MINISTRY OF MUNITIONS.
MUNITIONS INVENTIONS DEPARTMENT.
NITROGEN PRODUCTS COMMITTEE.

PHYSICAL AND CHEMICAL DATA OF NITROGEN FIXATION.

WITH 47 DIAGRAMS.

Specially Compiled for Use in Connection with the
SYNTHESIS AND OXIDATION OF AMMONIA
AND THE
PREPARATION AND PURIFICATION OF HYDROGEN.

M.I.D. RESEARCH LABORATORY,
UNIVERSITY COLLEGE,
DECEMBER, 1918.

Price 3s. Net.

INTRODUCTION.

THIS publication, containing a summary of physical and chemical data relating to the problems of nitrogen fixation, was first issued by the Munitions Inventions Department in April last and several hundred copies have now been circulated to British and Allied Government Departments and controlled works. Numerous enquiries have since been received from others desirous of obtaining copies and it has therefore been decided to place it on sale to the general public. At the suggestion of the Controller of Munitions Inventions, it may perhaps be useful if I indicate briefly its origin and objects.

In the course of the investigations proceeding at the M.I.D. Research Laboratory on certain processes for nitrogen fixation and allied problems, it became necessary to collect from all kinds of sources, some of which were not easily accessible, data relating to the subjects of the researches in question. At the outset, members of the Staff investigating the various branches had dealt with their different problems individually, but it became evident that much time would be saved if a more detailed critical examination of the chemical and physical constants available was undertaken and a compilation made summarising in a handy form the more important of these. I therefore requested Mr. G. W. Todd, D.Sc., B.A., Physicist to the M.I.D. Laboratory, to undertake this task, acting myself as general editor. This first publication has been compiled mainly by him after consultation with Lieut. H. C. Greenwood, D.Sc., Capts. J. R. Partington, D.Sc., and E. K. Rideal, Ph.D., and Dr. H. S. Taylor, the heads of sections of the Laboratory dealing with synthetic ammonia, the oxidation of ammonia, and the preparation and purification of hydrogen, respectively. On some of the subjects dealt with Dr. Todd has not been satisfied with gathering together from the different sources the meagre information available, but has exhibited considerable ingenuity in utilising these to advantage. In the majority of cases reference has been made to the original papers, instead of simply extracting the required figures from the usual books of constants.

The graphic form of presentation has been adopted deliberately, since for most purposes amply sufficient accuracy in the value required can usually be obtained by the use of graphs instead of a table, interpolation thus being altogether avoided. At the same time by means of a graph there is often also presented a general grasp of the facts not at once obvious from columns of figures. Thus the curve of freezing points of nitric acid (Fig. 25) shows that there are three different concentrations of acid having a freezing-point of – 30° C., and five strengths freezing at – 40° C.

Although only few of the data here presented depend on actual determinations carried out at the M.I.D. Laboratory, a considerable number of the tables and curves embody the results of special investigations and computations. Dr. Todd's mathematical treatment of the very important question of the oxidation of nitric oxide to peroxide, given in the Nitric Acid section, should be of distinct service in its application to tower design in the arc process for the fixation of nitrogen and in the ammonia oxidation and Häusser processes. So far as I am aware, his work offers the first general mathematical solution of the problem. Again, the data on the behaviour of oxygen, nitrogen and hydrogen gases under pressure depend on a theoretical investigation of the whole question of the departure from Boyle's law of gases under high pressure, made by Mr. C. Cochrane, M.A., B.Sc. His results, which have been closely confirmed by subsequent experiments, show that, contrary to preconceived ideas, the divergence is of an order which is much too large to be neglected in technical practice. As an example of specially computed tables may be instanced the series of curves representing the percentage of ammonia and of nitrogen peroxide theoretically removable from a mixture containing the gas in varying percentages. These have been calculated so as to give, in a convenient form, full details as to the theoretical possibilities of the process of separation of the liquefiable constituent by freezing.

This publication in its present form is to be regarded rather as an instalment than as a completed work, and the Munitions Inventions Department would be glad to have their attention drawn to any errors which it may contain, and to receive from users any criticisms or suggestions for its improvement, especially in regard to data the incorporation of which would render it more valuable. One or two minor corrections only have been introduced into this second issue, which is substantially a reprint of the earlier edition. That the errors frequently found in the first edition of a book of this kind were so few is due to the care with which the original manuscript was prepared for the press and the proofs corrected by Mr. William Hill, B.A., of the Headquarters Staff of the Munitions Inventions Department.

J. A. HARKER,
Director of Research.

Munitions Inventions Research Laboratory,
University College, London,
December, 1918.

CONTENTS.

GAS DATA.

Section I. PAGE

Section II.

AMMONIA DATA.

Section III.

NITRIC ACID DATA.

x (33)12343 Wt 17171—153 1000 9/20 E & S

SECTION III.—*cont.*

HYDROGEN PURIFICATION DATA.

SECTION IV.

SECTION V.

MISCELLANEOUS DATA.

Further general information on Chemical and Physical Constants may be obtained from :—

Physical and Chemical Constants.—Kaye and Laby (Longmans). 1916, 2nd ed., pp. 153. Referred to in the text as "Kaye and Laby."

Smithsonian Physical Tables.—Fowle (Smithsonian Institution). 1916, 6th ed., pp. 343.

Recueil de Constantes Physiques.—Abraham and Sacerdote (Gautier-Villars). 1913, pp. 753.

Tables Annuelles Internationales de Constantes.—1912 *et seq.* (Gautier-Villars).

Physikalisch-Chemische Tabellen.—Landolt-Bornstein-Roth. 1912, 4th ed., pp. 1313. Referred to in the text as "Landolt."

Physico-Chemical Tables.—Castell-Evans (Griffin). 2 vols., pp. 1235.

Also from :—

Ready Reference Tables.—Hering (Chapman and Hall). 1914, pp. 196.

Technical Chemist's Handbook.—Lunge (Gurney and Jackson). 1916, pp. 264.

Chemist's Year-Book.—Atack (Sherratt and Hughes). 1917, 2 vols. pp. 990.

SECTION I.

GAS DATA.

1. Deviation of Hydrogen and Nitrogen from Boyle's Law at High Pressures.

A "perfect" gas obeys Boyle's law $PV = RT$, where P = pressure, V = volume, and T = absolute temperature. When T is constant, PV should be constant. Real gases follow this law closely up to pressures of the order of 50 atmospheres, but depart from it considerably at high pressures (*see* Amagat's curves, Fig. 1). According to Boyle's law, the pressure is proportional to the density, provided the temperature is constant.

Natterer (*Pogg. Ann.*, LXII., p. 139; XCIV., p. 436) put equal increments of gas into a constant volume and measured the resulting pressures. His values for hydrogen and for nitrogen are given below:—

HYDROGEN.

No. of Masses introduced.	1	8	28	68	128	138	238	248	418	498	608	758	908	1,008
Pressure in Atmos.	1	8	28	68	134	146	274	287	539	685	958	1,434	2,044	2,790

NITROGEN.

No. of Masses introduced.	1	15	75	225	235	355	415	495	605	705
Pressure in Atmos.	1	15	75	240	252	444	600	882	1,640	2,790

Evidently P is not proportional to the density even in the cases of the nearly "perfect" gases hydrogen and nitrogen. In high-pressure gas work this divergence from Boyle's law must be taken into account.

The most reliable data for hydrogen and nitrogen are those of Amagat, given graphically in Fig. 1, where the product PV is plotted against P, the temperatures being given on the curves.

Since no gas obeys Boyle's law exactly, a cylinder of gas at n atmospheres will not yield exactly n times its volume of gas at atmospheric pressure. If gas cylinders of equal volume contain respectively hydrogen, nitrogen, and carbon dioxide at 16° C. and at a pressure of 120 atmospheres, they will yield at the same temperature and at atmospheric pressure 111·3 times their volume of hydrogen, 120 times their volume of nitrogen and 485 times their volume of carbon dioxide.

The following table, which Mr. C. Cochrane has deduced from the PV curves of Amagat and other observers, gives the relative volumes occupied by various gases when the pressure is reduced from the value given at the head of the column to 1 atmosphere:—

Gas (Temp. = 16° C.)	Relative volume which the Gas will occupy when the Pressure is reduced to Atmospheric from					
	1 atm.	50 atm.	100 atm.	120 atm.	150 atm.	200 atm.
"Perfect" gas	1	50	100	120	150	200
Hydrogen	1	48·5	93·6	111·3	136·3	176·4
Nitrogen	1	50·5	100·6	120·0	147·6	190·8
Air	1	50·9	101·8	121·9	150·3	194·8
Oxygen	1	—	105·2	—	—	212·6
Oxygen (at 0° C.)	1	52·3	107·9	128·6	161·9	218·8
Carbon dioxide	1	69·0	477*	485*	498*	515*

* Carbon dioxide is liquid at pressures greater than 90 atmospheres.

This table shows that the departures from Boyle's law, even for a gas such as hydrogen, are of considerable technical importance. Thus a purchaser buying hydrogen according to an accurate pressure gauge would be receiving, if the cylinder had its nominal capacity at 120 atmospheres (the usual working pressure), only 92·7 per cent. of his proper amount, and if the pressure were higher a still smaller proportion. For oxygen, on the contrary, the error is in the reverse direction, the table showing that the purchaser would receive over 5 per cent. too much at 100 atmospheres.

These considerations are of importance in estimating, for example, the number of cylinders of compressed hydrogen required to fill a balloon or airship of given volume.

2. Hydrogen-Nitrogen Mixture ($N_2 + 3H_2$) at High Pressures.

In connection with the synthesis of ammonia, it is often necessary to fill cylinders with the component gases in the right proportions at 100 to 200 atmospheres pressure. One accurate method of doing this would be to mix the gases in the correct proportions at atmospheric pressure before compression, but it is often much more convenient to compress first one gas into the cylinder and then add the other. If the final pressure of a ($N_2 + 3H_2$) mixture is to be, say, 200 atmospheres, it will not be correct, even for technical purposes, to add nitrogen at 50 atmospheres and fill up with hydrogen to 200 atmospheres, on account of the deviations from Boyle's law. Mr. C. Cochrane, assuming Leduc's law that "the volume occupied by a mixture of gases is equal to the sum of the volumes which the component gases would separately occupy at the same temperature and under the same pressure as the mixture," has deduced the following table for use when the gases are pumped separately into the cylinders:—

GAS MIXTURES FOR THE SYNTHESIS OF AMMONIA.

Temperature = 16° C.

If Final Pressure of Mixture is to be	Then Initial Pressure of Hydrogen should be	Or Initial Pressure of Nitrogen should be
atm. (abs.)	atm. (abs.)	atm. (abs.)
25	19·0	6·0
50	38·0	12·2
75	56·0	18·0
100	75·0	23·6
125	94·0	29·3
150	111·0	34·4
175	130·0	39·5
200	148·0	44·5

Thus, if it is desired to fill a cylinder to a final pressure of 200 atmospheres and the hydrogen is put in first, the pressure of hydrogen should be adjusted to 148 atmospheres, the nitrogen being afterwards added up to a gauge reading of 200 atmospheres. But if the nitrogen is filled in first, only 44·5 atmospheres are required, instead of 50, which would be the case if Boyle's law were obeyed, the ratio of the partial pressure of the nitrogen to that of the hydrogen being actually 1 to 3·49, instead of the theoretical 1 to 3.

The figures in the table have been calculated from Amagat's *PV* curves, and it has been found that cylinders pumped up with the gases according to them contain the correct ($N_2 + 3H_2$) mixture for the synthesis of ammonia.

3. Van der Waals' Constants and Critical Data.

Several "real" gas equations have been proposed, the best known being that of Van der Waals :

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT,$$

where a, b are constants characteristic of the gas. The following table has been taken from *Physical and Chemical Constants* (Kaye and Laby), p. 34 :—

GAS.	CRITICAL TEMPERATURE. ° C.	CRITICAL PRESSURE. Atmospheres.	CRITICAL VOLUME. cc.	a	b
H_2	−234·5	20	0·00264	0·00042	0·00088
N_2	−146	33	·00517	·00257	·00156
NH_3	+130	115	·00481	·00798	·00161
NO	− 93·5	71·2	·00347	·00257	·00116
NO_2	+171·2	147	·00413	·00756	·00138
N_2O	+ 38·8	77·5	·00436	·00710	·00184
Air	−140	39	·00468	·00257	·00156
O_2	−118	50	·00426	·00273	·00142
A	−117·4	52·9	·00404	·00259	·00135
CH_4	− 95·5	50	·00488	·00357	·00162
CO	−141·1	35·9	·00505	·00275	·00168
CO_2	+ 31·1	73	·0066	·00717	·00191

The *critical temperature* is the highest temperature at which a gas can be liquefied by compressing it.

