheres, it may be assumed that the transition point is close to this temperature.

Under a pressure of 4 atmospheres the transition point was found to be 95°.6 [1], an increase of pressure of 15.8 — 4 = 11.8 atmospheres has therefore raised it from 95°.6 to 96°.2, or 0°.6; the elevation of the transition temperature by an increase of pressure of one atmosphere is therefore given by experiment as 0°.05.

The same quantity may be calculated by means of the formula

$$\frac{dT}{dp} = 10333 \; \frac{T\,(\sigma - \tau)}{425.7\,r},$$

by introducing the following numerical values;

$$T = 273 + 95.6 = 368.6$$
$$\sigma - \tau = 0.00001252$$
$$r = 2.52.$$

This gives

$$\frac{dT}{dp} = \frac{10333 \times 368.6 \times 0.00001252}{425.7 \times 2.52} = 0^\circ.044,$$

a value which agrees sufficiently well with that obtained by experiment.

The experiments of S. Lussana were made with the various modifications of ammonium nitrate [2]. He determined the transition temperatures at different pressures, the determinations being made both with rising and falling temperature [3].

The results are given in the following tables in which, however, only those results which were obtained with rising temperature are included. The results obtained with rising temperature always differ from those obtained with falling temperature by some degrees, the influence of the pressure on the transition point was however found to be the same in both cases. [4]

---

[1] See page 184.

[2] See page 164

[3] No agreement was found between the experiments and the values obtained from the equation for $\frac{dT}{dp}$ in the case of $Hg\,I_2$; he ascribes this to the inaccuracy of Rodwell's determinations of the value of $(\sigma - \tau)$.

[4] For example, with ammonium nitrate (first modification).

Transition temperature at	On heating.	On cooling.
1 atmosphere	35°.45	30°.55
250 "	42 .76	37 .95
	Δ t = 7°.31	Δ t = 7°.40

See also Bellati and Romanese, Atti dell' Instituto Veneto, (6), 4, 1395, 1885—6.

	Pressure in atmos.	Transition temperature.	△ T observed.	△ T calculated.
Ammonium nitrate, first modification.	1	35°.45		
	50	37 .05	+ 1°.60	+ 1.42
	100	38 .59	3 .14	2.88
	150	39 .77	4 .32	4.33
	200	41 .47	6 .02	5.79
	250	42 .76	7 .31	7.24
Ammonium nitrate, second modification.	1	85°.85		
	50	85 .15	— 0°.70	—0.68
	100	84 .38	1 .47	1.37
	150	83 .73	2 .12	2.06
	200	83 .03	2 .82	2.75
	250	82 .29	3 .56	3.44

From the equation for $\frac{dT}{dp}$ it follows that when $\sigma - \tau$ is negative $\frac{dT}{dp}$ will also be negative, when r is positive; this conclusion is confirmed by the above results. According to the observations of Bellati and Romanese $\sigma - \tau = - 0.00854$ for the second modification of ammonium nitrate, and therefore, it is to be expected that the transition temperature will be depressed by an increase of pressure; as the table shows this is what occurs. Silver idiode also shows a similar behaviour, being analogous to ice in this respect.

Another change of this kind is the decomposition of copper calcium acetate into its components, studied by Reicher;[1]

$$CuCa(C_2H_3O_2)_4 . 6H_2O \rightleftarrows Cu(C_2H_3O_2)_2 . H_2O + Ca(C_2H_3O_2)_2 . H_2O + 4H_2O.$$

This occurs between 76°.2 and 78° at atmospheric pressure, and since the change of the first into the second system is accompanied by a contraction it is to be expected that the transition temperature will be depressed by an increase in the pressure. Spring and van 't Hoff have shown, experimentally, that this is the case by exposing copper calcium acetate, in

---

[1] See p. 171.

Spring's compression apparatus,[1] to a great pressure. The change occurred quite unmistakably at 40° under a pressure of about 6000 atmospheres, that is, the transition temperature was depressed by the application of this pressure by about 40°.

3. *Calculation of the transition point.*

a. The allotropic modifications of sulphur.

The diagram on page 242, being quite generally applicable to equilibrium in condensed systems, applies also to the simple cases of fusion and solidification.

In these cases the line qP represents the work which can be done by the forces producing solidification or fusion when Oq represents the latent heat of fusion q, and OP the melting point on the absolute scale of temperature. It must be pointed out, however, that qP here, in contradistinction to the case of chemical equilibrium, only represents the work in question near the transition point P, because q is a function of the temperature, the difference between the specific heats of a substance in the solid and liquid states being not inconsiderable[2].

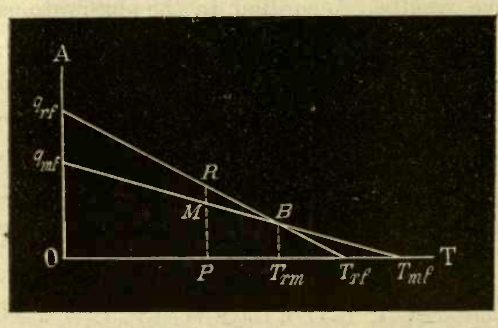


Fig. 48.

By means of this diagram it is possible to calculate the transition temperature of the allotropic modifications of sulphur. To do so, we will first represent the work which may be done by the solidification or fusion of the two modifications of sulphur in a diagram, fig. 48. Let the quantities of heat q_{rf} and q_{mf} which are evolved during the solidification of liquid sulphur to rhombic or monosymmetric sulphur respectively be measured along O A, and let the melting points T_{rf} and T_{mf} (on the absolute scale) be measured along O T. The straight lines $q_{rf}\,T_{rf}$, and $q_{mf}\,T_{mf}$ will then represent the quantities of work in question.

---

[1] Bull. de l'Acad. Roy. de Belgique, 49, 344.

[2] Appendix, note 3.

At any point P in OT erect a perpendicular, then P M and P R are the quantities of work which can be obtained when liquid sulphur solidifies in the form of monosymmetric or rhombic sulphur respectively, and therefore their difference R M represents the quantity of work which can be obtained from the change of monosymmetric into rhombic sulphur at the temperature given. Since there is a point of intersection at B, it is evident that at the corresponding temperature T_{rm} the sign of this quantity of work will change and that its value at this temperature will be zero; these are the characteristics of the transition temperature of the two modifications.

From the figure we see that,

$$T_{rf} - T_{rm} : T_{rf} = B\,T_{rm} : q_{rf},$$

$$\text{and} \quad T_{mf} - T_{rm} : T_{mf} = B\,T_{rm} : q_{mf}.$$

Therefore

$$\frac{T_{rf} - T_{rm}}{T_{mf} - T_{rm}} : \frac{T_{rf}}{T_{mf}} = 1 : \frac{q_{rf}}{q_{mf}},$$

or

$$T_{rm} = \frac{\dfrac{q_{rf}}{q_{mf}} - 1}{\dfrac{q_{rf}}{q_{mf}}\left(\dfrac{1}{T_{rf}} - \dfrac{1}{T_{mf}}\right)}.$$

Introducing the numerical values (page 215)

$$\frac{q_{rf}}{q_{mf}} = \frac{0.19}{0.15}, \quad T_{rf} = 273 + 114.5, \text{ and } T_{mf} = 273 + 120$$

we obtain

$$T_{rm} = 273 + 95.2.$$

The transition temperature calculated is therefore 95°.2, that found experimentally being 95°.4.[1]

Another (approximate) calculation on page 216 gave 96°.3.

---

[1] REICHER found 95°.6 at 4 atmospheres pressure, p. 246; the change for 1 atmosphere being 0°.05, the transition temperature under the pressure of sulphur vapour at 95°—6° will be 95°.4.

b. The transformation of a mixture of sodium ammonium lævo- and dextro-tartrates into sodium and ammonium racemates.

This case is analogous to that which we have just considered. van 't Hoff, van Deventer, Goldschmidt, and Jorissen[1] have described the following changes: —

At 26°.6,

$$2\,(NaNH_4\,C_4H_4O_6.\,4\,H_2O) = (NaNH_4\,C_4H_4O_6.\,H_2O)_2 + 6\,H_2O\,.\,.\quad(1)$$

The so-called racemate of Scacchi is here formed from the mixture of lævo- and dextro-tartrates.

At 34°.5,

$$2\,(NaNH_4\,C_4H_4O_6.\,H_2O)_2 = (Na_2\,C_4H_4O_6)_2 + [(NH_4)_2\,C_4H_4O_6]_2 + 4\,H_2O\,.\,.\,.\,.\,.$$

The salt of Scacchi decomposes at temperatures higher than 35° into the individual racemates.

The temperature at which the change of the mixture of lævo- and dextro-tartrates into the individual racemates occurs, according to the equation

$$4\,(NaNH_4\,C_4H_4O_6.\,4\,H_2O) = (Na_2\,C_4H_4O_6)_2 + [(NH_4)_2\,C_4H_4O_6]_2 + 16\,H_2O\,.\,.\,.\,.$$

may be calculated in the same way as before in the case of sulphur.

The work which can be done by reaction (2) may be represented as a function of the temperature by the line A B, fig. 49, OB representing the transition temperature on the absolute scale (273 + 34.5) and O A the heat absorbed by the change.