The *critical pressure* is the pressure which produces liquefaction at the critical temperature.

The *critical volume* is given in the above table as the ratio of the volume that the gas occupies at the critical temperature and pressure to the volume it would occupy at 0° C. and 760 mm.

Taking pressures in atmospheres and the volume at 0° C. and 1 atmosphere as 1, then

$$R=\frac{PV}{T}=\frac{1}{273}$$

In these units b is in terms of the volume of the gas at 0° C. and 1 atmosphere.

$$a=\frac{27R^2T_c^{\,2}}{64P_c} \quad \text{and} \quad b=\frac{RT_c}{8P_c}$$

Van der Waals' equation affords an explanation of the form of Amagat's curves. The equation may be written—

$$\left(PV+\frac{a}{V}\right)\left(1-\frac{b}{V}\right)=RT. \quad \therefore PV=\frac{RT}{1-b\rho}-a\rho, \text{ where } \rho=\frac{1}{V}.$$

$$\therefore \frac{d}{d\rho}(PV)=\frac{b\,RT}{(1-b\rho)^2}-a.$$

Hence there is a minimum value of PV for a density given by $\dfrac{bRT}{(1-b\rho)^2}=a$.

If this equation gives a positive value for ρ the curves are like those of N_2. If ρ is negative the PV curves are like those of H_2 (Fig. 1). As T diminishes, ρ for the minimum PV increases. This can be seen in the N_2 curves. At much lower temperatures, PV for H_2 should also show an initial diminution with increasing P or ρ.

4. Density of Gases.

The following table, from the figures given in "Kaye & Laby" (p. 26), gives the density of various gases at 0° C. and 760 mm. pressure:—

DENSITY OF GASES.

Gas.	Density (gms. per litre).	Density relative to Oxygen.	Density relative to Hydrogen.
Air - - - - -	1·2928	0·9047	14·385
Oxygen - - - - -	1·4290	1·0000	15·900
Hydrogen - - - -	0·08987	0·06289	1·000
Nitrogen - - - -	1·2507	0·8752	13·916
Argon - - - - -	1·7809	1·2463	19·816
Nitrous oxide - - -	1·9777	1·3840	22·006
Nitric oxide - - - -	1·3402	0·9379	14·912
Ammonia - - - -	0·7708	0·5394	8·577
Carbon monoxide - - -	1·2504	0·8750	13·913
Carbon dioxide - - -	1·9768	1·3833	21·996

DENSITY OF NITROGEN PEROXIDE.

The density (oxygen = 16) of nitrogen peroxide at different temperatures and 760 mm. pressure ("Kaye & Laby," p. 26) is given below:—

Temp. ° C. - - -	26°·7	39°·8	60°·2	80°·6	100°·1	121°·5	154°·0	183°·2
Density - - -	38·37	35·62	30·12	26·06	24·33	23·46	22·88	22·73

These figures indicate that, while at the lower ranges the gas is almost completely N_2O_4, at the higher temperatures above, say 140° C., it is practically completely dissociated.

5. Viscosity of Gases.

The viscosity of a fluid is measured by the tangential force on unit area of either of two parallel planes at unit distance apart, one of which is fixed while the other moves with the unit of velocity, the space between being filled with the fluid. Or, we may say that the viscosity coefficient η is the ratio of the tangential stress T to the velocity gradient $\frac{dv}{dx}$.

$$T = \eta \frac{dv}{dx}.$$

T is measured in dynes per sq. cm.; v is measured in cm. per sec.; x is measured in cm.

The viscosity of a gas changes considerably with temperature, but is practically independent of pressure.

(*a*)—VISCOSITY OF GASES.

GAS.	TEMPERATURE ° C.	VISCOSITY (η_t).
Air - - - -	– 21 0	0·000164 0171
Hydrogen - - -	– 21 0 15 99 302	0·0000819 0841 0889 0·000106 139
Nitrogen - - -	– 21 0 11 54 183	0·000157 166 171 190 246
Oxygen - - - -	0 15 54	0·000187 195 216
Nitric Oxide - - -	0 20	0·000165 186
Water Vapour - - -	0 15 100	0·000090 097 132

Sutherland gives for the variation with temperature:—

$$\eta_t = \eta_0 \frac{273 + C}{\theta + C}\left(\frac{\theta}{273}\right)^{\frac{3}{2}},$$

where θ = absolute temperature and C = constant.

(*b*)—VISCOSITY OF N_2 AND H_2 MIXTURES.

Reference:—Kleint, *Ver. phys. Ges.*, 7, 146, 1905.

PER CENT. H_2.	PER CENT. N_2.	TEMPERATURE ° C.	$\eta_t \times 10^7$	$\eta_0 \times 10^7$	SUTHERLAND'S C.
0·0	100·0	14·6 99·8 182·7	1742 2125 2459	1671	118
19·97	80·03	15·7 99·6 183·1	1714 2077 2405	1639	114
36·20	63·80	14·2 99·7 183·4	1659 2011 2321	1595	104

[*Table continued over*

(*b*)—VISCOSITY OF N_2 AND H_2 MIXTURES (*continued*).

PER CENT. H_2.	PER CENT. N_2.	TEMPERATURE °C.	$\eta_t \times 10^7$	$\eta_0 \times 10^7$	SUTHERLAND'S C.
53·55	46·45	14·6 99·8 183·4	1583 1921 2216	1522	104
82·61	17·39	17·0 99·9 183·2	1328 1593 1829	1269	94
93·62	6·38	16·7 99·9 183·7	1116 1329 1529	1067	86
100·0	0·0	13·0 100·4 183·8	873 1050 1212	841	91

From Kleint's results we can deduce the viscosity of $N_2 + 3H_2$ mixture at different temperatures. The following table is deduced from Kleint's figures :—

(*c*)—VISCOSITY OF $N_2 + 3H_2$ MIXTURE AT VARIOUS TEMPERATURES.

TEMP. ° C. - -	0	17	100	183
$\eta \times 10^7$ - -	1350	1450	1710	1970

Putting these figures into Sutherland's formula gives C = 96, whence—

$$\eta_{500} \times 10^7 = 2760 \qquad \eta_{600} \times 10^7 = 2950.$$

(*d*)—VISCOSITY OF NH_3 AND H_2 MIXTURES AT 12° TO 13° C.

Reference :—Thomsen, *Ann. d. Phys., 36*, pp. 825, 832.

VOL. OF H_2 IN 100 VOLS. MIXTURE	0·0	8·2	20·1	33·9	53·6	68·4	79·1	90·2	100·0
$\eta \times 10^7$ - - - - - - -	1005	1017	1042	1068	1102	1104	1089	1036	915

NOTE ON THE FLOW OF GASES THROUGH PIPES.

When the velocity of flow of a gas is below a critical value, depending on the density and viscosity and on the diameter of the tube, the gas moves in stream-lines parallel to the axis of the tube Above this critical velocity the stream-lines disappear and the flow becomes turbulent.

The critical velocity $V_c = k \dfrac{\eta}{\rho r}$ for small pipes up to, say, 5 cm. diam., where k is a constant, ρ is the gas density and r is the tube radius. When V_c, η, ρ and r are in C.G.S. units, k is 10^3 in round numbers.

Below the critical velocity the pressure drop along a tube is proportional to the velocity of gas flow. Above the critical velocity the pressure drop is practically proportional to the square of the velocity.

6. Specific Heat of Gases.

The specific heat of a substance is the quantity of heat in gm. calories required to raise 1 gram of it through 1° C. The specific heat of a gas at constant pressure C_p is always greater than the specific heat at constant volume C_v.

Thermodynamics gives

$$C_p - C_v = T\left(\frac{dp}{dT}\right)_v \left(\frac{dv}{dT}\right)_p.$$

Whence for a gas which follows Boyle's law, $C_p - C_v = R$; and for a gas which follows Van der Waals' law, $C_p - C_v = R\left\{1 + 2a\,\frac{(v-b)^2}{RTv}\right\}$ R in gm. cals. per gm. mol. $= 1{\cdot}985$.

(a) SPECIFIC HEATS AT CONSTANT PRESSURE.

AIR.

The following Table for Air (C_p and its variation with temperature) is taken from Landolt, p. 773 :—

TEMP. ° C. - -	− 183°	−30° to +10°	0° to 100°	20° to 440°	20° to 630°	20° to 880°
C_p - - -	0·253	0·238	0·237	0·237	0·243	0·243

Witkowski gives variation with temperature and pressure as follows :—

1 atmosphere - - -	− 102° to + 98° C.	0·237
40 atmospheres - - -	− 140°	2·607
40 " - - - -	− 120°	0·470
40 " - - - -	− 50°	0·274
70 " - - - -	− 120°	0·777
70 " - - - -	− 50°	0·312

The following table, showing the variation with pressure of C_p for air at 60° C., is given by Holborn and Jakob (*Z. Ver. deut. Ing.*, *58*, 1429, 1914). Three observers are in fair agreement.

PRESSURE. (Atmospheres).	HOLBORN AND JAKOB'S VALUES.	LUSSANA'S VALUES.	VOGEL'S VALUES.	NOELL'S VALUES.
1	0·2415	0·2370	—	—
25	·2490	·2711	0·2480	0·2490
50	·2554	·3061	·2543	·2568
100	·2690	·3675	·2664	·2701
150	·2821	·4195	·2770	·2812
200	·2925	—	·2853	·2893

6. Specific Heat of Gases *(continued).*

Recent experiments of Holborn and Jakob (*Z. Ver. deut. Ing., 61*, p. 146, 1917) give for air at 60° C. between pressures of 1 and 300 atmospheres :—

$$10^4C_p = 2414 + 2\cdot86p + 0\cdot0005p^2 - 0\cdot0000106p^3.$$

Hydrogen.

Regnault	− 28° to + 9° C.	3·400
Wiedemann	+ 21° to + 100°	3·410
Regnault	+ 12° to + 198°	3·409

Lussana gives variation with pressure :—
1 atmosphere, 3·402 ; 30 atmospheres, 3·788.

Nitrogen.

Scheele and Heuse	at 20° C.	0·249
Regnault	0° to 200°	0·244
Alt gives for liquid nitrogen	− 208° to − 196°	0·430

Ammonia.

Wiedemann	23° to 100° C.	0·520
„	27° to 200°	0·536
Nernst	365° to 680°	0·65

Tamaru (*Z. Electroch., 21*, p. 240, 1915) gives for ammonia—

$$C_p = 8\cdot62 + 0\cdot0035t + 5\cdot1 \times 10^{-6}\, t^2,$$

where C_p is the heat in gm. cals. required to raise 1 gm. mol. through 1° C. at a temperature t° C.

Nitrous Oxide :		
Wiedemann	26° to 103° C.	0·213
Nitric Oxide :		
Regnault	13° to 172° C.	0·232
Nitric Peroxide :		
Berthelot and Ogier	27° to 67° C.	1·625
Water Vapour :		
Holborn and Henning	at 100° C.	0·465

(b) SPECIFIC HEATS AT CONSTANT VOLUME.

Air.

Holborn and Henning	at 100° C.	0·163
	„ 600° C.	0·173
	„ 1100° C.	0·191

Hydrogen.

Joly	at 50° C.	2·40
Pier	0° to 2500° C.	2·89

Nitrogen.

Pier	0° to 2500° C.	0·215

Mallard and Le Chatelier give for N_2 up to 3000° C.

$$C_v = 0\cdot170 + 0\cdot0000872t.$$

Ammonia

Voller	at 18° C.	0·390

Water Vapour.

Pier	at 100° C.	0·340

(*c*) SPECIFIC HEAT AT CONSTANT PRESSURE OF $N_2 + 3H_2$ MIXTURE UNDER VARIOUS PRESSURES.

Assuming, as is justifiable, that the heat capacity of the mixture is the sum of the heat capacities of the constituents, we obtain

$$C_P = 0{\cdot}806 \text{ between } 0^\circ \text{ and } 100^\circ \text{ C. and at 1 atm. pressure.}$$

Holborn and Jakob's figures show that *for air* at 60° C. a linear law holds, namely:—

$$C_p = C_1 \left\{ 1 + (P - 1)a \right\},$$

where P = absolute pressure in atmospheres, $a = 0{\cdot}0013$, and C_1 = specific heat at 1 atmosphere.

Assuming the linear law and taking Witkowski's values at low temperatures, we get

for air at -50° C. $a = 0{\cdot}0056$; at -120° C. $a = 0{\cdot}011$.

These scanty data suggest that aT^2 (where T is the absolute temperature) is constant, so that

$$\frac{da}{dT} = -\frac{\text{constant}}{T}.$$

When T is great, the change of a with T will be small and negative.

The only other datum on change of specific heat with pressure is that of Lussana, given above for *hydrogen*. Assuming the linear law, then, for hydrogen at ordinary temperatures $a = 0{\cdot}0037$.* If we take a for nitrogen to be the same as a for air, *i.e.*, $0{\cdot}0013$, we shall not make a grave error in putting a for $N_2 + 3H_2$ mixture equal to $0{\cdot}0025$ at ordinary temperatures.

Hence we may take the specific heat at constant pressure of $N_2 + 3H_2$ mixture as given by:

$$C_P = C_1 \left\{ 1 + 0{\cdot}0025\,(P-1) \right\} \text{ ; or, } C_P = 0{\cdot}80 + 0{\cdot}002\,(P-1).$$

At high temperatures the coefficient of $(P - 1)$ may be slightly less.

The following values are deduced from this expression* :—

P atmospheres - - - - - -	1	30	50	100	150	200
Specific heat at cons. press. - - -	0·80	0·85	0·90	1·00	1·10	1·20

Thermodynamics gives

$$\frac{d}{dp}\left(C_p\right) = -T\left(\frac{d^2v}{dT^2}\right)_p$$

whence

$$C_p - C_1 = -T\int_1^P \left(\frac{d^2v}{dT^2}\right) dp.$$

Modifying Van der Waals' equation to

$$pv = RT + pb - \frac{ap}{RT}, \text{ we get } \left(\frac{d^2v}{dT^2}\right)_p = -\frac{2a}{RT^3}.$$

Whence

$$C_p - C_1 = \frac{2a}{RT^2}(P-1), \text{ or, } C_p = C_1\left\{1 + \frac{2a}{RT^2}(P-1)\right\}.$$

This gives

$$\frac{da}{dT} = -\frac{\text{constant}}{T^3}.$$

Modifications of the other gas equations also give approximately linear relations between C_p and pressure.

---

* Experiments made in the M.I.D. laboratory on hydrogen suggest a much lower value for a, so that the figures in the table may be too high.—G.W.T.

6. Specific Heat of Gases *(continued)*.

(*d*) SPECIFIC HEAT OF $N_2 + 3H_2 + n$ Per Cent. NH_3 MIXTURES.

Assuming that the heat capacity of the mixture is the sum of the heat capacities of the constituents, the following table has been calculated for 1 atmosphere pressure at ordinary temperatures :—

Per cent. NH_3 (by vol.) - - - - -	0	1	2	3	4	5
Specific heat - - - - - -	0·806	0·802	0·797	0·790	0·782	0·779

Taking the pressure coefficient as 0·025, approximate values of the specific heat at higher pressures can be obtained.

At temperatures of 365° C. to 680° C. Nernst gives C_p for ammonia as 0·65. This, however, does not affect the figures in the above table, the percentages of ammonia being so small.

(*e*) RATIO OF THE SPECIFIC HEATS (γ).

The ratio of the specific heats of air, nitrogen and hydrogen is for all practical purposes independent of the temperature.

AIR.

γ at different temperatures (various observers). *Reference* :—Landolt, p. 775.

TEMP. ° C. - -	– 181°	– 156°	0°	18°	100°	900°	950°
γ - - - - -	1·34	1·39	1·405	1·405	1·403	1·39	1·34
OBSERVER - -	Cook		Wüllner	Röntgen	Leduc	Kalähne	Stevens

Partington (*Phys. Zeit.*, 1913) gives at 18° C., $\gamma = 1·403$.

Holborn and Henning obtain from explosion experiments (*Ann. d. Phys.*, 23, 1907) :—

TEMP. ° C. - - -	100°	600°	1100°
γ - - - - -	1·404	1·38	1·345

The ratio γ may change considerably with pressure, as the following table for air at – 79° C. (Koch) shows :—

PRESS. (atm.) -	1	25	50	100	150	200
γ - - -	1·405	1·569	1·767	2·200	2·469	2·333

Apparently γ has a maximum value in the neighbourhood of 150 atmos., where its value is 75 per cent. greater than its value at 1 atmosphere. It is impossible to say whether this same increase would take place if the temperature were 500° or 600° C., instead of – 79° C.

HYDROGEN.

$\gamma = 1{\cdot}41$ - - - - - - - - - Cazin.
$= 1{\cdot}38$ - - - - - - - - - Maneuvrier and Fournier.
$= 1{\cdot}408$ (4° to 16° C.) - - - - - - Lummer and Pringsheim.

No data are available for different pressures.

NITROGEN.

$\gamma = 1{\cdot}45$ (at – 192° C.) - - - - - - Valentiner.
$= 1.41$ - - - - - - - - Cazin.
$= 1{\cdot}389$ - - - - - - - - Rohlf.

No data are available for different pressures.

AMMONIA.

$\gamma = 1{\cdot}262$ (21° to 40° C.) - - - - - - Müller.
$= 1{\cdot}317$ (0°) - - - - - - - - Wüllner.
$= 1{\cdot}277$ (100°) - - - - - - - - ,,

No data are available for different pressures.

HYDROGEN-NITROGEN MIXTURES.

For any mixtures of N_2 and H_2 at ordinary temperatures and pressures, $\gamma = 1{\cdot}40$. The same value may be taken when a small percentage of NH_3 is present.

At high pressures the value of γ may be considerably changed. (*See* AIR.)

NITRIC OXIDE:
$\gamma = 1{\cdot}394$ - - - - - - - - - - Masson.

NITRIC TETROXIDE (N_2O_4):
$\gamma = 1{\cdot}172$ (20° C.) (15 per cent. dissociated; press. = 641 mm.). Natanson.
$= 1{\cdot}274$ (22° C.) (60 ,, ,, ; press. = 44 mm.). Natanson.

NITRIC PEROXIDE:
$\gamma = 1{\cdot}31$ (150° C.) - - - - - - - - Natanson.

WATER VAPOUR:
$\gamma = 1{\cdot}305$ (100° C.) - - - - - - - - Makower.

7. Thermal Conductivity of Gases.

If two opposite faces of a cm. cube of substance are maintained at temperatures differing by 1° C., then the heat in gm. cals. which passes through the cube in 1 second is the thermal conductivity of the material.

The kinetic theory of gases leads to the expression for thermal conductivity

$$k = A\eta C_v,$$

where $A = 1{\cdot}6$ for diatomic gases or $2{\cdot}6$ for monatomic gases; η = viscosity coefficient; C_v = specific heat at constant volume.

Pollock (*Phil. Mag.*, *31*, p. 52) gives A as a function of γ.

$$A = \frac{7{\cdot}32\,(\gamma - 1)}{\gamma^{1{\cdot}3}}.$$

According to the kinetic theory the viscosity coefficient η should be independent of pressure, and for a wide range of pressures experiment agrees with theory. It follows that k should be independent of pressure *provided C_v is also independent of pressure.* We have seen that both C_p and γ may have pressure coefficients and, if these pressure coefficients are unequal, C_v will not be independent of pressure. The thermal conductivity of a gas may, therefore, have a different value at pressures of 200 atmospheres.

In this connection it is interesting to see what the application of thermodynamics suggests. We have

$$\frac{d}{dv}\left(C_v\right) = T\left(\frac{d^2p}{dT^2}\right)_v.$$

A gas which follows Van der Waals' law gives $\left(\frac{d^2p}{dT^2}\right)_v = 0$, whence C_v is independent of the volume of gas and therefore independent of the pressure.

Other gas equations (such as that of Clausius) give, however,

$$\left(\frac{d^2p}{dT^2}\right)_v = f(T, v)$$

so that C_v is *not independent* of the pressure. Investigation shows that C_v may be taken approximately as a linear function of the pressure, the coefficient not necessarily being the same as the pressure coefficient of C_p.

(*a*) THERMAL CONDUCTIVITY OF GASES.

Nearly all experiments on thermal conductivity of gases have been carried out at pressures of a few cm. of mercury to avoid convection difficulties.

GAS.	TEMPERATURE ° C.	k	TEMPERATURE COEFFICIENT.	OBSERVER.
AIR at low pressures (1 – 3 cm.)	0°	0·0000492	—	Kundt and Warburg.
	”	568	0·00203	Winkelmann.
	”	483	183	Graetz.
	”	562	281	Schleiermacher.
	”	557	—	Müller.
	”	467	360	Eckerlein.
	”	479	—	Compan (*Landolt*, p. 742).
	at 1 atmosphere 55°	0·0000571		Todd (*Proc. Roy. Soc.*, A. 83, 1909).
HYDROGEN at low pressures (1 – 3 cm.)	0°	0·000327	0·00206	Winkelmann.
	”	319	22	Graetz.
	”	410	275	Schleiermacher.
	”	318	42	Eckerlein.
	”	387	—	Günther (*Landolt*, p. 742).
NITROGEN at low pressures (1 – 3 cm.)	0°	0·0000569	—	Günther.
	8°	524	—	Winkelmann (*Landolt*, p. 742).
	at 1 atmosphere 55°	0·0000569	—	Todd (*Proc. Roy. Soc.*, A. 83, 1909).
AMMONIA at low pressure	0°	0·0000458	0·00513	Winkelmann (*Landolt*, p. 742).
	100°	709	—	

[*Table continued on p.* 17.

(*a*) THERMAL CONDUCTIVITY OF GASES (*continued*).

GAS.	TEMPERATURE ° C.	k	TEMPERATURE COEFFICIENT.	OBSERVER.
NITROUS OXIDE at low pressure	0° 100°	0·0000350 506	—	Winkelmann.
NITRIC OXIDE	8°	0·0000460	—	Winkelmann.
	at 1 atmosphere 55°	0·0000539	—	Todd.
NITRIC PEROXIDE	at 1 atmosphere 55°	0·0000888	—	Todd.

(*b*) CONDUCTIVITY OF GASEOUS MIXTURES.

When the constituents of the mixture have nearly the same viscosities and not very different specific heats, the thermal conductivity may be obtained from the *viscosity of the mixture* by applying the formula :—

$$k = A\eta\, C \;= A\eta\, \frac{C_p}{\gamma}$$

This equation, however, gives incorrect values when the viscosities of the constituents are not of the same magnitude. Thus, for air, the above formula gives a value for the thermal conductivity in fair agreement with experimental determinations. For $(N_2 + 3H_2)$ mixture the formula gives a value which is probably much too low.

It can be shown theoretically that the thermal conductivity of a mixture of two gases is given by

$$k = \frac{k_1}{1 + A\,\dfrac{p_2}{p_1}} + \frac{k_2}{1 + B\,\dfrac{p_1}{p_2}}$$

where k_1 and k_2 are the conductivities of the constituents,
„ p_1 „ p_2 „ „ partial pressures of the constituents,

$$\text{and } A = \tfrac{1}{4}\sqrt{\tfrac{1}{2}\left(1 + \frac{m_1}{m_2}\right)}\,\left\{1 + \left(\frac{\eta_1}{\eta_2}\right)^{\frac{1}{2}} \times \left(\frac{m_2}{m_1}\right)^{\frac{1}{4}}\right\}^2$$

where η_1 and η_2 are viscosities, m_1 and m_2 are masses of molecules and $B = \dfrac{\eta}{\eta_1} A$.

(*c*) CONDUCTIVITY OF $(N_2 + 3H_2)$ MIXTURE.

Let us take the following data for the constituent gases :—

at 0° C.	Hydrogen	$k_1 = 0·00035$	$\eta_1 = 0·0000841$.
	Nitrogen	$k_2 = 0·000052$	$\eta_2 = 0·000166$.
at 100° C.	Hydrogen	$k_1 = 0·00044$	$\eta_1 = 0·000106$.
	Nitrogen	$k_2 = 0·000068$	$\eta_2 = 0·00021$.

At each temperature,

$$\frac{m_2}{m_1} = 14\,,\ \frac{\eta_1}{\eta_2} = 0·51\,,\ \frac{p_1}{p_2} = 3\,.$$

Whence $A = 1·14$, and $B = 2·24$, giving

$$k_0 = 0·00026 \text{ and } k_{100} = 0·00033.$$

SECTION II.

AMMONIA DATA.

1. Ammonia Equilibrium.

PERCENTAGE OF AMMONIA IN EQUILIBRIUM WITH THE MIXED GASES ($N_2 + 3H_2$).