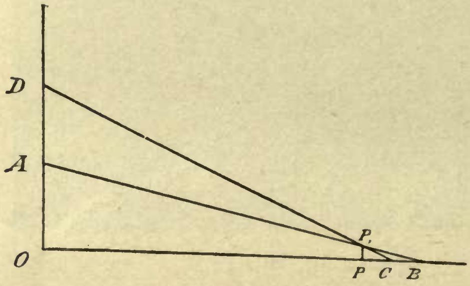


Fig. 49.

Similarly the work which can be done by the change (3) may be represented by a line D C, C being the transition temperature to be calculated, and O D the quantity of heat absorbed by the change.

The point of intersection P_1, corresponds therefore to the temp-

---

[1] Zeit. phys. Chem. 1, 173, 1887; 17, 49, 1895; see also p. 170.

REESE LIBRA
OF THE
UNIVERS
OF CA

erature at which no work can be obtained from the change of the mixture of lævo- and dextro-tartrates into the racemate of SCACCHI, that is, the transition point of change (1), (273 + 26.6).

The quantities of heat evolved by the changes may be taken as approximately equal to the differences between the heats of solution of the different systems concerned. These are as follows: —

$NaNH_4\,C_4H_4O_6.\,4\,H_2O$ — 11726 cals.
$NaNH_4\,C_4H_4O_6.\,H_2O$ — 7922 „
$1/2\,(Na_2\,C_4H_4O_6 + (NH_4)_2\,C_4H_4O_6)$ — 5660 „

therefore

$$OD : OA = 11726 - 5660 : 7922 - 5660 = 6066 : 2262.$$

The figure shows further that

$$P_1\,P : AO = PB : OB$$
$$\text{and}\quad P_1\,P : DO = PC : OC.$$

Since OC differs very little from OB, we may write

$$AO : DO = PC : PB.$$

Introducing numerical values we obtain, since

$$PB = 34.5 - 26.6 = 7.9,$$

$$PC = 7.9\,\frac{2262}{6066} = 2.9.$$

The transition temperature required is therefore 26.6 + 2.9 = 29.5; dilatometric experiments gave 29°.

V. THE ELECTRICAL WORK PERFORMED BY A CHEMICAL CHANGE.

1. *General considerations.*

It has been proved above that the work which can be done by the force of affinity which brings about a chemical reaction may be represented by the equation

$$A = q\,\frac{P - T}{P}.$$

The magnitude of this quantity of work is independent of the way in which the chemical reaction takes place, *provided that it is reversible.*

Helmholtz[1] has shown that a chemical reaction which occurs in such a way that it does electrical work is reversible.

The chemical change may take place in the one direction producing a current of electricity, or it may be made to proceed in the opposite direction by passing a current from an external source. In such cases the electromotive force prouced by the reaction is the same as that required to reverse it. It is evident, from these considerations, that the expression for A represents the electrical work which the chemical change is capable of producing. This may also be proved by means of the following cycle of reversible operations: —

At the transition temperature P let unit quantity of the system undergo chemical change absorbing q calories. Let the temperature be then depressed from P to T. At the latter temperature the chemical change, which will now occur in the opposite direction, is allowed to take place in a galvanic cell so as to produce a current of electricity; it will do a quantity of electrical work equivalent to A calories, a quantity of heat, q — A calories, being simultaneously evolved. The system is then brought back to its initial condition by raising the temperature to P.

This cycle of changes is reversible; we might begin by cooling the original system from P to T, at which temperature it might be caused to undergo the chemical change by passing a current of electricity. This would do a quantity of work equivalent to A calories on the system, and q — A calories would be absorbed. The temperature might then be raised from T to P and the chemical change allowed to take place, evolving q calories.

The cycle being reversible, we may apply the second law of thermodynamics to it, and obtain

$$\frac{q}{A-q}=\frac{P}{T},$$

---

[1] Sitzungsberichte der Kön. Preuss. Akad. 1882, p. 823. Gesammelte Abhandlungen, II, 958 and 979; III, 92.

or

$$A = q \frac{P - T}{P},$$

This result may be further simplified by considering as unit quantity of the system, its equivalent weight in kilograms. The electrical work, A, which is done by the change of unit quantity of the system is then proportional to the electromotive force produced by the reaction[1]. The connexion between A and the heat evolved by the reaction may therefore be expressed in words as follows: —

The electromotive force which a chemical change can produce is proportional to the heat evolved by the reaction, q, divided by the absolute temperature of the transition point, P, and multiplied by the difference between it and the temperature T *at which the reaction occurs.*

Since the electromotive force is thus shown to be proportional to the work done by affinity, the diagram (p. 241) representing the latter may evidently be applied to the former also.

By differentiating the equation for A with respect to T we obtain[2]

$$\frac{dA}{dT} = - \frac{q}{P}.$$

Eliminating P by means of the original equation we obtain

$$\frac{dA}{dT} = \frac{A - q}{T},$$

or

$$A = q + T \frac{dA}{dT}.$$

$\frac{dA}{dT}$ is the temperature coefficient of the electrical work done by the change.

Helmholtz has already obtained this equation in another way in his memoir "On the thermodynamics of chemical processes,"[3] and it has been confirmed experimentally in a number of cases by Czapski[1], Gockel[2], and Jahn[3].

---

[1] [According to Faraday's law the quantity of electricity carried by an equivalent of any substance is constant, it is found to be 96587 × 10^3 coulombs per kgrm. equivalent. If E be the electromotive force produced by a reaction, the electrical work done by a kgrm. equivalent of change will be $A = E \times 96587 \times 10^3$ volt-coloumbs. 1 volt-coulomb = 10^7 ergs = 0.0002395 kgrm. degree calorie, so that the above quantity of electrical work $A = 23116$ E kgrm. degree calories. T. E.]

[2] This is also evident from figure 45.

[3] See the note on page 252.

As is well known, the view that in reversible processes the chemical energy is completely converted into electrical has been advanced by Joule, William Thomson (Lord Kelvin), and also by Helmholtz; accordingly we should have $A = q$. That this view is incorrect has been proved by Braun[4], Gibbs, and Helmholtz, the latter giving the above-mentioned equation for the electrical work.

2. *Thermodynamics of the transition cell.*

The equation

$$A = q \frac{P - T}{P}$$

shows that if the electrical work in a galvanic cell be furnished by the change of one of two mutually convertible systems into the other, it being of course assumed that the change takes place in a reversible way, then at the transition point, where $P = T$, this work will have the value zero.

Cohen's electrical method of determining the transition temperature, using both stable and meta-stable phases, (page 193) is implicitly based on this deduction from the above equation.

Since the change in the transition cell used in this method is reversible we may at once apply to it the equation

$$A = q + T \frac{dA}{dT}, \quad \ldots\ldots (1)$$

and see to what results it leads.

It has already been proved that A and q have the same sign at temperatures below the transition temperature, while at temperatures above it they have opposite signs.

Since A vanishes at the transition temperature it is obvious that its magnitude (considered without reference to its sign) must decrease, with rising temperature, below the transition temperature, and increase above it. The values of the electromotive force which are proportional to A show similar behaviour, as is shown by the table on page 198. A little consideration will show that q and $T \frac{dA}{dT}$ are always quantities of opposite sign below the transition temperature; at this temperature $A = 0$, and therefore

---

[1] Wied. Ann. 21, 209, 1884.

[2] Wied. Ann. 24, 618, 1885. See also W. Nernst, Zeit. phys. Chem. 2, 23, 1888.

[3] Wied. Ann. 29, 21, 1886.

[4] Wied. Ann. 5, 182, 1878; 16, 561, 1882; 17, 593, 1882.

$$q = - T \frac{dA}{dT} \;\ldots\ldots (2)$$

This equation may be called the *equation of the transition cell.*

The results obtained with the transition cell with stable and meta-stable phases show clearly that the view put forward by W. Thomson (Lord Kelvin), i. e. that $A = q$, is erroneous, for at the transition temperature where q has a large value A is zero.

The value of $\frac{dA}{dT}$ at the transition temperature may be calculated by means of equation (2); it may also be determined by experiment and the two values so obtained compared. Taking the case of Glauber's salt, which has been investigated experimentally, q will be the heat evolved by the change which produces the quantity of work A, A being the electrical work obtainabel from the change when the quantity of electricity carried by one equivalent of the salt is set in motion.

If a transition cell (fig. 37), in which the change occurring below the transition point is the conversion of anhydrous sodium sulphate and saturated solution of Glauber's salt into solid Glauber's salt, were connected up against a Daniell cell and the current allowed to flow, then after 1 kgrm. equivalent of zinc had passed into solution in the latter an equivalent quantity (200 kgrms.) of mercury would have separated in the metallic state at the electrode contained in the saturated solution of the anhydride, and an equivalent quantity of mercurous sulphate would have been formed at the electrode in the saturated solution of Glauber's salt. A corresponding quantity of Na and SO_4 ions would also have passed through the solutions. The transference of the SO_4 ions does not affect the concentrations of the solutions since the SO_4 combines with mercury to form insoluble mercurous sulphate. If the transition cell were allowed to furnish the same quantity of electricity everything would take place in the reverse order. Everything would also be reversed above the transition point.

Suppose the cell to be working in its normal way below the transition point, let n be the migration constant[1] for Na in $Na_2 SO_4$, then n sodium ions migrate from the more concentrated (anhydride) solution to the weaker (Glauber's salt) solution, while $(1-n)\frac{SO_4}{2}$ ions migrate in the opposite direction.