Haber gives the following table for the equilibrium at various temperatures and pressures (*Z. Electroch.*, *20*, 600, 1914). The figures have been plotted in Figs. 2 and 3 :—

t° C.	Per Cent. NH_3 in Equilibrium at Pressures (in Atmospheres) of			
	1	30	100	200
200	15·3	67·6	80·6	85·8
300	2·18	31·8	52·1	62·8
400	0·44	10·7	25·1	36·3
500	·129	3·62	10·4	17·6
600	·049	1·43	4·47	8·25
700	·0223	0·66	2·14	4·11
800	·0117	·35	1·15	2·24
900	·0069	·21	0·68	1·34
1,000	·0044	·13	·44	0·87

Haber gives the following formula for the equilibrium constant at a pressure of 1 atmosphere, which agrees well with experimental determinations between the temperatures 500° C. and 1000° C.

$$\log_{10} K_p = \frac{13200}{4{\cdot}571\,T} - 6{\cdot}134,\ T \text{ being the absolute temperature.}$$

If the partial pressures of NH_3, N_2, and H_2 are respectively p_{NH_3}, p_{N_2} and p_{H_2}, then

$$K_p = \frac{p_{NH_3}}{p_{N_2}^{\frac{1}{2}} \times p_{H_2}^{\frac{3}{2}}}.$$

If the percentage of NH_3 is small and the total pressure is 1 atmosphere, we may take

$$p_{NH_3} = (\tfrac{1}{4})^{\frac{1}{2}} \times (\tfrac{3}{4})^{\frac{3}{2}} \times K_p = 0{\cdot}325\,K_p\ ,\ p_{NH_3} \text{ being in atmospheres.}$$

Hence, if E is the equilibrium percentage of NH_3, we have at 1 atmosphere between 500° C and 1000° C.

$$\log_{10} E = \frac{13{,}200}{4{\cdot}571\,T} - 4{\cdot}622\,,$$

which agrees well with the figures for 1 atmosphere given in the table.

2. Vapour Pressure of Anhydrous Ammonia.

The results obtained by various experimenters (*see* Landolt's tables, p. 379) on the vapour pressure of anhydrous ammonia are given in the following table. The results have been plotted in the graphs in Fig. 4, which also give, of course, the boiling points of anhydrous ammonia at different pressures. The data deduced therefrom concerning the condensation of ammonia from gaseous mixtures are given in paragraphs (*a*) and (*b*).

VAPOUR PRESSURE OF ANHYDROUS AMMONIA.

R—Regnault	*Mém. de l'Acad.*, *26*, 535.	B—Brill	*Ann. Phys.* (4), *21*, 170.
P—Pictet	*Arch. de Genève*, *13*, 212.	D—Davies	*Proc. Roy. Soc.*, A., *78*, 42.

Temperature ° C.	Pressure of Saturated Vapour.		
– 80 (Solid)		35·2 mm. (B)	
– 77·6 (M.pt.)		44·1 „ „	
– 70		77·2 „ „	
– 60		166·6 „ „	
– 50		323·3 mm. (B)	293 mm. (D)
– 40		563·1 „ „	557 „ „
– 30	867 mm. (D)	1·14 atm. (P)	1·14 atm. (R)
– 25	1098 „ „	1·45 „ „	1·45 „ „
– 20	1393 „ „	1·83 „ „	1·83 „ „
– 15	1726 „ „	2·28 „ „	2·24 „ „
– 10	2146 „ „	2·82 „ „	2·82 „ „
– 5	2617 „ „	3·45 „ „	3·45 „ „
0°		4·19 „ „	4·19 „ „
+ 5		5·00 „ „	5·04 „ „
10		6·02 „ „	6·02 „ „
15		7·12 „ „	7·14 „ „
20		8·40 „ „	8·41 „ „
25		9·80 „ „	9·84 „ „
30		11·44 „ „	11·45 „ „
35		13·08 „ „	13·25 „ „
40		15·29 „ „	15·26 „ „
45		17·38 „ „	17·48 „ „
50		19·98 „ „	19·95 „ „
55		22·66 atm. (R)	
60		25·63 „ „	
65		28·90 „ „	
70		32·47 „ „	
75		36·35 „ „	
80		40·59 „ „	
85		45·17 „ „	
90		50·14 „ „	
95		55·52 „ „	
100		61·32 „ „	

(*a*) CONDENSATION OF AMMONIA FROM A GASEOUS MIXTURE.

In Figs. 5 and 6 graphs have been constructed from Fig. 4 showing at what temperatures and total pressures, condensation should begin for various percentages (by volume) of ammonia in a gaseous mixture. These graphs give the maximum percentages of ammonia that can exist in a gaseous mixture under various temperatures and pressures. Thus at — 10° C and 140 atmospheres the ammonia content cannot be greater than 2 per cent. (Fig. 5).

The graphs were obtained by reasoning as follows. Let the vapour pressure of anhydrous ammonia at t° C. be p_t. In other words, the boiling point of liquid ammonia under a pressure p_t is t° C.

2. Vapour Pressure of Anhydrous Ammonia (*continued*).

If a not easily liquefiable gas contains 50 per cent. NH_3 at a temperature of $t°$ C., obviously the total pressure must be $2p_t$ before liquefaction of the NH_3 sets in. Generally, if x per cent. NH_3 is present at $t°$ C., the pressure required for liquefaction to begin will be $\frac{100}{x} p_t$.

(*b*) PERCENTAGE OF AMMONIA THEORETICALLY REMOVABLE BY COOLING.

Further graphs (Figs. 7, 8 and 9) have been constructed from Figs. 5 and 6 showing the percentage of ammonia which, theoretically, can be removed from gaseous mixtures by cooling under pressures of 50, 100, 150 and 200 atmospheres.

These have been obtained in the following way. Let the NH_3 content be x per cent. By increasing the pressure on the gas or by lowering the temperature we can reach a point (shown by Figs. 5 and 6) at which condensation will begin in a mixture containing, say, y per cent. NH_3; that is to say, $x - y$ per cent. will have been liquefied, *i.e.*, a fraction $\frac{x-y}{x}$ of the original content of ammonia.

3. Vapour Pressure of Ammonia Solutions.

(*a*) TOTAL PRESSURE (AMMONIA + WATER VAPOUR) AT DIFFERENT TEMPERATURES AND CONCENTRATIONS.

The following table (Hilde Mollier, *Fors. d. ver. deutsch. Ing.*, Berlin, 1909) gives the total pressures *in mm.* In Fig. 10 the results are graphed in convenient form, the pressures being given in *atmospheres* :—

Per cent. NH_3	Pressure in MM. of Mercury.													
	20°	30°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°
5								972	1342	1831	2447	3235	4200	5350
10						770	1091	1520	2060	2745	3620	4672	5890	7500
15					823	1166	1616	2200	2937	3850	4980	6350		
20				840	1200	1670	2270	3055	4030	5210	6708			
25			837	1208	1680	2308	3120	4145	5400	6950				
30		820	1197	1676	2320	3155	4200	5510	7070					
35	793	1157	1652	2305	3142	4238	5570	7155						
40	1103	1594	2260	3120	4190	5550	7135							
45	1487	2138	3000	4080	5410	7030								
50	1960	2790	3850	5210	6810									

(*b*) PARTIAL PRESSURES OF AMMONIA AND WATER VAPOUR ABOVE SOLUTIONS.

Perman (*J. Chem. Soc.*, *83*, 2, 1169, 1903) has measured the partial pressures at different temperatures for various concentrations of ammonia. Some of his figures are given in the Table below.

These have been plotted in Fig. 11 and the graphs in Figs. 12 and 13 have been constructed from Fig. 11 to give at a glance the value of the partial pressure at any temperature. Figures 12 and 13 have been deduced from Perman's figures and must be considered as approximate only.

It is interesting to note that according to Perman's figures the partial pressure of water vapour above a 5 or 6 per cent. solution at 0° C. is greater than the vapour tension of pure water at that temperature.

PARTIAL PRESSURE OF NH_3 AND OF H_2O ABOVE SOLUTIONS.

t° C.	Per Cent. NH_3	Partial Pressure—mm.	
		NH_3	H_2O
0	4·72	11·4	5·1
	9·15	24·8	5·3
	14·73	51·3	4·1
	19·62	82·5	3·0
	22·90	116·6	2·8
10	4·16	16·5	9·1
	8·26	37·2	8·8
	12·32	64·2	7·6
	15·88	95·1	7·0
	20·54	149·2	7·2
	21·83	169·8	5·5
19·9	4·18	27·4	16·4
	6·55	46·0	16·0
	10·15	80·6	15·1
	16·64	166·1	12·9
	23·37	302·4	10·3
30·09	3·93	41·2	31·1
	7·43	86·3	29·2
	12·77	175·0	26·6
	17·84	291·1	24·3
	21·47	404·6	22·1
40	3·79	61·1	53·5
	11·06	218·5	49·1
	15·55	353·6	44·1
	20·85	576·1	37·8
50	3·29	79·1	89·6
	8·91	246·6	83·0
	14·15	451·4	77·0
	14·94	487·1	75·2
60	3·86	136·9	144·1
	7·78	300·4	138·5
	11·31	475·8	130·4

4. Density of Anhydrous Ammonia at different Temperatures.

Fig. 14 has been plotted from the results of Lange (*Z. Ges. Kälte-Ind.*, *5*, 39, 1898) and Dieterici (*Z. Ges. Kälte-Ind.*, *11*, 21 and 47, 1904). Tables are not given, but the experimental determinations are shown in the graphs, and the density of saturated vapour is also given.

5. Melting Point and Boiling Point of Anhydrous Ammonia.

Melting Point :—

— 75° C.	Faraday	1845
— 75·5° C.	Ladenburg	1900
— 77·7° C.	Brill	1906

Boiling Point :—

— 33·46° C.	Gibbs	1905
— 33·1° C.	Brill	1906
— 33·5° C.	Perman	1906
— 34·6° C.	Burrell and Robertson	1916

6. Density of Ammonia Solutions at 15° C.

The figures of Lunge and Wiernik (*Z. angew. Chem.*, *2*, 181, 1889) are plotted in Fig. 15. The graph gives :—(*a*) percentage NH_3 from specific gravity or from Twaddell degrees; (*b*) gms. NH_3 per litre solution from specific gravity; (*c*) lb. of NH_3 per gallon from specific gravity.

7. Solubility of Ammonia at different Temperatures and Pressures.

These graphs (Fig. 16) show what weight of NH_3 will dissolve in unit weight of *water* at temperatures from 0° C. to 100° C. under pressures up to $2\frac{1}{2}$ atmospheres. Since the heat of solution is great, it is to be understood that the temperatures referred to are *final* temperatures.

8. Freezing Points for various Concentrations of Ammonia.

The experimental determinations of F. H. Rupert (*J. Amer. Chem. Soc.*, *32*, 749) lie very closely on the graph in Fig. 17.

9. Heats of Solution of Liquid and Gaseous Ammonia.

Hilde Mollier (*Z. Ver. deut. Ing.*, p. 424, 1909) has measured the heat of solution of 1 kgm. of ammonia when dissolved in various percentage solutions of ammonia. The graph in Fig. 18A explains itself.

10. Heat of Formation of Ammonia from its Elements.

Fig. 18B gives Nernst's values of the heat of formation in gm. cals. per gm. mol. at different temperatures. (Nernst, *Z. Electroch.*, p. 100, 1910).

Tamaru (*Z. Electroch.*, *21*, 201, 1915) gives for the heat of formation in gm. cals. per gm. mol. at 1 atm. pressure :—

Temp. ° C.	659°	554°	503°	466°
Ht. F.	13,100	12,900	12,700	12,670

11. Specific Heats of Anhydrous and Aqueous Ammonia.

(a) *Anhydrous Ammonia.*

The following table shows the specific heat of Anhydrous Ammonia at different temperatures :—

TEMP. ° C.	SPECIFIC HEAT.	OBSERVER.
– 103 to – 188 (solid)	0·50	Dewar.
0 to 26 (liquid)	0·878	Lüdeking and Starr.
26 " 46 "	0·894	
10 "	1·021	Elleau and Ennis.
0 "	0·876	Drewes.
10 "	1·140	
20 "	1·190	
30 "	1·218	
40 "	1·231	
50 "	1·239	
60 "	1·240	
70 "	1·233	
0 " 20 "	1·152	Keyes and Babcock. *J. Am. Ch. S.*, *39*, 1917.
20 " 50 "	1·172	

(b) *Ammonia Solutions.*

$NH_3 + 31\ H_2O$ (3 per cent. solution) - - 18° C. 0·997
$NH_3 + 51\ H_2O$ (1·8 " ") - - 18° C. 0·999 } Thomsen.
$NH_3 + 101\ H_2O$ (0·9 " ") - - 18° C. 0·999

12. Latent Heats of Ammonia.

The following table shows the latent heats of fusion and vaporisation of Ammonia in kgm. Calories :—

——	TEMPERATURE ° C.	LATENT HEAT (KG. CALS.) FOR		OBSERVER.
		1 kgm.	1 gm. mol.	
FUSION - -	— 75° C.	108·1	1·84	Massol.
VAPORISATION -	— 33·4	321·3	5·46	Estreicher and Schnerr.
	— 33·46	341·0	5·81	Franklin and Kraus.
	7·8	294·21	5·01	Regnault.
	11·04	291·32	4·961	”
	16·0	297·38	5·064	”
	17·0	296·5	5·05	v. Strombeck.

SECTION III.

NITRIC ACID DATA.

1. Specific Gravity of HNO_3 Solutions at 15° C.

Various observers closely agree. The graph (Fig. 19) has been plotted from Lunge and Rey (*Z. angew. Chem.*, *4*, 165, 1891). It gives Twaddell degrees, specific gravity, percentage HNO_3, gms. HNO_3 per litre of solution, lb. HNO_3 per gall. of solution.

2. Boiling Points of Pure HNO_3 (99·79 per cent.) at different Pressures.

The data for the graph (Fig. 20) have been taken from Creighton and Githens (*J. Franklin Inst.*, p. 161, 1915). The experimental points lie very closely on the given curve. The graph gives also the *total vapour pressure above pure HNO_3 at different temperatures.*

3. Boiling Points of Aqueous HNO_3 at different Pressures.

The data for this graph (Fig. 21) have been taken from the same source as for the preceding graph.

4. Vapour Pressure of Aqueous HNO_3 at different Temperatures.

Two graphs (Figs. 22 and 23), plotted from Creighton and Githens' paper, give:—

(*a*) total pressure against molecular percentage HNO_3, and
(*b*) total pressure against percentage HNO_3 by weight.

The graphs in Fig. 23 also give the Boiling Points of Aqueous Solutions of HNO_3 at different pressures.

5. Influence of Non-volatile Water-retaining Agents on the Maximum Boiling-point Mixture.

Reference: Creighton and Smith (*J. Franklin Inst.*, p. 703, 1915).

The presence of $KHSO_4$ produces no change in the position of the maximum boiling-point.

The presence *of H_2SO_4 raises the boiling point* of HNO_3 solutions and also *decreases the HNO_3 content of the maximum boiling-point mixture.* The decrease is greater the greater the addition of H_2SO_4.

Diminution of pressure causes a very slight decrease in the HNO_3 content of the maximum boiling-point mixture.

The graphs (Fig. 24) are taken from Creighton and Smith's paper. The percentage HNO_3 refers to dehydrating-agent-free solution.

6. Freezing Points of Aqueous HNO_3.

Fig. 25 has been plotted from the determinations of F. W. Kuster and R. Kremann (*Zeit. anorg. Chem.*, *41*, 1, 1904).

7. Heat of Solution of Nitric Acid.

The following table gives the heat of solution in kgm. Calories when 1 gm. mol. of HNO_3 is dissolved in m gm. mols. of H_2O. Thomsen's figures are for 18° C. Berthelot's are for 10° C.:—

m	0·5	1	1·5	2	2·5	3	4	5	6	8	10	20	40	80	100	160	200	320
Thom.	2·00	3·29	4·16	—	5·27	5·71	—	6·66	—	—	7·32	7·46	7·44	7·42	7·44	7·45	—	7·49
Bert.	2·03	3·34	4·16	4·86	—	5·76	6·39	6·76	6·98	7·22	7·27	7·36	7·27	—	7·21	—	7·18	—

Reference: Thomsen, *Thermochem. Untersuch.*, Bd. 3. Leipzig, 1883.
Berthelot, *Ann. Ch. Phys.*, *5*, 4, 468, 1875.

8. Vapour Pressures of Oxides of Nitrogen.

The experimental data on Vapour Pressures of Oxides of Nitrogen have been plotted in Figs. 26, 27, and 28, the authors and their papers being given at the head of the graphs. Egerton (*Trans. Chem. Soc.*, p. 652, 1914) states that his results for solid N_2O_4 closely follow the equation $\log p = \overline{14}\cdot 9166 + \theta\ (0\cdot 0604)$. The following data concerning the Condensation of Nitrogen Peroxide from Gaseous Mixtures have been deduced from these experimental curves.

(*a*) *Condensation of Nitrogen-Peroxide from a Gaseous Mixture.*

Fig. 29 has been constructed from the vapour pressure curves of nitrogen peroxide. It shows at what temperatures and (total) pressures condensation should begin for various percentages by volume of peroxide present in the gas. For example, take Curve IV., which is for a 10 per cent. gas. At − 10° C. condensation will begin at a pressure of 2 atmospheres; any peroxide in excess of 10 per cent. will be liquefied. For the method of construction of these graphs *see* AMMONIA, p. 19.

(*b*) *Percentage of the total Peroxide theoretically removable by Cooling.*

Two sets of graphs (Figs. 30 and 31) have been constructed from Fig. 29 showing the percentage of peroxide theoretically removable by cooling from a 10 per cent. and from a 15 per cent. mixture at different pressures. The pressure in atmospheres is given by the number on the curve.

Example.—90 per cent. removal required from a 15 per cent. mixture :—From the curves we see that this can be done (*a*) at − 15° C. by the application of 10 atmospheres; (*b*) at − 28° C. by 5 atmospheres; (*c*) at − 36° C. by 3 atmospheres, and so on. For the method of construction of these graphs *see* AMMONIA, p. 20.

9. The Velocity of Reaction between Nitric Oxide and Oxygen.*

This has been experimentally investigated *at constant pressure* by Lunge and Berl (*Z. angew. Ch.*, *20*, 1716, 1907). Their results are given in Fig. 32, which shows the percentage of NO converted at any given time from the beginning of the reaction. It has been found possible to construct general curves for the reaction at constant volume and constant pressure.

The following table (*see* Fig. 32, Curve II.) gives some of the actual experimental values obtained by Lunge and Berl :—

Initial mixture : 125 cc. NO + 500 cc. Air.
Temperature : 20° C. Pressure constant.

TIME : Seconds.	PERCENTAGE BY VOLUME OF	
	NO.	NO_2.
0	100·	0
1·76	47·51	52·49
2·64	38·67	61·33
3·96	30·95	69·05
7·92	19·44	80·56
13·78	14·72	85·28
29·92	8·23	91·77

---

* This subject has been deliberately dealt with in detail in the text partly because of its novelty, and partly in order to render possible its application by the user of the tables to any technical process involving the oxidation of nitric oxide.—J.A.H.

9. The Velocity of Reaction between Nitric Oxide and Oxygen *(continued).*

At *constant volume* it is immaterial whether NO_2 or N_2O_4 is produced. Fig. 33 gives the velocity of reaction when oxygen is in excess. The presence of an inert gas has very little, if any, effect on the reaction. Fig. 34 is obtained from Fig. 33 and explains itself.

The reaction at *constant pressure* is complicated by volume changes and two sets of curves (Figs. 35 and 36) have been constructed assuming :—(*a*) that the reaction is $2NO + O_2 \rightarrow 2NO_2$, (*b*) that the reaction is $2NO_2 + O_2 \rightarrow N_2O_4$. For warm gases at ordinary pressures, when the concentration is small, the tetroxide is practically all dissociated and the reaction may be taken as $2NO + O_2 \rightarrow 2NO_2$.

Lunge and Berl's Curve I. (Fig. 32) corresponds to $p = 8$, p being the ratio of the concentration of the O_2 to NO_2. Curve II. corresponds to $p = 1{\cdot}6$.

On comparing the sets of curves it will be observed that the reaction is slowest at constant volume and quickest when N_2O_4 is formed at constant pressure.

The following indicates the method by which the curves have been obtained :—

1. Constant Volume Reaction.

The velocity of reaction is given by

$$\frac{dx}{dt} = k(a - x)^2 (b - x)$$

where a = initial concentration of NO in gm. mols. per litre.
b = ,, ,, ,, O_2 ,, ,, ,,
x = change in concentration in time t.

Since there are 2 molecules of NO in the reaction we take,

$$a = \frac{1}{2} \textit{ total No. of gm. mols. of NO in 1 litre of the reaction space,}$$

while b = *total No. of gm. mols. of* O_2 *in* 1 *litre of the reaction space.*

Putting $\frac{x}{a} = X$, *i.e.*, the fraction of NO converted, and $\frac{b}{a} = p$, we get

$$\frac{dX}{dt} = ka^2(1 - X)^2 (p - X). \quad k \text{ is the velocity constant.}$$

Integrating gives

$$ka^2t = \int_0^X \frac{dX}{(1 - X)^2 (p - X)},$$

from which the curves (Fig. 33) have been constructed. (*See* Todd, *Phil. Mag.*, *35*, 281.)

2. Constant Pressure Reaction.

In this case the volume changes. If the volume of the reaction space at time t is v, then the velocity of the reaction is given by

$$\frac{d}{dt}\left(\frac{x}{v}\right) = k\left(\frac{a - x}{v}\right)^2 \left(\frac{b - x}{v}\right)$$

where a is now $\frac{1}{2}$ (total No. of gm. mols. of NO in the reaction space v),

and b = (total No. of gm. mols. of O_2 in the space v),

,, $x = \frac{1}{2}$ (No. of gm. mols. of NO converted),

= (No. of gm. mols. of O_2 used up).

On putting $\frac{x}{a} = X$, the fraction of NO converted

and $\frac{b}{a} = p$, we get by a treatment which is too long to be given here :—

$$k\left(\frac{a}{v_0}\right)^2 t = \int_0^X \frac{1 + \frac{3a}{p + 2} X}{(1 - X)^2 (p - X)} \, dX$$

from which the curves (Figs. 35 and 36) have been constructed. (*See* Todd, *Phil. Mag.*, *35*, 435.)

In this equation $\left(\frac{a}{v_0}\right)$ is the initial concentration, defined as above, of the NO in gm. mols. per litre; (it corresponds to a in the previous equation).

When the reaction is $2NO + O_2 \rightarrow 2NO_2$, $a = -\frac{1}{3}$

" " " " $2NO + O_2 \rightarrow N_2O_4$, $a = -\frac{2}{3}$.

USE OF THE CURVES.

(*a*) *To find the Velocity Constant.*

As an example of the use of the curves let us find *the velocity constant k*, using Lunge and Berl's Curve I., Fig. 32. At the beginning of the reaction Lunge and Berl had present 125 cc. NO + 500 cc. O_2, *i.e.*, the value of a for NO was 62·5 cc. per 625 cc. Since 1 gm. mol. occupies 22·4 litres at 0° C. (say, 24 at Lunge and Berl's temperature) the initial concentration of NO in gm. mols. per litre was

$$\frac{62{\cdot}5}{24000} \div \frac{625}{1000} = \frac{1}{240} = \frac{a}{v_0}$$

Lunge and Berl's Curve I. (Fig. 32) corresponds to $p = \frac{500}{62{\cdot}5} = 8$ on the theoretical curves.

For the reactions $2NO + O_2 \rightarrow 2NO_2$, and $2NO + O_2 \rightarrow N_2O_4$ we get:—

REACTION.	PER CENT. NO CONVERTED.	TIME FROM LUNGE AND BERL'S CURVE. Seconds.	$k\left(\frac{a}{v_0}\right)^2 t$ FROM THE THEORETICAL CURVE.	WHENCE $k =$
$2NO + O_2 \rightarrow 2NO_2$	75	1	0·375	21800
	85	2	0·75	21800
	90	3	1·15	22000
	94	5	1·95	22400
$2NO + O_2 \rightarrow N_2O_4$	75	1	0·370	21300
	85	2	0·67	19200
	90	3	1·05	20100
	94	5	1·70	19600

Since the product of the reaction at ordinary temperatures is chiefly NO_2 we will take the velocity constant as $k = 22000$ (Temp. = 20° C.).

(*b*) *To find the Time required for Oxidation.*

Let us further illustrate the application of the curves by finding *the time required for the oxidation of* NO to NO_2 for a definite initial concentration of NO and for various excesses of O_2.

Take, for example, the oxidation of NO in the *ammonia oxidation* process. Suppose that the gas produced after passing through the converter and condensing arrangements consists of oxygen-free nitrogen containing 1 volume of NO in 7 volumes. Let air be admitted for the conversion to NO_2. Since there is a large excess of inactive gas the reaction may be regarded as taking place at constant volume (Fig. 33).