The n sodium ions combine with SO_4 from the mercurous sulphate and so form $\frac{n}{2}$ molecules of sodium sulphate, this causes the precipitation of x molecules of Glauber's salt from the saturated solution according to the equation

$$\frac{n}{2}\, Na_2SO_4 + \frac{(x-n)}{2}\, Na_2SO_4 . \, bH_2O = \frac{x}{2}\, Na_2SO_4 . \, 10\, H_2O$$

where b is the number of molecules of water to each molecule of sodium sulphate in the saturated solution of Glauber's salt.

We obtain from the above equation

$$x = n \frac{b}{b-10}.$$

The migration of the sodium ions towards the Glauber's salt solution has, further, the effect of removing $\frac{n}{2}$ molecules of sodium sulphate from the saturated solution of the anhydride, thus causing $\frac{n}{2}$ molecules of the anhydride to dissolve. The final result is therefore

$$\frac{n}{2} Na_2 SO_4 + \frac{n}{2}\left(\frac{10}{b-10}\right) Na_2SO_4 . \, bH_2O = \frac{n}{2}\,\frac{b}{b-10} Na_2SO_4 . \, 10\, H_2O,$$

or in words, $\frac{nb}{2(b-10)}$ molecules of Glauber's salt are formed from $\frac{n}{2}$ molecules of the anhydride and $\frac{10n}{2(b-10)}$ molecules of the saturated solution of Glauber's salt.

---

[1] Appendix, note 4.

The quantity of heat to be taken into account in equation (2) is therefore the quantity evolved by the formation of $\frac{nb}{2(b-10)}$ molecules of $Na_2SO_4 . 10\,H_2O$; the value of b depends on the temperature and may be obtained from the tables of solubility given by Loewel[1]. The latent heat of fusion of Glauber's salt, for a kgrm. molecule, has been determined by means of the calorimeter as — 16509 calories.[2]

Equation (2) (p. 255) may now be written

$$-\frac{dA}{dT} = \frac{Q}{T_0}\,\frac{n\,b_0}{2\,(b_0 - 10)} \quad . \; . \; . \; . \; . \; . \quad (3)$$

where b_0 is the number of molecules of water to each molecule of sodium sulphate in the saturated solution of Glauber's salt at the transition temperature T_0.

The numerical values of the quantities occurring in equation (3) are the following:

$Q = 16509$ calories.
$n = 0.36$ according to Hittorf.[3]
$b_0 = 15.6$,, ,, Loewel.
$T_0 = 305.6$.

Introducing these into (3) we obtain

$$-\frac{dA}{dT} = \frac{16509}{305.6} \times \frac{0.36 \times 15.6}{2(15.6-10)}$$

or

$$\frac{dA}{dT} = -\ 27.09 \text{ calories}$$

and since (note p. 253) $E = \frac{A}{23116}$, E being the electromotive force in volts, we obtain

$$\frac{dE}{dT} = -\ 1.2 \text{ millivolts.}$$

---

[1] Ann. Chim. Phys. (3), 49, 1857.

[2] E. Cohen, Zeit. phys. Chem. 14, 85, 1894.

[3] Pogg. Ann. 106, 377, 1859. This value was obtained at 9°. At the transition temperature of Glauber's salt it should be somewhat higher, since Bredig, Zeit. phys. Chem. 13, 191, 1894, found $n = 0.4$ at 25°.

The electromotive force of this sodium sulphate transition cell with both stable and meta-stable phases was determined by E. Cohen and G. Bredig[1] by means of the apparatus represented on page 196; the following numbers were obtained.

Temperature.	Electromotive force in millivolts. E.
28°.2	5.2
30 .2	2.9
32 .7	— 0.5

These data may be represented by the formula

$$E = -2.05 + 1.57\,t - 0.0466\,t^2,$$

from which we obtain, at the transition point, $t = 32.6$,

$$\frac{dE}{dT} = -1.5 \text{ millivolts.}$$

This may be regarded as being in sufficiently good agreement with the number obtained by calculation (— 1.2 millivolts), the smallness of the electromotive forces measured being taken into consideration.[2]

The equation obtained above is also applicable to the transition cell containing no meta-stable phase[3] described on page 198.

If we consider a cell of this kind (fig. 40) containing a solution maintained in a condition of saturation by the presence of the modification of the system which is stable above the transition temperature T_0, we have

$$A_1 = q_1 + T\,\frac{d\,A_1}{d\,T}, \quad . \ . \ . \ . \ . \ . \ (4)$$

where q_1 is the chemical energy of the cell, that is, the quantity of heat evolved by the solution of the modification which is stable at temperatures above T_0, calculated for the quantity which passes into solution at T during the passage of unit quantity of electricity[1] through the cell, and A_1 is the electrical energy obtainable under the same circumstances.

---

[1] Zeit. phys. Chem. 14, 546, 1894.

[2] According to the note on page 257 the result given by the calculation should probably be higher.

[3] E. Cohen and G. Bredig, Zeit. phys. Chem. 14, 535, 1894.

Similarly, for a cell containing the saturated solution of the modification of the system which is stable at temperatures below the transition point, we have

$$A_2 = q_2 + T \frac{d\ A}{d\ T} \quad . \ . \ . \ . \ . \ . \ (5)$$

Since the two saturated solutions have the same concentration at the transition point the two cells have the same electromotive force at that temperature, and therefore at T_o,

$$A_1 = A_2,$$

from which we obtain (at T_o)

$$\frac{d\ A_2}{d\ T} - \frac{d\ A_1}{d\ T} = \frac{q_1 - q_2}{T_o} \quad . \ . \ . \ . \ . \ . \ (6)$$

$\frac{dA_2}{dT} - \frac{dA_1}{dT}$ affords a measure of the angle between the two branches of the curve representing the connexion between the electromotive force of the cell and the temperature. $q_1—q_2$ represents the quantity of heat which is evolved by the transformation of that modification of the system stable at temperatures below the transition point into that stable at higher temperatures, calculated for the quantity which dissolves at T_o when unit quantity of electricity passes through the cell.

The graphical representation, on page 202, of the connexion between the electromotive force of a cell of this type and the temperature shows that the curve consists of two parts meeting at an angle. Each of these parts may be represented by an empirical equation of the form,

$E_1 = Q_1 + R_1t + S_1t^2$ for temperatures between 35° and 45° (7)

and $E_2 = Q_2 + R_2t + S_2t^2$ for temperatures between 20° and 30° (8),

where t is the temperature centigrade.

By differentiating these empirical equations with respect to t, and subtracting, we obtain the value of the sudden change in the temperature coefficient of the cell which occurs at the transition temperature (32°.6): —

---

[1] Unit quantity of electricity is taken to mean that quantity which migrates with a kgrm. equivalent of an ion (96587 × 1000 coulombs).

$$\frac{dE_2}{dT} - \frac{dE_1}{dT} = (R_2 - R_1) + 2\,t_o\,(S_2 - S_1) \ldots\ldots (9)$$

The values of $\frac{dE_2}{dT} - \frac{dE_1}{dT}$ found experimentally were: —

For cell I (p. 201)	+ 1.6	millivolts.
,, ,, II (p. 202)	+ 1.2	,,
,, ,, III (p. 203)	+ 1.1	,,

The mean value being 1.3 millivolts.

The same quantity may be calculated from other data by means of equation (6), in which T_o, the transition temperature on the absolute scale, is 305°.6; q, for Glauber's salt at its transition temperature is $\frac{nb_o}{2\,(b_o - 10)}\,W_1$, and similarly $q_2 = \frac{nb_o}{2\,(b_o - 10)}\,W_2$, where n and b_o have the meanings already ascribed to them (page 257), and

W_1 is the heat evolved by the solution of 1 kgrm. molecule of Na_2SO_4 at temperatures above T_o, and

W_2 is the heat evolved by the solution of 1 kgrm. molecule of $Na_2SO_4 . 10H_2O$ at temperatures below T_o.

$W_2 - W_1$ is therefore the heat evolved by the fusion of Glauber's salt (— 16509 cals.). Equation (6) may thus be written

$$\frac{dA_2}{dT} - \frac{dA_1}{dT} = \frac{W_1 - W_2}{T_o}\;\frac{nb_o}{2\,(b_o - 10)} \ldots\ldots (10).$$

From this, introducing numerical values,

$$\frac{dA_2}{dT} - \frac{dA_1}{dT} = \frac{16504 \times 0.36 \times 15.6}{305.6 \times 2\,(15.6 - 10)} = 27.09 \text{ calories,}$$

or, since A = 23116 E, where E is the electromotive force of the cell, $\frac{dE}{dT} = 1.2$ millivolts.

This number is in satisfactory agreement with that found experimentally, i. e. 1.3 millivolts.

Van 't Hoff, Cohen and Bredig[1] have shown that the equation

$$\frac{dA}{dT} = \frac{A - q}{T} \quad \ldots\ldots \quad (1)$$

may be used to calculate the electromotive force of transition cells of the type which we have just considered. To do this we may set out from the temperature at which $A = 0$, and sum the increments of A with T, taking sufficiently small finite increments of A and T to make it permissible to regard their ratio as constant during the increment.

Taking first cell III, in which the one electrode is immersed in a saturated solution of Glauber's salt and the other in a $^1/_4$ normal solution of sodium sulphate, the temperature at which $A = 0$ is that at which the saturated solution of Glauber's salt is $^1/_4$ normal; this temperature, however, cannot be observed since it lies below the cryohydratic temperature. It may be calculated with considerable accuracy from the formula

$$\frac{d \log C}{dT} = \frac{Q}{T^2} \quad \ldots\ldots \quad (2)$$

which is strictly true for dilute solutions, and in which C is the concentration and Q a quantity connected with the heat of solution and varying but little with the temperature.