Take $p = 1$, *i.e.*, just sufficient O_2 for complete oxidation. To 7 volumes of gas we must add $2\frac{1}{2}$ volumes of air, making the total volume $9\frac{1}{2}$; therefore the initial concentration of NO is a $\frac{1}{2}$ vol. in $9\frac{1}{2}$ vols., or in gm. mols. per litre

$$a = \frac{\frac{1}{2}}{24000} \div \frac{9\frac{1}{2}}{1000} = 0{\cdot}00218, \quad \therefore \quad ka^2 = 22000 \times (0{\cdot}00218)^2 = 0{\cdot}105.$$

9. The Velocity of Reaction between Nitric Oxide and Oxygen (*continued*).

For 90 per cent. conversion, $ka^2t = 50\,, \quad \therefore \quad t = \dfrac{50}{0\cdot105} = 476 \text{ sec.} = 7 \text{ min. } 56 \text{ sec.}$

Take $p = 2$, *i.e.*, add 5 vols. air to 7 vols. gas,

$$a = \frac{\frac{1}{2}}{24000} \div \frac{12}{1000} = 0\cdot00174\,, \quad \therefore \quad ka^2 = 22000 \times (0\cdot00174)^2 = 0\cdot066\,.$$

For 90 per cent. conversion, Fig. 33 gives $ka^2t = 7\cdot5\,, \quad \therefore \quad t = \dfrac{7\cdot5}{0\cdot066} = 113 \text{ sec.} = 1 \text{ min. } 53 \text{ sec.}$

For 95 per cent. conversion, $ka^2t = 17\,, \quad \therefore \quad t = \dfrac{17}{0\cdot066} = 256 \text{ sec.} = 4 \text{ min. } 16 \text{ sec.}$

Proceeding in the same way we obtain the results in the following table, assuming that initial content of NO = 1 vol. in 7 vols., *air* is added to convert to NO_2, temperature = 20° C. :—

	FOR 90 PER CENT. CONVERSION.					FOR 95 PER CENT. CONVERSION.			
$\dfrac{\text{Vol. of air added}}{\text{Orig. vol. of mixture}}$	$\frac{2\frac{1}{2}}{7} = 0\cdot36$	$\frac{5}{7} = 0\cdot71$	$\frac{7\frac{1}{2}}{7} = 1\cdot1$	$\frac{10}{7} = 1\cdot4$	$\frac{12\frac{1}{2}}{7} = 1\cdot8$	$\frac{5}{7} = 0\cdot71$	$\frac{7\frac{1}{2}}{7} = 1\cdot1$	$\frac{10}{7} = 1\cdot4$	$\frac{12\frac{1}{2}}{7} = 1\cdot8$
Time (min.) - -	7·9	1·9	1·5	1·4	1·5	4·3	3·5	3·1	3·3

N.B.—It is impossible to get 90 per cent. conversion with a contact time of less than 1·4 minutes; or to get 95 per cent. conversion with a contact time of less than 3·1 minutes. For quicker reaction times for the above concentration of NO, pure oxygen would have to be introduced. The calculation of the times of reaction would be done as has been indicated.

It should be remembered that the above calculations assume no absorption of the NO_2 produced.

In the *arc processes* the percentage of NO is very low. Assuming the mixture is air containing 2 per cent. NO we have $p = 19$ approximately. The curves in Fig. 33 do not go up to $p = 19$, but we proceed thus :—

$$ka^2t = \int_0^X \frac{dX}{(1-X)^2(p-X)} = \frac{1}{(p-1)^2}\left\{\log_e \frac{p(1-X)}{p-X} + \frac{X(p-1)}{1-X}\right\}$$

$$a = \frac{1}{24000} \div \frac{100}{1000} = 0\cdot00042 \quad \therefore \; ka^2 = 22000 \times (0\cdot00042)^2 = 0\cdot00388.$$

For 50 per cent. conversion, *i.e.*, $X = 0\cdot5 \quad ka^2t = 0\cdot0502 \quad \therefore \; t = 13\cdot0$ secs.
For 90 „ „ *i.e.*, $X = 0\cdot9 \quad ka^2t = 0\cdot495 \quad \therefore \; t = 128$ secs.

These figures hold good at a temperature of 20° C. The temperature coefficient of the reaction up to temperatures such as are met with in tower practice has not been definitely established, but is probably small.

Working on lines indicated in the preceding pages, it has been possible to deduce a general expression for the time of oxidation of nitric oxide in arc gases.

The time *in seconds* required for the oxidation of a fraction X of the nitric oxide present in an arc process gas consisting of air containing P per cent. of nitric oxide is given by

$$t = \frac{2\cdot62 \times 10^4}{(200-7P)^2}\left\{\frac{X(200-7P)}{5P(1-X)} + \log_e \frac{(200-2P)(1-X)}{(200-2P-5X)}\right\}$$

when the gases are at a temperature of 20° C.

From this expression we get the following table, the results being plotted in Fig. 37 :—

X	$P = 0{\cdot}5$ per cent.	$P = 1$ per cent.	$P = 1{\cdot}5$ per cent.	$P = 2$ per cent.
	t (sec.)	t (sec.)	t (sec.)	t (sec.)
0·5	52·9	26·7	17·9	13·5
·6	79·5	40·0	26·9	20·4
·7	124·0	62·4	41·5	32·0
·8	213·0	108·0	72·3	55·1
·9	480·0	250·0	164·0	125·0

To be completely general the expression for t should contain a function of the temperature as a factor. No data appear to be available for the determination of this function.

10. Equilibria.

The reaction velocity of the reversible reaction

$$A + B + \; . \; . \; . \; . \rightleftarrows X + Y + \; . \; . \; . \; .$$

is given by

$$\frac{dC}{dt} = k_1(C_A\, C_B \; . \; . \; . \; . \;) - k_2(C_X\, C_Y \; . \; . \; . \; . \;),$$

where C denotes concentration, k_1 and k_2 are the velocity constants of the forward and backward reactions respectively.

Equilibrium is reached when $\frac{dC}{dt} = 0$,

$$\text{or} \qquad \frac{k_1}{k_2} = \frac{C_X\, C_Y \; . \; . \; . \; .}{C_A\, C_B \; . \; . \; . \; .}.$$

The ratio $\frac{k_1}{k_2} = K$ is called the equilibrium constant. From it is determined the constitution of the equilibrium mixture. It must be remembered that when partial pressures are substituted for concentrations, K may depend on the total pressure. It is much safer to measure concentrations in gm. mols. per litre. K is then only dependent on temperature.

In what follows, unless otherwise stated, concentrations in gm. mols. per litre are shown thus [NO], temperatures Centigrade are denoted by t, absolute temperatures by T, and logs are to the base 10.

$N_2O_4 \rightleftarrows 2NO_2$:—

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}; \quad \log_{10} K_c = 7{\cdot}3374 - \frac{266}{T}.$$

Reference: Natanson, *Wied. Ann.* [3], *24*, 454, 1885; *27*, 606, 1886. Bodenstein, *Z. physik. Chem.*, *69*, 43, 1909.

Haber (*Technical Gas Reactions*) gives at 1 atmosphere pressure :—

t° C.	0°	18·3°	49·9°	73·6°	99·8°
K_p	8·06	3·71	1·116	0·544	0·273

where $K_p = \frac{p^{\frac{1}{2}}_{N_2O_4}}{p_{NO_2}}$

10. Equilibria (*continued*).

If x = degree of dissociation

$$K_p = \frac{\sqrt{1-x^2}}{2x} \times \frac{1}{P^{\frac{1}{2}}}\text{, where } P = \text{total pressure in atmos.}$$

For $P = 1$ and $x = \frac{1}{2}$, then $K_p = 0{\cdot}865$. According to the table, this is for a temperature of approximately 64° C., *i.e.*, N_2O_4 is half dissociated at 1 atmosphere at 64° C. (Compare with Fig. 38).

Richardson's experimental results (*J. Chem. Soc.*, *51*, 402) are given in Fig. 38.

$2NO_2 \rightleftarrows 2NO + O_2$:—

$$K_c = \frac{[NO]^2\ [O_2]}{[NO_2]^2}\text{; } \log K = -\frac{6000}{T} + 0{\cdot}75 \log T + 4{\cdot}086.$$

T° abs. -	500°	600°	700°	800°	900°	1,000°
K_c - -	$1{\cdot}32 \times 10^{-6}$	$1{\cdot}51 \times 10^{-4}$	$4{\cdot}55 \times 10^{-3}$	$5{\cdot}90 \times 10^{-2}$	0·436	2·19

Reference: Bodenstein and Katayama, *Z. physik. Chem.*, *69*, 44, 1909.
See Fig. 38 for Richardson's experimental results.

$2NO \rightleftarrows N_2 + O_2$:—

$$K_c = \frac{[NO]^2}{[N_2]\ \ [O_2]}\text{; } \log \sqrt{K_c} = \log 0{\cdot}0249 - 2{\cdot}148\ \frac{2200 - T}{T}.$$

t° C. - - -	1227°	1727°	2227°	2727°
$\sqrt{K_c}$ - - -	$2{\cdot}48 \times 10^{-3}$	$15{\cdot}3 \times 10^{-3}$	$45{\cdot}5 \times 10^{-3}$	$93{\cdot}0 \times 10^{-3}$

Reference: Nernst, *Z. anorg. Chem.*, *49*, 226, 1906.

COMBUSTION OF AIR TO NO.

In Col. 5 of the following table

$$K = \frac{p_{NO}}{p_{N_2}^{\frac{1}{2}} \times p_{O_2}^{\frac{1}{2}}}$$

N. = Nernst, *Göttinger Nachrichten* (1904), p. 261.
J. & F. = Jellinek and Finckh, *Z. anorg. Chem.*, *45*, 116, 1905; *49*, 212 and 229, 1906.

T° abs.	Per cent. N_2	Per cent. O_2	Per cent. NO.	K	OBSERVER.
1811	78·92	20·72	0·37	0·0091	N.
1877	78·89	20·69	0·42	—	J. & F.
2023	—	—	0·52–0·80	—	„
2033	78·78	20·58	0·64	·0159	N.
2195	78·61	20·42	0·97	·0242	„
2580	78·08	19·88	2·05	—	J. & F.
2675	77·98	19·78	2·23	—	„
3200	76·60	18·4	5·0	·1331	N.

10. Equilibria (*continued*).

$4NH_3 + 5O_2 \rightleftarrows 4NO + 6H_2O$:—

$$K = \frac{p^4_{NO} \times p^6_{H_2O}}{p^4_{NH_3} \times p^5_{O_2}}$$

Partington (*The Alkali Industry*, 1918, p. 228) gives

$$\log K = \frac{44280}{T} + 32{\cdot}14$$

$N_2 + 2H_2O \rightleftarrows 2NO + 2H_2$:—

Reference: O. F. Tower, *Ber. d. ch. Ges.*, *38*, 2945, 1905.

SECTION IV.

HYDROGEN PURIFICATION DATA.

The data contained in this section deal chiefly with those equilibria which form the basis of the more important methods for the technical preparation and purification of hydrogen.

The remarks on equilibrium made on p. 29 apply to this section also.

1. Water-gas Equilibrium.

$H_2O + CO \rightleftarrows CO_2 + H_2$.

$$K_p = K_c = \frac{[H_2O]\,[CO]}{[H_2]\,[CO_2]};$$

$$\log K = -\frac{2170}{T} + 0{\cdot}979 \log T - 1{\cdot}082 \times 10^{-3}\,T + 1{\cdot}734 \times 10^{-7}\,T^2 - 0{\cdot}02858.$$

$T°$ abs.	1000°	1200°	1300°	1400°	1500°	1600°	1700°	1800°	1900°	2000°
K -	0·68	1·34	1·73	2·12	2·52	2·92	3·31	3·69	4·07	4·45

Reference :—F. Haber, *Z. physik. Chem.*, *68*, 731.

Figures for lower temperatures calculated from the above formula are given in the following table :—

$t°$ C.	127°	227°	327°	427°	527°	627°	727°
K	0·00049	0·0059	0·031	0·085	0·221	0·369	0·676

These values of K have been plotted in Fig. 39.

Abegg (*Handbuch der anorg. Chemie*) gives :—

$$\log K = -\frac{2232}{T} - 0{\cdot}0836 \log T - 0{\cdot}00022\,T + 2{\cdot}5084.$$

2. Carbon—Carbon dioxide Equilibrium.

$2\,CO \rightleftarrows CO_2 + C$.

Rhead & Wheeler (*J. Chem. Soc. 99*, 1151) give a modified form of Le Chatelier's formula for the equilibrium constant, namely :—

$$K = \frac{38{\cdot}055 + 2{\cdot}02\,T - 0{\cdot}0031\,T^2}{2T} + \log_e P + \log_e \frac{C_1^2}{C_2},$$

where P = total press. in atm., C_1 = conc. of CO, C_2 = conc. of CO_2, $C_1 + C_2 = 1$.

$t°$ C.	P	Per Cent. CO_2.	Per Cent. CO.
800 - - - - -	1·23 to 3·05	16·12 to 28·40	83·88 to 71·60
900 - - - - -	0·65 to 2·90	2·17 to 9·05	97·80 to 90·95
950 - - - - -	0·69 to 3·18	1·11 to 4·42	98·89 to 95·58
1000 - - - - -	0·66 to 3·78	0·65 to 3·17	99·35 to 96·83
1050 - - - - -	0·83 to 3·06	0·52 to 1·42	99·53 to 98·53
1100 - - - - -	1·33 to 3·64	0·35 to 0·92	99·65 to 99·08

The effect of pressure on the equilibrium percentage of CO_2 at temperatures between 900° C. and 1100° C. is shown in Fig. 40 taken from Rhead and Wheeler's paper.

Boudouard (*Ann. Ch. Phys.*, VIII., *24*, 5, 1901) gives the equilibrium percentage of CO_2 as follows:—

t° C - -	445°	650°	800°	925°
Per Cent. CO_2 -	100	61	6·6	4·0

Abegg (*Handbuch der anorg. Chemie*) gives

$$\log K = \frac{9130}{T} - 9 \cdot 3 \quad \text{where } K = \frac{p_{CO_2}}{p^2_{CO}}.$$

Rhead and Wheeler (*J. C. S.*, *97*, 2189) have determined the velocity constants for the separate reactions $2CO \rightarrow CO_2 + C$ and $CO_2 + C \rightarrow 2CO$.

In the following tables the velocity constant k has been obtained from $\frac{1}{t} \log \frac{C_0}{C_t} = k$.

TIME. (HOURS.)	TEMPERATURE = 850° C.			TIME. (HOURS.)	TEMPERATURE = 850° C.		
	P at 0° C.	P_{CO_2}	k_{CO_2}		P at 0° C.	P_{CO}	k_{CO}
0	258·6	257·6	--	0	463·0	453·7	—
1	292·3	224·9	0·0590	24	459·2	446·1	0·00030
2	317·8	199·4	·0555	48	453·9	435·5	·00037
4	356·3	160·9	·0511	72	452·1	431·9	30
6	389·0	128·2	·0505	96	448·0	423·7	31
8	415·8	101·4	·0506	120	447·2	422·1	26
12	439·5	77·7	·0434				

3. Carbon monoxide—Oxygen Equilibrium.

$$\underline{2CO_2 \rightleftharpoons 2CO + O_2.}$$

$$K_C = \frac{P}{RT} \frac{x^3}{(2+x)(1-x)^2} = \frac{[CO]^2 [O_2]}{[CO_2]^2}.$$

According to Nernst and v. Wartenberg (*Z. physik. Chem.*, *56*, 548, 1906)—

$$\log K_C = 15 \cdot 48 - \frac{29600}{T} + 2 \cdot 93 \log \frac{T}{1000} - 1 \cdot 286 \times 10^{-3} (T - 1000) + 1 \cdot 61 \times 10^{-7} (T^2 - 1000^2).$$

The following figures give the percentage dissociation observed by Bjerrum (*Z. physik. Chem*, *79*, 1912):—

t° C. - -	2367°	2606°	2627°	2672°	2843°
Per Cent.	21·0	51·7	49·2	64·7	76·1

Haber (*Technical Gas Reactions*) gives for the most probable values for the percentage dissociation of CO_2 at different temperatures and pressures :—

$T°$ abs.	10 atm.	1 atm.	0·1 atm.	0·01 atm.
1000	$7{\cdot}31 \times 10^{-6}$	$1{\cdot}58 \times 10^{-5}$	$3{\cdot}4 \times 10^{-5}$	$7{\cdot}31 \times 10^{-5}$
1500	$1{\cdot}88 \times 10^{-2}$	$4{\cdot}06 \times 10^{-2}$	$8{\cdot}72 \times 10^{-2}$	0·188
2000	0·818	1·77	3·73	7·88
2500	7·08	15·8	30·7	53·0

4. Dissociation of Water Vapour.

$2\ H_2O \rightleftarrows 2\ H_2 + O_2.$

$$K_c = \frac{P}{RT} \times \frac{x^3}{(2+x)(1-x)^2} = \frac{[H_2]^2\,[O_2]}{[H_2O]^2}\,.$$

Nernst and v. Wartenberg (*Z. physik. Chem.*, *56*, 534, 1906) give

$$\log K_c = 11{\cdot}46 - \frac{25030}{T} + 2{\cdot}38 \log \frac{T}{1000} - 1{\cdot}38 \times 10^{-4}(T - 1000) - 6{\cdot}85 \times 10^{-8}(T^2 - 1000^2).$$

Bjerrum (*Z. physik. Chem.*, *79*, 1912) observed the following percentage dissociation at various temperatures :—

$t°$ C. - -	2027°	2369°	2425°	2488°	2561°	2656°
Per Cent. -	2·6	4·3	7·5	8·6	9·8	11·1

Haber (*Technical Gas Reactions*) gives for the most probable values for the percentage dissociation of H_2O at different temperatures and pressures :—

$T°$ abs.	10 atm.	1 atm.	0·1 atm.	0·01 atm.
1000	$1{\cdot}39 \times 10^{-5}$	$3{\cdot}00 \times 10^{-5}$	$6{\cdot}46 \times 10^{-5}$	$1{\cdot}39 \times 10^{-4}$
1500	$1{\cdot}03 \times 10^{-2}$	$2{\cdot}21 \times 10^{-2}$	$4{\cdot}76 \times 10^{-2}$	0·103
2000	0·273	0·588	1·26	2·70
2500	1·98	3·98	8·16	16·6

5. Equilibrium between the Oxides of Iron and Carbon.

$(a)\ Fe_3O_4 + CO \rightleftarrows 3\ FeO + CO_2.$

$(b)\ FeO + CO \rightleftarrows Fe + CO_2.$

The equilibrium percentages, by volume, of CO_2 at different temperatures for the equilibria (*a*) and (*b*) have been experimentally determined by Baur and Glaessner (*Z. physik. Chem.*, *43*, 358, 1903). The curves given in Fig. 41 are taken from their paper.

6. Iron Oxide—Hydrogen Equilibrium.

$3\,Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$.

The equilibrium pressure of hydrogen at different temperatures is given by Deville (*Lieb. Ann.*, *157*, 71, 1871) as follows:—

Temperature ° C. - - -	200°	265°	360°	440°	765°	920°	1000°
Partial Pressure of H_2 in cms. -	9·59	6·42	4·04	2·58	1·28	0·92	0·51

Preuner (*Z. physik. Chem.*, *47*, 385, 1904) gives—

$t°$ C.	900°	1025°	1150°
$\dfrac{p(H_2O)}{p(H_2)}$	0·69	0·78	0·86

7. Methane—Hydrogen Equilibrium.

$C.\,(\text{amorph.}) + 2H_2 \rightleftarrows CH_4$.

Abegg (*Handbuch der anorg. Chemie*) gives—

$$\log K = \frac{4050}{T} - 3{\cdot}027 \log T - 0{\cdot}0006424\,T + 4{\cdot}617$$

$$\text{where } K = \frac{p_{CH_4}}{p^2_{H_2}}$$

whence

$t°$ C. - -	300°	400°	500°	600°	700°	800°
Per Cent. CH_4 -	96·90	86·16	62·53	31·68	11·07	4·41
Per Cent. H_2 -	3·10	13·84	37·47	68·32	88·93	95·59

Mayer and Altmayer (*Ber. Berichte*, *40*, 2134, 1907) give for 1 atmosphere pressure—

$t°$ C. - - -	250°	450°	550°	750°	850
Per Cent. CH_4 -	98·79	76·80	46·69	6·08	1·59

Pring (*J. Chem. Soc.*, *97*, 509) gives—

$t°$ C.	WITH *C*.	WITH *C + Pt*.
1200 - - - -	0·35 per cent. CH_4	0·55 per cent CH_4
1500 - - - -	0·17 „ „	0·30 „ „

8. Dissociation of Sulphuretted Hydrogen.

$2H_2S \rightleftharpoons 2H_2 + S_2$.

$$K_p = P\frac{x^3}{(2+x)(1-x)^2} = \frac{p^2_{H_2} \times p_{S_2}}{p^2_{H_2S}};$$

Preuner and Schupp (*Z. physik. Chem.*, *68*, 157, 1909) give :—

t° C.	750°	830°	945°	1065°	1132°
$K_p \times 10^4$ - -	0·89	3·8	24·5	118	260
Per Cent. - -	5·5	8·7	15·6	24·7	30·7

9. Dissociation of Carbon Bisulphide.

C (amorph.) + $S_2 \rightleftharpoons CS_2$.

$$K_c = \frac{[S_2]}{[CS_2]};$$

t° C.	823°	906°	1009°	1110°
K_c	0·078	0·115	0·179	0·258

Reference : Koref, *Z. anorg. Chem.*, *66*, 88.

SECTION V.

MISCELLANEOUS DATA.

1. Hydrometer Readings.

A graph is given showing the relation between Twaddell and Baumé degrees and specific gravity (Fig. 42). Twaddell degrees are a linear function of specific gravity, Baumé degrees are not.

$$\text{sp. gr.} = 1 + \frac{\text{Twaddell degrees}}{200}. \quad \text{Twaddell degrees} = 200\ (\text{sp. gr.} - 1).$$

2. Specific Gravity of Solutions at Ordinary Temperatures.

The graphs in Fig. 43 give the percentage salt in a solution when the specific gravity is known. (Taken from various sources.)

3. Specific Gravity and Percentage of Salt in Solutions saturated at ordinary Temperatures.

(The percentage refers to weight of anhydrous salt in 100 parts by weight of solution.)

SALT.	Temp.° C.	Per Cent.	Sp. Gr.	° Tw.
Ammonium chloride - - -	15	26·3	1·078	15·5
„ sulphate - - -	19	50·0	1·289	57·8
Barium chloride - - - -	15	25·97	1·283	56·5
Calcium „ - - - -	15	40·66	1·411	82·2
Magnesium sulphate - - -	15	25·25	1·288	57·6
Potassium chloride - - - -	15	24·90	1·172	34·4
„ carbonate - - -	15	52·02	1·571	114·0
„ nitrate - - - -	15	21·07	1·144	28·8
„ sulphate - - - -	15	9·92	1·083	16·6
Sodium chloride - - - -	15	26·39	1·204	40·8
„ carbonate - - - -	15	14·35	1·154	30·7
„ nitrate - - - -	19·5	46·25	1·380	76·0
„ sulphate - - - -	15	11·95	1·112	22·3

4. Solubilities at Different Temperatures.

Graphs are given (Fig. 44) showing the amount of salt which will dissolve in 100 grams of H_2O at different temperatures. (From various sources.)

5. Vapour Tension of Water at Different Temperatures.

The numbers given in Landolt's tables (page 360) have been plotted in Fig. 45. To get the vapour tension in mm. at any temperature, multiply the ordinate by the factor on the curve.

6. Vapour Tension of $NaNO_3$ and KNO_3 Solutions.

The graphs (Fig. 46) show the vapour tension of $NaNO_3$ solutions for varying concentrations and temperatures. The curves also give the boiling points of the solutions under reduced pressure.

7. Freezing Points.

The graphs (Fig. 47) show at what temperature solidification begins for

(1) $Ca(NO_3)_2$ and H_2O
(2) NH_4NO_3 and H_2O

solutions for various concentrations, and indicate the nature of the solid.

FREEZING POINTS OF MIXTURES OF NO_2 AND NO.

Percentage by Weight of NO_2.	Nature of Solid.	Temperature ° C.
99·9	NO_2	– 10·0°
91·2		– 18·0°
82·9		– 31·7°
80·0		– 37·7°
71·0		– 73·0°
65·5	$NO_2 + N_2O_3$	– 112·5°
63·6	N_2O_3	– 108·5°
61·3		– 104·5°
$\geq$ 61·3		

8. Heats of Formation.

The following table gives the molecular heat of formation, from the elements, in *kilogram Calories* per gram-molecule, at 15° C. to 20° C. :—

——	Mol. H.F. in Kgm. Cals.	——	Mol. H.F. in Kgm. Cals.
H_2O liq.	69·0	NH_4Cl aq.	72·4
„ gas	58·1	$(NH_4)_2 SO_4$	283·0
NH_3	12·0	$(NH_4)_2 SO_4$ aq.	280·6
N_2O	– 19·0	NH_4OH aq.	90·0
NO	– 21·6	$Ca(NO_3)_2$	202·0
N_2O_3	– 21·4	KNO_3	119·0
NO_2 (22° C.)	– 1·7	NaOH	102·3
„ (150° C.)	– 7·6	NaOH aq.	112·2
N_2O_5 liq.	3·6	$NaNO_3$	111·0
H_2SO_4 liq.	193·0	Na_2SO_4	328·3
HNO_3 aq.	41·6	Na_2CO_3	272·0
CH_4	21·7	$(NH_4)_2 SO_3$	215·4
CO (from amorph. C.)	29·0	$(NH_4) NO_2$	64·9
CO_2 „ „	96·9	$NH_4 NO_3$	88·0
CO_2 aq. „ „	102·8	$(NH_4)_2 CO_3$ aq.	222·0
CuS	10·0	FeO	65·7
Cu_2S	18·3	Fe_2O_3	198·0
CuO	37·2	Fe_3O_4	271·0
Cu_2O	40·8	CaO	140·0
FeS	23·7		

9. Heats of Modification-change.

The following table gives the heat of change of modification (solid to solid) in *kgm. Calories* per gm. molecule :—

		Kgm. Cals.	
NaOH		0·990	v. Hevesy.
KOH		1·522	„
NH_4NO_3	rhomb→rhomb (31° to 35° C.)	– 0·402	Bellati and Romanese.
„	rhomb→rhomboid (82·5° to 86° C.)	– 0·427	„ „
„	rhomboid→regular	– 0·950	„ „
KNO_3	rhomboid→prismatic	1·189	„ „

10. Latent Heats of Fusion.

The following table gives the latent heat of fusion in *kgm. Calories* per kgm. and per gm. molecule :—

—	MELTING POINT. ° C.	LATENT HEAT FOR		OBSERVER.
		1 KGM. (kgm. Cals.).	1 GM. MOL. (kgm. Cals.).	
NH_3	— 75	108·1	1·84	Massol.
$Ca(NO_3)_2\,4H_2O$	+ 42·4	33·49	7·94	Pickering.
KNO_3	339	47·37	4·79	Person.
„	308	25·5	2·57	Goodwin and Kalmus.
KOH	360·4	28·6	1·61	v. Hevesy.
CO_2 (5·1 atm.)	— 56·29	43·8	1·93	Kuenen and Robson.
$NaOH$	+ 318·4	40·0	1·60	v. Hevesy.
$NaNO_3$	333	45·3	3·69	Goodwin and Kalmus.
HNO_3	— 47	9·54	0·601	Berthelot.
H_2SO_4	+ 10·35	24·031	2·358	Pickering.
$H_2SO_4H_2O$	8·53	39·92	4·63	„
N_2O_5	30	76·67	8·28	Berthelot.
N_2O_4	— 10·14	32·2	2·96	Ramsay.