According to Loewel 100 parts of water at 0° dissolve 5.02 parts of sodium sulphate and 9 parts at 10°. Substituting these values in (2) (after integration), and replacing the Naperian logarithm by that to the base 10, we obtain

$$\mathrm{Log}\ \frac{9}{5.02} = \frac{Q}{2.3026}\left(\frac{10}{273 \times 283}\right).$$

At a temperature x degrees below zero the saturated solution of Glauber's salt will be $^1/_4$ normal, and will therefore contain $^{71}/_{40} = 1.775$ grams (approximately) of sodium sulphate to 100 grams of water, whence as before

$$\mathrm{Log}\ \frac{5.02}{1.775} = \frac{Q}{2.3026}\left(\frac{x}{273\,(273 - x)}\right).$$

---

[1] Zeit. phys. Chem. 16, 453, 1895.

By eliminating Q from these two equations we obtain $x = 16.2$, that is, $A = 0$ at $-16°.2$.

In order to calculate the electromotive force of the cell at 20°, it is sufficient to make use of the values of $\frac{dA}{dT}$ at fairly large intervals of temperature, say at -16.2, 0°, 10°, and 20°.

The most important quantity entering into the calculation is q in equation (1); it represents the quantity of heat which is evolved by the process which produces the current. This process is the transference of 0.36 molecule of $\frac{1}{2}(Na_2SO_4)$ from the saturated solution, the composition of which may be represented by $\frac{1}{2}(Na_2SO_4)\,bH_2O$, to the $\frac{1}{4}$ normal solution $\frac{1}{2}(Na_2SO_4)\,222.4H_2O$. The heat evolved by this process may be considered to consist of three parts: —

1. λ_1 evolved by the removal of $\frac{1}{2}(Na_2SO_4)\,b\,H_2O$ from an indefinitely large quantity of the saturated solution, and by the return to it of $b\,H_2O$ which would then become saturated in accordance with the equation

$$\frac{b}{b-5}\,\frac{1}{2}(Na_2SO_4)\,5\,H_2O + b\,H_2O = \frac{b}{b-5}\,\frac{1}{2}(Na_2SO_4)\,b\,H_2O.$$

The following are the quantities of heat evolved when $\frac{1}{2}(Na_2SO_4)\,5\,H_2O$ is dissolved in a quantity of water such that the solution formed contains n molecules of water to $\frac{1}{2}(Na_2SO_4)$.

n =	400	200	100	50	25	7.8
Heat evolved	— 9430	— 9380	— 9255	— 9021	— 8689	— 7495

The first five numbers have been determined by Thomsen, the last is calculated from Cohen's determination of the latent heat of fusion of Glauber's salt and from Thomsen's determination of the heat of hydration of Na_2SO_4.

2. λ_2 is the heat evolved by diluting $\frac{1}{2}(Na_2SO_4)\,b\,H_2O$ to $\frac{1}{2}(Na_2SO_4)\,222.4H_2O$; it also may be calculated from the above numbers.

3. λ_3 is the heat evolved by removing $222.4\,H_2O$ from an indefinitely large quantity of a $\frac{1}{4}$ normal solution of sodium

sulphate. λ_1 and λ_2 are negative quantities, while λ_3 is positive and its value is approximately $\frac{9430-9380}{200} = 56$ calories.

We thus obtain the following numbers.

Temperature.	b (Loewel).	λ_2.	λ_1.	E.	$\frac{dE}{dT}$
— 16°.2	222.4	0	— 9602	0	0.58
0	78.6	— 234	— 9773	9.4	0.60
10	43.8	— 450	— 10086	15.4	0.63
20	20.3	— 1023	— 11096	21.7	0.72

A somewhat more exact result is perhaps obtained by using the mean values of the temperature coefficients in the different intervals of temperature. By doing so we obtain

$$E_{20^\circ} = 16.2 \times 0.59 + 10 \times 0.615 + 10 \times 0.675 = 22.5$$

millivolts, the number found experimentally being 21 millivolts.

Following the curve to 33°.2, at which temperature Cohen and Bredig observed the transition to anhydride, it is necessary to calculate the temperature coefficients at temperatures somewhat nearer to each other, since they increase more rapidly with the temperature, this is done in the following table.

Temperature.	b.	λ_2.	λ_1.	E.	$\frac{dE}{dT}$
20°	20.3	— 1023	— 11096	22.5	0.72
25	14.1	— 1453	— 12292	27.1	0.8
30	9.86	— 1748	— 15496	32.9	0.99
32.6	7.8	— 1891	— 20879	36.3	1.27

A more exact result is again perhaps to be obtained by making use of the mean values of the temperature coefficients in the different intervals of temperature; the following numbers have been calculated in this way.

Temperature.	E observed.	E calculated.
20°	21 millivolts.	22.5 millivolts.
25	24.8 „	26.3 „
30	31.4 „	30.8 „

Using now the mean temperature coefficient between 30° and 33°.2 the electromotive force at the latter temperature is found to be 34.5 millivolts. At this temperature the change of Glauber's salt into the anhydrous salt occurs and the value of $\frac{dA}{dT}$ undergoes a *per saltum* decrease owing to the change in λ_1. The quantities of heat evolved by the solution of $^1/_2(Na_2 SO_4)$ are obtained from the values of the heat of solution of $^1/_2(Na_2SO_4). 5H_2O$ previously given, by adding to them 9610 cals. which is, according to Thomsen, the heat of hydration of $^1/_2(Na_2SO_4)$.

The following are the numbers obtained: —

Temperature.	b.	λ_2.	λ_1	E	$\frac{dE}{dT}$
33°.2				34.5	
35	7.91	— 1883	+ 2107	34.8	0.101
40	8.08	— 1872	+ 2095	35.3	0.101
45	8.26	— 1859	+ 2083	35.8	0.101

Since the temperature coefficient here does not change appreciably the values of E obtained should be fairly accurate; they are compared in the following table with those found by experiment.

Temperature.	E observed.	E calculated.
35°	35.8 millivolts.	34.8 millivolts.
40	36.7 ,,	35.3 ,,
45	37.1 ,,	35.8 ,,

The numbers observed and those calculated are therefore fairly concordant. The electromotive force of cell I, containing a normal solution of sodium sulphate (see page 201), may be obtained by calculating the difference between it and that of cell III; this difference was found to be

$$\text{at } 20°, \quad 21 - 7.1 = 13.9,$$
$$\text{at } 45°, \quad 37.1 - 23.1 = 14.$$

The temperature at which the electromotive force of cell I is zero is calculated, in the same way as before, from the equations

$$\operatorname{Log} \frac{9}{5.02} = \frac{Q}{2.3026} \left(\frac{10}{273 \times 283}\right),$$

and

$$\operatorname{Log} \frac{9}{7.1} = \frac{Q}{2.3026} \left(\frac{1}{273 + x} - \frac{1}{283}\right),$$

from which $x = 5°.8$.

From the numbers already given, the electromotive force of the cell containing 1/4 normal sodium sulphate is, at this temperature,

$$E_{5°.8} = 16.2 \times 0.59 + 5.8 \times 0.609 = 13.1 \text{ millivolts},$$

from which value, neglecting its small variation with the temperature, the following numbers are obtained.

Temperature.	E observed.	E calculated.	E calculated with temp. corr^{n}.
20°	7.1 millivolts	9.4 millivolts.	8.7 millivolts.
25	10.8 ,,	13.2 ,,	12.3 ,,
30	16.6 ,,	17.7 ,,	16 6 ,,
35	22.2 ,,	21.7 ,,	20.4 ,,
40	22.5 ,,	22.2 ,,	20.7 ,,
45	23.1 ,,	22.7 ,,	21.0 ,,

The agreement is satisfactory and becomes somewhat better if the fact be taken into account that the difference between the electromotive forces of the cells containing normal and 1/4 normal solutions of sodium sulphate, is proportional to the absolute temperature just as in the case of a concentration cell[1] containing dilute solutions; allowance has been made for this in calculating the numbers in the fourth column.

The solutions of sodium sulphate contained in these cells being dilute the electromotive force of cell II containing a 1/2 normal solution may be calculated by taking the mean of those of the cells containing normal and 1/4 normal solutions. The following numbers are obtained in this way.

Temperature.	E observed.	E calculated.
20°	14.2 millivolts.	15.6 millivolts.
25	18.5 ,,	19.3 ,,
30	24.0 ,,	23.7 ,,
35	28.2 ,,	27.6 ,,
40	28.6 ,,	28.0 ,,
45	28.7 ,,	28.4 ,,

The electromotive forces of these cells may therefore be calculated with a maximum deviation of 2 millivolts.

From equations (3) p. 257, and (10) p. 260, the following deduction may be made: —

$$\frac{dA_2}{dT} - \frac{dA_1}{dT} = - \frac{dA}{dT}.$$

The negative temperature coefficient of the transition cell with both stable and meta-stable phases is, at the transition temperature, equal to the difference between the temperature coefficients of the two transition cells containing no meta-stable phase.

This has been confirmed by experiment; on page 260, $\frac{dE_2}{dT} - \frac{dE_1}{dT}$ was found to be 1.6 millivolts in cell I, while the temperature coefficient of the cell with both stable and metastable phases is — 1.5 millivolts (p. 258).

---

[1] Nernst, Zeit. phys. Chem. 4, 154, 1889.

3. *Equilibrium constant and electromotive force.*

From the equations

$$\frac{d \log K}{dT} = \frac{q}{2\,T^2} \ldots (1) \text{ and } A = q + T\,\frac{dA}{dT} \ldots (2)$$

we find, by solving (2) for q and substituting the value obtained in (1),

$$\frac{d \log K}{dT} = \frac{A - T\,\frac{d\,A}{d\,T}}{2\,T^2},$$

and therefore, by integration, putting the integration constant equal to zero,

$$\log K = -\frac{A}{2\,T}.$$

Since A is proportional to the electromotive force produced by a reaction, each determination of the value of a constant of equilibrium is at the same time a determination of this electromotive force[1].

The case of ammonium sulphide may be taken as an example,

$$NH_5S \rightleftarrows NH_3 + H_2S.$$

The experimental data have been given on page 157. The value of A at the temperature T may be calculated from them by means of the equations[2]

$$\log K = -\frac{A}{2T}, \text{ and } K = \frac{C_2^{\Sigma a_2 i_2}}{C_1^{\Sigma a_1 i_1}}.$$

Since a gaseous system is under consideration

$$i = 1;\ \Sigma a_1 i_1 = n_1, \text{ and } \Sigma a_2 i_2 = n_2,$$

where $n_1 = 0$, and $n_2 = 2$, and therefore

---

[1] Van 't Hoff, Lois de l'équilibre chimique, p. 54.

[2] See page 206.

$$A = -4\ T \log C_2,$$

C_2 being the concentration of the second system.

The unit of concentration of the second system is 17 kgrms. of ammonia and 34 kgrms. of sulphuretted hydrogen per cubic metre. If the pressure of the mixture of gases be p mm., the pressure of the ammonia will be $\frac{p}{2}$ mm.

Since the weight of a litre of ammonia gas at 0° and 760 mm. is 0.761 grams, its concentration under a pressure of $\frac{p}{2}$ mm. is

$$C_2 = \frac{0.761 \times p \times 273}{17 \times 2 \times 760 \times T} = \frac{p}{124.4T},$$

and therefore

$$A = 4\ T \log \frac{124.4T}{p}.$$

We thus obtain

Temperature.	A.
9°.5	5992 calories.
25 .1	5132 „

The number found, 6000 calories approximately at 10°, indicates that if the formation of ammonium sulphide from ammonia and sulphuretted hydrogen at concentrations of 17 and 34 kgrms. per cubic metre, were to take place in a galvanic cell at 10° producing a current, the electromotive force of the combination would be approximately $E = \frac{A}{2 \times 23116} = 0.129$ volt.

On the other hand it is clear that, a determination of an electromotive force, under definite conditions, must lead to a knowledge of the condition of equilibrium towards which the change tends.

For example, suppose that a Daniell cell at 0° can furnish a quantity of electrical energy equivalent to 50300 calories, during the separation of a kgrm. atom of copper from the copper sulphate solution of unit concentration, that is, containing 159 kgrms. of $CuSO_4$ per cubic metre, and the solution of the zinc in a liquid already containing 161 kgrms. of zinc sulphate per cubic metre, then the final condition of the equilibrium

$$ZnSO_4 + Cu \rightleftarrows CuSO_4 + Zn,$$

at 0°, is known.

We have, namely,

$$\log K = -\frac{A}{2T}, \text{ and } \frac{C_2^{\Sigma a_2 i_2}}{C_1^{\Sigma a_1 i_1}} = K,$$

therefore

$$\log \frac{C_2^{\Sigma a_2 i_2}}{C_1^{\Sigma a_1 i_1}} = -\frac{A}{2T} = -\frac{50300}{2 \times 273} = -92.1.$$

In this expression

$$i_{CuSO_4} = i_{ZnSO_4} = 1,$$

therefore

$$\Sigma a_2 i_2 = \Sigma a_1 i_1 = 1,$$

from which

$$\log \frac{C_1}{C_2} = 92.1 \text{ or } \frac{C_1}{C_2} = 10^{40}.$$

At 0° therefore, equilibrium between the copper and zinc and the sulphates will be reached when there is a certain definite ratio between the concentrations of the two salts. The calculation shows that the concentration of the zinc sulphate would be 10^{40} times that of the copper sulphate.

It is further possible to show that a general relationship exists between the values of K in a cycle of chemical equilibria.

The equilibrium which is reached when an alkaloid is brought together with the hydrochloride of another alkaloid has been studied by JELLETT.[1] The alkaloids used were Quinine (Q), Codeïne (C), and Brucine (B), the following equilibria being investigated: —

1. Equilibrium between Quinine, Codeïne and their hydrochlorides.

$$Q + C.\ HCl. \rightleftarrows C + Q.\ HCl.$$

---

[1] Transactions of the Royal Irish Academy, 25, 371, 1875.

2. Equilibrium between Codeïne, Brucine, and their hydrochlorides,

$$C + B.\,HCl \rightleftarrows B + C.\,HCl.$$

3. Equilibrium between Brucine, Quinine, and their hydrochlorides,

$$B + Q.\,HCl \rightleftarrows Q + B.\,HCl.$$

The determinations of the ratios of the quantities of the different salts in these three cases gave the following results: —

$$\frac{Q.\,HCl}{C.\,HCl} = 2.03, \quad \frac{C.\,HCl}{B.\,HCl} = 1.58, \quad \frac{B.\,HCl}{Q.\,HCl} = 0.32.$$

Jellett observed further that the product of the numbers obtained is approximately unity.

$$2.03 \times 1.58 \times 0.32 = 1.026.$$

It is possible to show that this relationship, found in a special case by Jellett, holds good quite generally.

Let the values of K in the three equilibria be K_1, K_2 and K_3 at any given temperature; the changes which lead to these equilibria will be able to do quantities of electrical work A_1, A_2, and A_3 for a gram equivalent of change when the concentrations of the mutually convertible systems are unity. We have then,

$$\log K_1 = -\frac{A_1}{2T}, \quad \log K_2 = -\frac{A_2}{2T}, \quad \text{and} \log K_3 = -\frac{A_3}{2T}$$

and therefore,

$$\log K_1 K_2 K_3 = -\frac{A_1 + A_2 + A_3}{2T}.$$

Since the initial condition of the system remains unaltered after these isothermal changes have taken place, the sum of the quantities of electrical work done by them must be zero, that is,

$$A_1 + A_2 + A_3 = 0,$$

and therefore,

$$K_1 K_2 K_3' = 1,$$

that is, the product of the constants of equilibrium is equal to unity.

Since the same is true of any similar series of equilibria, independent of their number, the following general proposition may be enunciated. *The product of the values of K in a cycle of chemical equilibria is equal to unity.*

The case studied by Jellett is an example of this, for since

$$K = \frac{C_2^{\Sigma a_2 i_2}}{C_1^{\Sigma a_1 i_1}},$$

and the values of Σai differ from each other very little, the equilibria studied being similar, and further

$$K_1 K_2 K_3 = 1,$$

we obtain

$$\left(\frac{C_2}{C_1}\right)_1 \times \left(\frac{C_2}{C_1}\right)_2 \times \left(\frac{C_2}{C_1}\right)_3 = 1.$$

We have also

$$\left(\frac{C_2}{C_1}\right)_1 = \frac{Q.\ HCl}{C.\ HCl},\quad \left(\frac{C_2}{C_1}\right)_2 = \frac{C.\ HCl}{B.\ HCl},\quad \text{and}\quad \left(\frac{C_2}{C_1}\right)_3 = \frac{B.\ HCl}{Q.\ HCl},$$

from which the result obtained by Jellett is found.

From the electromotive force produced by a change it is possible to predict the direction in which it will proceed.

Taking for example a case of equilibrium between condensed systems such as

$$2\,Ag + Cu_2Cl_2 \rightleftarrows 2\,AgCl + 2\,Cu,$$

the sign of the quantity of heat evolved determines the direction in which the reaction will proceed at absolute zero; that system which is formed with evolution of heat will alone be present in a condition of equilibrium at this temperature.

The following data have been obtained by F. Braun.[1]

Reaction.	Heat evolved q.	Electrical work A.
$2\,Ag + Cl_2$	117500	97000
$2\,Cu + Cl_2$	131600	99200
$2\,Ag + Br_2$	90800	85000

---

[1] Wied. Ann. 17, 633, 1882.

From these numbers the formation of the first system from the second is accompanied by an evolution of heat of 131600—117500 = 14100 calories; at absolute zero, therefore, it will be formed at the expense of the second. This is, however, not necessarily the case at the ordinary temperature; the heat evolved is no longer equivalent to the work which the change is capable of producing, and it cannot therefore be used to predict the direction of the reaction. The work which the reaction can do may be measured by means of the electromotive force produced by it. When the first system is formed from the second this work is, according to the numbers given above, 99200—97000 = 2200 calories.

The first system thus represents the condition of the system when it is in equilibrium at the ordinary temperature, the change still occurring in the same direction as at absolute zero. The first system will continue to be present alone, in equilibrium, until the transition temperature is reached; at which point both systems may exist together, above it the first system will give place to the second.

We must now calculate the transition temperature; having done so the condition of the system in a state of equilibrium is known at all temperatures.

In the equation

$$A = q\,\frac{P - T}{P}$$

all the quantities, are known with the exception of P. At T (273° approximately) the value of A is 2200 calories, that of q is 14100 calories. From these numbers we find P = 324, that is, the transition temperature lies at 51° C. It is however to be noted that small changes in the values of A, q, and T have a considerable influence on the value of P obtained.

As a further example we may consider a case of heterogeneous equilibrium such as

$$2\ \mathrm{Ag\,Br} \rightleftarrows 2\ \mathrm{Ag} + \mathrm{Br_2}.$$

According to the laws governing equilibria of this kind the bromine must, at each temperature, attain a maximum pressure, which vanishes only at absolute zero.

Silver bromide, when placed in a vacuum at the ordinary temperature, must therefore lose bromine until the latter has attained the extremely small maximum pressure corresponding to the prevailing temperature. This pressure may be calculated in the following way.

The quantity of work which may be obtained from the combination of metallic silver and liquid bromine is known; it has been determined by measuring the electromotive force to which this reaction gives rise. From the table on page 271 it is equivalent to 85000 calories.

This quantity of work may also be calculated from the equation

$$A = 2T \log \frac{S_{Br}}{S_{AgBr}},$$

where S_{Br} is the vapour pressure of liquid bromine, S_{AgBr} that of the bromine from silver bromide at the temperature T. At the boiling point of bromine (about 60°) we have

$$T = 273 + 60, \quad S_{Br} = 760 \text{ mm.},$$

and therefore

$$S_{AgBr} = 2.9 \times 10^{-53} \text{ mm.}$$

That is, silver bromide will decompose when exposed to a vacuum at 60° until the bromine vapour evolved has reached a pressure of 2.9×10^{-53} mm.

A similar calculation shows that the pressure of chlorine evolved from silver chloride at the ordinary temperature is

$$S_{AgCl} = 5.4 \times 10^{-75} \text{ mm.}$$

THE END.

APPENDIX[1].

Note 1, (page 2).

There are, to begin with, C_0 kilogram molecules of arsenic hydride in a cubic metre. At the time t a fraction x of them has undergone decomposition; the concentration of the arsenic hydride is then $C_t = (1 - x) C_0$, and that of the hydrogen molecules $\frac{3 x C_0}{2}$. Since the pressure of the gas is proportional to the concentration we have

$$\frac{P_t}{P_0} = \frac{(1 - x) C_0 + \frac{3}{2} x C_0}{C_0} = 1 + \frac{x}{2},$$

or

$$x = \frac{2 P_t}{P_0} - 2.$$

Therefore

$$C_t = (1 - \frac{2 P_t}{P_0} + 2) C_0$$

$$= C_0 \left(3 - \frac{2 P_t}{P_0}\right).$$

Note 2, (page 95).

32.7 cc. of pure air (saturated with aqueous vapour at 0°, and under a pressure of 760 mm.) would occupy 32.45 cc. when dry, and would contain 6.78 cc. of oxygen. The hydrogen added (13.8 cc.) is in excess; the quantity of electrolytic gas is thus $3 \times 6.78 = 20.34$ cc. initially. At the time t a fraction n has undergone change, that is 20.34 n cc. The fraction of the whole quantity of gas which has disappeared at this time is $\frac{P_0 - P_t}{P_0}$, or, since the lengths L of the column of air are inversely proportional to the pressures, $\frac{L_t - L_0}{L_t}$.

We thus obtain the expression

$$46.5 \left(\frac{L_t - L_0}{L_t}\right) = 20.34\ n.$$

---

[1] By the translator.

Note 3, (pp. 123 and 248).

The connexion between the quantities of heat evolved by the conversion of a material system, A, into another, B, at different temperatures may be obtained as follows: —

At the temperature T, let one gram of A be converted into B, q_T calories being evolved. Now let the temperature of B change to T_0, C_B $(T-T_0)$ calories being evolved, where C_B is the specific heat of B. At T_0 let the substance be reconverted into A, with evolution of $-q_0$ calories, and finally let the system be brought back to the temperature T, the quantity of heat evolved being C_A $(T_0 - T)$ calories, where C_A is the specific heat of A. If the external work done during these changes be zero or negligible we may write

$$q_T - q_0 + C_B (T - T_0) + C_A (T_0 - T) = 0,$$
$$\text{or}\quad q_T = q_0 + (C_A - C_B)(T - T_0).$$

Note 4, (page 256).

If we call u the velocity with which Na ions move through a solution of Na_2SO_4 under the influence of a given E. M. F., and v the velocity of the SO_4 ions under the same circumstances, the quantity of Na ions which move out of the solution surrounding the anode, i. e. the loss of Na_2SO_4 there, will be proportional to u, and similarly the loss of Na_2SO_4 from the solution round the kathode will be proportional to v, the whole quantity of Na_2SO_4 decomposed being proportional to $(u + v)$. The migration constant for the Na ion is the ratio between the diminution in the quantity of Na_2SO_4 in the solution round the anode, and the whole quantity decomposed, i. e. $n = \frac{u}{u+v}$.

If we call the whole quantity decomposed unity, n is the quantity of Na ions which moves out of the solution round the anode, and $\frac{v}{u+v} = (1 - n)$ the quantity of SO_4 ions which moves out of the solution surrounding the kathode.

Note 5, p. 89. *Valvolin* is a trade name for vaseline, used in Hamburg.

NAME INDEX.

Alexejeff 208
Arrhenius 123, 131, 133
Askenasy 42, 47, 48, 49
Aubel (van) 94

Baker 32, 33, 59, 81, 86
Baur 169, 203
Baeyer 92
Bellati 246, 247
Berthelot 28, 30, 36, 52, 92, 93, 123, 124, 145, 146, 151, 154, 163, 215, 224, 225, 242
Bodenstein 32
Boguski 27
Bois-Reymond (du) 201
Bordet 168
Boyle 205, 210, 222
Braun 254, 271
Bredig 169, 198, 257, 258, 261, 263
Bremer 159, 178
Brodie 215
Buchanan 14, 32
Bunsen 33, 39, 48, 91, 93, 136

Cailletet 168
Chancel 168
Chappuis 83, 85
Charles 205, 210
Clausen 126
Clausius 242
Cohen 169, 188, 193, 198, 254, 257, 258, 261, 262, 263.
Conrad 125, 133
Czapski 254

Davy 51
Dent 25
Deventer (van) 150, 165, 169, 170, 173, 187, 207, 208, 250.
Deville 152, 223
Dewar 81
Dixon 32, 33, 59
Docters van Leeuwen 163
Duclaux 168
Dumas 51

Engelmann 52, 196
Esson 13, 93, 124, 135
Ettling 171
Evans 125
Ewan 33, 56, 61, 82
Eykman 189

Faraday 253
Forcrand (de) 168
Fourcroy 51
Friedel 52
Frowein 158, 161, 162, 178, 211, 221, 235, 236.

Gay-Lussac 205
Gibbs 254
Gockel 254
Goldschmidt 81, 170, 171, 250
Graham 32
Guldberg 145, 206, 233

Harcourt 13, 93, 124, 135
Harker 33
Hautefeuille 173, 221
Hecht 125, 133
Heide (van der) 172
Helmholtz H. 252, 253, 254
Helmholtz R. 82
Hemptinne (de) 116, 118, 119, 121
Henry 12
Hittorf 257
Hoff (van 't) 24, 30, 32, 34, 36, 49, 57, 59, 82, 123, 138, 145, 147, 148, 151, 165, 169, 170, 171, 173, 187, 206, 208, 243, 247, 250, 261, 267
Hofmann 36
Hood 20, 125, 132
Horstmann 143, 145, 151
Houton de Labillardière 51, 52

Ikeda 56, 61
Isambert 156, 157

Jahn 254
Jellett 269, 270, 271
Jorissen 52, 171, 250
Joubert 52, 61, 62, 66, 86, 141, 254
Joule 254

Kahlbaum 75
Konowalow 93, 125
Kooy 32, 49, 123, 125, 125, 126, 134, 169.
Kopp 171, 181
Krauel 42, 47, 48

Laar (van) 208, 210
Ladenburg 52
Landolt 28, 29
Le Chatelier 208, 243
Leeds 83, 96
Lehmann 164, 168, 221
Lemoine 36
Lescoeur. 193
Leverrier. 81
Ley 133
Linebarger 189
Loewel 168, 175, 187, 257, 261, 263
Löwenherz 118, 119, 180
Luff 92
Lussana . . . 167, 243, 244, 246

Mallard . - 243
Marchand 82
Marignac 208
Marum (van) 51
Meissner. 82
Menschutkin . . 28, 29, 93, 95
Meyer L 28, 30, 136
Meyer V . . 42, 47, 48, 49, 137
Meyerhoffer 172, 186
Miller (Lash) 199
Mitscherlich . . . 221, 230, 234
Moser. 193, 194
Mulder 168

Naumann . . . 43, 44, 93, 211
Nernst 188, 194, 254
Noyes. 102, 104, 111
Ogier 154

Ostwald 12, 13, 27, 115, 116, 119 125, 193, 199, 233.

Pareau 235
Parmentier. 168
Péan de Saint Gilles 28, 30 36, 92, 93, 145, 146.
Pfaundler 143, 145, 161
Pfeffer 230, 231, 232, 233, 234, 235
Pfeiffer 191
Poggendorff 201
Pringsheim. 33

Raoult 234
Raum 137
Reicher 4, 9, 30, 52, 94, 105, 115, 116, 119, 125, 130, 168, 171, 173, 181, 183, 207, 216, 243, 244, 247, 249.
Reinizer 81
Rennie 92
Rodwell 246
Romanese 246, 247
Röntgen 30, 31
Roozeboom (Bakhuis) 168, 176, 184, 187, 207.
Roscoe 33, 48, 91, 93
Rose 51
Rüdorff 171

Sabatier 125
Salzer. 85
Scacchi 170, 186, 250
Schiff. 173, 178
Schönbein 83
Schwab . . . 15, 17, 28, 129, 130
Schwarz . . 167, 181, 185, 203, 244
Schwicker 105
Scott 104
Shenstone 34
Skalweit. 83
Smithells 25
Spohr. 125, 133
Spring 27, 30, 93, 94, 243, 247, 248
Stadt (van de) 20, 33, 54, 57, 58, 59, 60, 207, 208.
Stefan. 63
Swart 152

Tammann 31

Than 33
Thomsen 161, 224, 225, 262, 264
Thomson J. J. 80, 81
Thomson W. 254, 255
Thorpe 86
Tollens 37
Troost 152, 173, 221
Tutton 86

Urech 32, 90, 91, 94, 107, 133

Verschaffelt . . . 169, 188, 199
Vriens 161, 172, 221

Waage 145, 206
Walker 199
Warder 4, 33, 116, 125, 130, 133
Weltzien 173
Wiedemann E. 169, 184
Wiedemann G. 236
Wilhelmi 13
Wittwer 13
Wright 92
Wyrouboff 170, 186

SUBJECT INDEX.

Acetamide, decomposition of, by acids, ... 12, 125
Acetic acid, etherification of, 28
Acids, influence of the nature of, on the hydrolysis of their esters 116, 120
Active oxygen, ... 82—86
Activity coefficient. 208
Affinity 229
„ at absolute zero, . . 241
„ measurement of, 230—235
„ of salts for water of crystallisation, . . 230, 234
„ work done by, . 235—240
Alcohol, influence of the nature of, on the hydrolysis of its esters, ... 116, 119
„ retarding action of, 28, 34, 35
Aldehyde, rate of oxidation of, 73--80
Alkaloids, ... 269, 271
Ammonia, decomposition of . 33
Ammonium carbamate, 34, 89, 94
„ carbonate, . . . 34
„ nitrate, 164, 168, 221 246, 247
„ sodium racemate, transition point of, 170, 171, 250
„ sulphide, dissociation of, 155, 156, 157, 205 219, 223, 267
Amyl alcohol, solubility of, in water. 189, 190
Aniline, action of, on acetic acid, 28, 93
Anti-benzaldoxime acetate . . 133
Arsenic compounds, preparation of by pressure, ... 30
„ hydride, decomposition of 1, 2, 20, 32, 99, 134
Arsenic oxidation of, ... 52
Astrakanite, transition point of 169, 176, 178, 179, 184, 187
Atomic condition of oxygen gas, 80, 82—86

Barium chloride, affinity of, for water, . . 234
„ „ hydrated, heat of formation of, ... 161
Benzene, nitration of,. . . . 28
Bimolecular reaction . . 4, 9, 15
Birotation of milk sugar, . . 32
Bloedite (astrakanite) 169, 176, 178 179, 184, 187
Bromic acid, action of hydriodic acid on, ... 140

Cadmium choride (hydrated), transition point of, ... 169
Calcium carbonate, dissociation of, 218
Calcium oxalate, action of acids on, ... 155
Cane sugar, inversion of, 30, 32 125, 133
Carbon, oxidation of 33
„ monoxide, explosion of with oxygen, 33
„ „ action of, on metallic oxides, 92
„ „ action of, on water, . . 151
Catalytic action,. . . . . 31—34
„ „ of hydrogen and hydroxyl ions, . . . 116, 121
Chemical induction . . 91—98
Chloracetic acid, action of water on, 14, 32, 125, 130
Chloracetate of sodium, action of NaOH on, ... 15, 125, 129

Chlorine, action of, on hydrogen, 33, 91, 93
Colour, determination of the transition point by, ... 203
Concentration currents, . 193, 194
„ gaseous, . . . 18
„ of a system,. . 12
„ unit of, . . . 4
Condensed systems, ... 163
„ „ incompatibility of 165
Contact action, . . 26—29, 31—34
Copper, action of on $ZnSO_4$, 269
„ bipotassium chloride, decomposition of, 161, 162, 172, 229
„ calcium acetate, 30, 171, 172, 247
„ sulphate, affinity of for water, 234, 235
„ „ dissociation of hydrated, 158, 160
„ „ heat of formation of hydrated, ... 160, 161
Crystallisation method of determining the transition temperature, 186
Cuprous chloride, action of, on silver, 271
Cyamelide, see cyanic acid. .
Cyanic acid, polymerisation of, 36—38, 43—45, 88, 96, 97, 107—110, 173, 174, 220—223
Cyanogen, ... 25
Cyanuric acid, see cyanic acid
Cycle of chemical equilibria, 271

Depression of freezing point, 233
Devitrification, ... 47
Dibromsuccinic acid, 30, 113, 114, 115, 125, 127, 128
α-Dichlorhydrine, decomposition of 125
Differential tensimeter, . . . 178
Dilatometer, ... 94, 181
Dimethyl ethylene hydrochloride, decomposition of, ... 125
Dissociation, . 144, 152, 155—157
„ pressure of hydrated salts, 158—161, 188
Disturbing actions, elimination of 86—91
„ „ in gases, 31, 43, 50
„ „ in liquids, . 26
Double decomposition, transition temperature in cases of, 169, 173, 229

Electrical conductivity, . . . 203
„ methods of determining the transition point, 193-203
„ work done by chemical change, 251, 252, 254, 255
Electrodes, unpolarisable, 195, 196, 199
Electrolytic gas, transformation into water. . 36, 39—42, 45—49, 95
Electromotive force, . . 253, 264
„ „ connexion of with equilibrium constant 267
Electromotive force, determination of direction of change by means of, ... 272
Electromotive force, measurement of 196
Electromotive force, produced by chemical change 253
Equilibrium, chemical, . . . 143
„ „ analogy with physical, ... 211
Equilibrium, chemical, in condensed systems, . . 163—180, 219
Equilibrium, chemical, in heterogeneous systems, . 155—168, 218
Equilibrium, chemical, in homogeneous systems, . 143—155, 222
Equilibrium, influence of temperature on, 148, 212, 217, 223—228
Equilibrium, constant. . . . 145
„ „ connexion of of with E. M. F.. 267
Equilibrium, physical, . . . 204
„ „ in condensed systems, ... 210, 219
Equilibrium, physical, in heterogeneous systems, . . . 205, 217
Equilibrium, physical, in homogeneous systems, . . 205, 222
Equilibrium, principle of mobile, 217, 228

REESE LIB OF THE UNIVERS OF CALIFOR

Esters, formation of, 28, 36, 92, 146, 151
Esters, hydrolysis of, 4, 11, 32, 115—121, 130, 131, 133
Etherification, 28, 36, 92, 146, 151
„ influence of pressure on, ... 30
Ethyl acetate, 4, 8, 11, 28, 115, 125, 130, 131, 133, 147
Ethylene hydrochloride, decomposition of 125
Evaporation, equilibrium of, 204—206, 217
Evaporation, rate of, . . . 63, 64
Explosive limit for dry phosphine and oxygen, ... 56
Explosive limit for moist phosphine and oxygen, ... 57—61
Explosion, velocity of, in dry gases, 33

Fatty acids, action of bromine on, 94
Ferric chloride, action of, on $SnCl_2$, 110—112
Ferrous sulphate, action of, on $KClO_3$, 132
Formaldehyde, polymerisation of, 36, 89
Freezing point, depression of, 233
Fumaric acid, action of bromine on, 105, 106
Fusion, ... 210, 219, 243

Gaseous concentration . . . 18
Glauber's salt, action of on ammonium chloride, ... 173
Glauber's salt, action of on potassium chloride. . 173, 177, 178
Glauber's salt, transition point of, 168, 169, 175, 179, 180, 184, 188, 191, 192, 193, 198—203, 230, 255—257

Heat evolved by reactions at high or low temperatures, 224—228
Heat evolved by reactions, connexion of, with equilibrium constant, ... 148—150
Heat evolved by reactions, connexion of, with velocity constant, 122—126
Heat of solution, . . . 207, 208
Hexane, rate of reactions in, 28
Hydrated salts, dissociation of, 158—161, 188
Hydrated salts, transition point of, 168, 179, 180
Hydrates, transition point of, 168
Hydriodic acid, action of, on bromic acid, ... 104
Hydriodic acid, action of, on hydrogen peroxide, ... 104
Hydriodic acid, decomposition of, 32, 36
Hydrolysis of esters, apparatus and methods, ... 6, 10
Hydrolysis of esters by acids, 116—121
Hydrolysis of esters by bases, 4, 11, 32, 115, 116, 130, 131, 133
Hypophosphoric acid, . . . 85

Identity methods of determining the transition point, . . . 186
Ignition temperature, . . 136—142
Incompatible systems. . 165, 219
Induction, chemical, . . . 91—98
Initial acceleration, . . . 91—98
Inversion of cane sugar, 30, 32, 133
Invert sugar, action of, on Fehling's solution, ... 90
Ionisation, effect of pressure on, 31
Isodibrom succinic acid, 113, 114, 115
Isomers, equilibrium of optical, 151
„ transition point of, . 173

Lactic acid, action of bromine on, 92
Lactones, action of bases on, . 12
Light, effect of, on chemical change, 33, 91, 92, 93
Limiting equation, ... 146

Magnesium sulphate, heat of formation of hydrated, . . . 161
Marble, rate of solution of, 27, 94
Maximum work, principle of, 224, 242
Medium, action of the, 26, 27, 43
Mercuric iodide, transition temperature of, ... 203
Metaphosphoric acid, action of water on, ... 125
Metaphosphorous acid, 21, 22, 23

Methyl ethylene hydrochloride, decomposition of, ... 125
Methyl iodide, action of, on sodium ethylate, ... 125, 133
Micro-organisms, behaviour of, to oxygen, ... 52
Milk-sugar, birotation of, . . 32
Minimum work, principle of, 225, 242
Mixtures, recognition of, 113—115
Moisture, influence of, on chemical change, . . 32—35, 58, 59, 81
Moistening the walls of the vessel, 89—91
Molecular volume, influence of on the rate of reaction, . . . 15
Monomolecular reaction, . 1, 13

Nickel carbonyl, oxidation of, 52
Nitration of benzene, ... 28
Nitriles, formation of, . . . 133
Nitrogen peroxide, 122, 144, 205, 222
Nitrogen peroxide, heat evolved by the dissociation of, . . 152—155
Normal reactions, ... 1
Number of molecules participating in a change, ... 99—112

Optical activity, ... 29
„ isomers, equilibrium between, ... 151
Osmotic pressure, . 189, 230—235
„ „ connexion of with vapour pressure . . . 232, 233
Oxalic acid, action of, on permanganate, ... 93
Oxidation of aldehyde, . 73—80
„ „ phosphine, 20—25, 33, 50—61
„ „ phosphorus, 32, 33, 51, 61—69, 81—86
„ „ sulphur, 33, 52, 69—73
Oxygen, atomic condition of, 80, 82
Ozone, formation by the silent discharge. 34
Ozone, formation during the oxidation of phosphorus, 82—86

Phosphine, decomposition of, 3, 20, 32, 43, 45, 49, 50, 99—101, 139
Phosphine, decomposition of, influence of temperature on, 126, 134, 135
Phosphine, oxidation of, 20—25, 33, 50—61
Phosphorescence, influence of temperature and pressure on, 61, 66, 141
Phosphorescence, intermittent, 86
Phosphorous acid, ... 21
Phosphorus, formation of active oxygen by oxidation of, . . 83
Phosphorus, oxidation of, 32, 33, 51, 61—69, 81—86
Platinum sponge, ... 27
Polymerisation, see cyanic acid and formaldehyde.
Polymolecular reaction, . . 4, 19
Polymorphous substances, transformation of, ... 167, 203
Potassium astrakanite . . . 173
„ chlorate, action of, on FeO, ... 20
Potassium chlorate, action of, on $FeSO_4$, ... 125, 132
Potassium hypoiodite, . . . 104
„ magnesium sulphates. 172, 173, 185
Potassium sodium racemate, 170, 171
Pressure, influence of, on the luminosity of phosphorus, 61, 66, 141
Pressure, influence of, on the oxidation of aldehyde,. . . . 79
Pressure, influence of, on the oxidation of phosphorus,. . 66, 69
Pressure, influence of, on the rate of reactions in liquids, . . 30
Pressure, influence of, on the transition temperature, . . 242, 243
Pressure, influence of, on the transition temperature of sulphur, 244—246
Principle of mobile equilibrium, 217—228

Racemates, . . 170, 171, 186, 250
Respiration of plants,. . . . 126
Rochelle salt, decomposition of, 162
Rotativity 29

Salts, hydrated, dissociation of, 158—161, 188

Schönite, ... 172, 185
Semipermeable membrane,. . 231
Silicon hydride, oxidation of, 52
Silver bromide, vapour pressure of, 273
Silver chloride, vapour pressure of 273
Silver iodide, transition temperature of, ... 247
Simonyite, see astrakanite.
Sodium ammonium racemate, 170, 171, 186, 250
Sodium ammonium tartrate, 170, 171, 186, 250
Sodium chloracetate, action of NaOH on, ... 15, 125, 129
Sodium ethylate, action of, on methyl iodide,. . . . 125, 133
Sodium hydrogen phosphate, hydrated, heat of formation of, 161
Sodium hydrogen phosphate, hydrated, transition temperature, 169, 203
Sodium potassium racemate, 170, 171
Sodium sulphate, anhydrous, 168, 169, 173, 175, 177—180, 184, 188, 191, 192, 193, 198-203, 230, 255-257
Sodium sulphate, decahydrated, 168 169, 173, 175, 177—180, 184, 188, 191, 192, 193, 198-203, 230, 255-257
Solubilities, product of, . . . 177
Solubility . . . . 206—209
Solubility at the transition temperature, . . 174—178, 186, 187
Solubility of water in amyl alcohol, 189, 190
Solution heat of, ... 207
„ pressure, . . . 188—192
„ „ of dissociation, 189, 192
Solutions, solid, ... 143
„ supersaturated, at the transition point, ... 175
Solvents, indifferent . . . 27—29
„ use of, in eliminating disturbing actions, ... 87—89
Stannous chloride, action of, on $FeCl_3$, ... 110—112
Steam, dissociation of, . . . 223
Sugar, osmotic pressure of solutions of, ... 231, 234
Sulphur compounds, preparation of by pressure, ... 30
Sulphur, oxidation of, 33, 52, 69—73
„ rate of change of rhombic into monosymmetric, . . 94, 95
Sulphur, transition point, 30, 94, 95, 168, 181—183, 210, 212—216, 220, 221, 244—246, 248, 249
Surface of the walls of the vessel, area of, ... 43
Surface of the walls of the vessel, nature of, ... 43—50
Synaldoxime acetates, . . . 133
System, unit of concentration of a, 12
„ „ quantity of a, . 253

Tartaric acid, action of bromine on, 92
Tartrates, transition temperature of, 163, 170, 171, 186, 250
Temperature coefficient of the transition cell, 199, 257—259, 266
Temperature, influence of, on equilibrium, ... 148, 212, 217
Temperature, influence of, on the velocity of reactions, 122—135
Temperature of ignition, 136—142
Tensimeter, ... 158, 187
Thermometric method of determining the transition point, 184, 185
Transition cell with stable and metastable phases, 194, 195, 254—259
Transition cell with stable and without metastable phases, 198—203, 258—266
Transition point (temperature), 164, 165
„ point, calculation of, 212—216, 248—251
„ determination of by the dilatometer, . . . 181—183
Transition point, determination of by electrical methods . . . 197
Transition point, influence of pressure on. 242, 243
Transition point, methods of determining the,. . . 180, 181, 203

Triethylamine, action of, on ethyl iodide, ... 28
Trimethylethylene hydrochloride, 125
Trimolecular reaction, 25, 110, 113
Turpentine, . . . : . . . 29

Units of concentration, . . 4, 12
Unit quantity of a system, . 253
" " " electricity . 259

Valvolin, ... 89, 275
Vapour pressure at the transition point, . . 178, 179, 180, 187, 188
Velocity constant, ... 1
" " influence of temperature on, ... 122—135
Velocity of explosion, effect of moisture on, ... 33
Velocity of reaction in mixtures, 113
Volume, change of, at the transition temperature, ... 184
Volume, influence of, on the rate of bimolecular reactions, . . 13
Volume, influence of, on the rate of monomolecular reactions, 3
Volume, molecular, influence of, on the rate of reactions, 13, 15, 18

Walls of vessel, effect of moistening, 86, 89, 90
Walls of vessel, influence of area of, 43
Walls of vessel, influence of nature of, ... 43, 50
Water, influence of, on chemical change, 32, 33, 34, 37, 58, 59, 81
Work done by chemical affinity, 235, 236, 238, 240
Work done by chemical affinity at absolute zero, ... 241
Work, electrical, done by chemical change, ... 251, 252
Work, principle of maximum, 224, 226, 242
Work, principle of minimum, 225, 242

Zinc, action of acids on, . . 94
Zinc sulphate, action of copper on. 269
Zinc sulphate, hydrated, affinity of for water, ... 234
Zinc sulphate, hydrated, heat of formation of, ... 161
Zinc sulphate, hydrated, transition temperature of, ... 169
Zinc sulphate transition cell, 194, 195

REESE LIBRARY
OF THE
UNIVERSITY
OF CALIFORNIA

THIS BOOK IS DUE ON THE LAST DATE STAMPED BELOW

AN INITIAL FINE OF 25 CENTS

WILL BE ASSESSED FOR FAILURE TO RETURN THIS BOOK ON THE DATE DUE. THE PENALTY WILL INCREASE TO 50 CENTS ON THE FOURTH DAY AND TO $1.00 ON THE SEVENTH DAY OVERDUE.

OCT 26 1938

FEB 25 1941M

JUN 23 1941

NOV 26 1943

FEB 21 1946

MAY 9 1946

NOV 1 1946

MAR 16 1948

LD 21-95m-7,'37

YD 04694

71504

QD501
H58

THE UNIVERSITY OF CALIFORNIA LIBRARY