11. Latent Heats of Vaporisation.

The table gives the latent heat of vaporisation in *kgm. Calories* per kgm. and per gm. molecule :—

—	VAPORISATION TEMPERATURE. ° C.	LATENT HEAT FOR		OBSERVER.
		1 KGM. (kgm. Cals.).	1 GR. MOL. (kgm. Cals.).	
NH_3	— 33·4	321·3	5·46	Estreicher and Schnerr.
„	— 33·46	341·0	5·81	Franklin and Kraus.
„	7·8	294·21	5·01	Regnault.
„	11·04	291·32	4·961	„
„	16·0	297·38	5·064	„
„	17·0	296·5	5·05	v. Strombeck.
NH_4Cl.	350	709·0	37·9	Marignac.
HNO_3	86	115·1	7·25	Berthelot.
H_2SO_4	326	122·1	11·98	Person.
N_2O	— 20	66·9	2·94	Cailletet and Mathias.
„	0	59·5	2·62	„ „
„	20	43·25	1·90	„ „
„	35	9·87	0·43	„ „
„	36·4	0·0	0·0	„ „
N_2O_5	50	44·8	4·84	Berthelot.
N_2O_4	18	93·5	8·66	Berthelot and Ogier.
H_2O (in terms of 15° cal.).	0	598·0	10·8	(Mean value). Dieterici, Henning, Griffiths.
„ „ „	100	539·0	9·67	(Mean value). Joly, Harker, Callendar, Henning, Smith.

MISCELLANEOUS CONVERSION TABLES.

LENGTH.

To convert	Multiply by Factor F.	Log₁₀ F.	To convert	Multiply by Factor F.	Log₁₀ F.
Yards to cm. -	91·44	1·9611	Feet to metres -	0·3048	$\bar{1}$·4840
Cm. ,, yds. -	0·01094	$\bar{2}$·03886	Metres to feet -	3·2808	0·5160
Feet ,, cm. -	30·48	1·4840	Yards to metres	0·9144	$\bar{1}$·9611
Cm. ,, ft. -	0·0328	$\bar{2}$·5160	Metres to yards	1·0936	0·03886
Inches ,, cm. -	2·540	0·4048			
Cm. ,, ins. -	0·3937	$\bar{1}$·5952			

AREA.

To convert	Multiply by Factor F.	Log₁₀ F.	To convert	Multiply by Factor F.	Log₁₀ F.
Sq. in. to sq. cm.	6·4516	0·8097	Sq. cm. to sq. ft.	0·001076	$\bar{3}$·0320
Sq. cm. to sq. in.	0·1550	$\bar{1}$·1903	Sq. yds. to sq. m.	0·8361	$\bar{1}$·9223
Sq. ft. to sq. cm.	929·03	2·9680	Sq. m. to sq. yds.	1·1960	0·0777

VOLUME.

To convert	Multiply by Factor F.	Log₁₀ F.	To convert	Multiply by Factor F.	Log₁₀ F.
Cu. in. to cu. cm.	16·387	1·2145	Pints to litres	0·5682	$\bar{1}$·7545
Cu. cm. ,, cu. in.	0·0610	$\bar{2}$·7855	Litres ,, pints	1·7598	0·2455
Cu. ft. ,, cu. m.	0·02832	$\bar{2}$·4520	Gals. ,, cu. in.	277·41	2·4431
Cu. m. ,, cu ft.	35·314	1·5480	Cu. in. ,, gals.	0·003605	$\bar{3}$·5569
Cu. ft. ,, litres	28·317	1·4520	Gals. ,, cu. ft.	0·1605	$\bar{1}$·2056
Litres ,, cu. ft.	0·03531	$\bar{2}$·5480	Cu. ft. ,, gals. -	6·2290	0·7944
Gals. ,, litres	4·546	0·6576			
Litres ,, gals.	0·2200	$\bar{1}$·3424			

MASS.

To convert	Multiply by Factor F.	Log₁₀ F.	To convert	Multiply by Factor F.	Log₁₀ F.
Lb. to kgm. -	0·45359	$\bar{1}$·6567	Grains to gms. -	0·0648	$\bar{2}$·8116
Kgm. to lb. -	2·2046	0·3433	Gms. to grains -	15·432	1·1884
Oz. to gms. -	28·350	1·4525	Tons to kgm. -	1016·0	3·0069
Gms. to oz. -	0·03527	$\bar{2}$·5475	Kgm. to tons -	0·000984	$\bar{4}$·9931

DENSITY.

To convert	Multiply by Factor F.	$\log_{10}$ F.
Lb. per cu. ft. to gms. per cu. cm. - - -	0·016018	$\bar{2}$·2046
Gms. per cu. cm. to lb. per cu. ft. - - -	62·428	1·7954

FORCE.

To convert	Multiply by Factor F.	$\log_{10}$ F.
Lb. weight to dynes - - - - - -	4·45 × 10	5·6482

VELOCITY.

Feet per Min.	Cm. per Sec.	Feet per Sec.	Miles per Hour.	Metres per Sec.
1	0·5080	0·01667	0·01136	0·00508
1·969	1	0·0328	0·02237	0·0100
60·0	30·48	1	0·6818	0·3048
88·0	44·70	1·467	1	0·4470
196·9	100·0	3·281	2·237	1

RATE OF FLOW.

Litres per Hour.	Cu. Cm. per Sec.	Cu. Ft. per Hour.	Litres per Min.	Cu. Metres per Hour.	Cu. Ft. per Min.	Cu. Ft. per Sec.
1	0·278	0·0353	0·0167	0·001	0·000588	$9·81 \times 10^{-6}$
3·60	1	0·1271	0·060	0·00360	0·002119	0·0000353
28·32	7·867	1	0·472	0·02832	0·01667	0·000278
60·0	16·67	2·119	1	0·060	0·0353	0·000588
1000·0	277·8	35·31	16·67	1	0·5885	0·00981
1699·0	472·0	60·0	28·32	1·699	1	0·01667
28317·0	7867·0	1000·0	472·0	28·32	16·67	0·2778
101940·0	28317·0	3600·0	1699·0	101·94	60·0	1

ENERGY.*

Joules.	Gm. Cals.	Brit. Therm. Units (B.Th.U.).	Pound-Deg. Cent. Heat Units (C.H.U.).	Watt. Hrs.	Kgm. Cals.	H.P.Hours.	Kilowatt Hours.
1	0·2389	$0{\cdot}0_{3}9480$	$0{\cdot}0_{3}5266$	$0{\cdot}0_{3}2778$	$0{\cdot}0_{3}2389$	$0{\cdot}0_{6}373$	$0{\cdot}0_{6}278$
4·186	1	0·00397	0·00221	0·001163	0·00100	$0{\cdot}0_{5}156$	$0{\cdot}0_{5}116$
1055	252·0	1	0·5555	0·2930	0·2520	$0{\cdot}0_{2}393$	$0{\cdot}0_{3}293$
1899	453·6	1·800	1	0·5274	0·4536	$0{\cdot}0_{3}707$	$0{\cdot}0_{3}527$
3600	860·0	3·413	1·896	1	0·8600	0·00134	0·00100
4186	1000	3·968	2·205	1·163	1	0·00156	0·00116
2684000	641200	2545	1414	745·6	641·2	1	0·7456
3600000	860000	3413	1896	1000	860	1·341	1

Heat Emission of 1 gm. cal. per sq. cm. per sec.

= 13270 B.Th.U. per sq. ft. per hour.
= 7372 C.H.U. „ „

Thermal Conductivity.

To convert thermal conductivities expressed in C.G.S. units into B.Th.U. per sq. ft. per hour for a fall of 1° F. difference of temperature through 1 in. thickness, multiply by 2903.

CALORIFIC VALUE.

Grm. Cals. Per Cu. Ft.	Pound-Deg. Cent. Heat Units (C.H.U.) Per Cu. Metre.	Kgm. Cals. Per Cu. Metre.	Brit. Therm. Units (B.Th.U.) Per Cu. Ft.	Pound-Deg. Cent. Heat Units (C.H.U.) Per Cu. Ft.
1	0·0778	0·0353	0·00397	0·00221
12·84	1	0·4536	0·0510	0·0283
28·31	2·205	1	0·1123	0·0624
251·9	19·62	8·90	1	0·555
453·5	35·32	16·02	1·8	1

---

* The subscript figures indicate the number of zeros in the conversion factor given.

POWER. RATE OF DOING WORK.*

Foot-lb. per Min.	Kgm.-Metres per Min.	Watts. (Joules per Sec.).	Foot-lb. per Sec.	Gram.-Cals. per Sec.	Kgm.-Metres per Sec.	Brit. Therm. Units. (B.Th.U.) per Min.	Pound-Deg. Cent. Heat Units. (C.H.U.) per Min.	Kgm.-Cals. per Min.	Horse-Power.	Kilowatts.
1	0·1382	0·02259	0·01666	0·005396	0·002303	0·001285	0·000714	0·0003238	0·0$_4$3030	0·0$_4$2260
7·233	1	0·1634	0·1205	0·03904	0·01666	0·009295	0·005164	0·002342	0·0002192	0·0001634
44·26	6·119	1	0·7376	0·2389	0·1020	0·05688	0·03160	0·01433	0·001341	0·00100
60·0	8·295	1·3557	1	0·3238	0·1382	0·0771	0·0428	0·0194	0·00182	0·001355
185·3	25·61	4·186	3·088	1	0·4270	0·2382	0·1322	0·0600	0·00561	0·00419
434·0	60	9·806	7·233	2·342	1	0·558	0·310	0·1405	0·01315	0·00981
778·1	107·6	17·58	12·97	4·200	1·793	1	0·556	0·2520	0·0236	0·01758
1400	193·6	31·65	23·33	7·561	3·227	1·800	1	0·4536	0·04244	0·03165
3088	426·9	69·77	51·47	16·67	7·115	3·968	2·205	1	0·0936	0·0698
33000	4562	746	550	178·1	76·03	42·41	23·56	10·69	1	0·746
44260	6119	1000	738	238·9	102·0	56·88	31·60	14·33	1·341	1

PRESSURE.

Dynes per Sq. Cm.	Lb. per Sq. Ft.	Mm. of Mercury.	Feet of Water.	Inches of Mercury.	Lb. per Sq. In.	Metres of Water.	Kg. per Sq Cm.	Atmospheres.	Tons per Sq. In.
1	0·002089	0·000750	0·0$_4$3346	0·0$_4$2954	0·0$_4$1451	0·0$_4$1019	0·0$_5$1019	0·0$_6$9860	0·0$_8$648
478·7	1	0·3591	0·01602	0·01414	0·00694	0·00488	0·000488	0·0$_3$472	0·0$_5$310
1333	2·785	1	0·0446	0·0394	0·01934	0·1359	0·001359	0·001316	0·0$_5$863
29885	62·43	22·42	1	0·8826	0·4335	0·3048	0·03048	0·02947	0·0$_3$193
33850	70·73	25·40	1·133	1	0·4912	0·3453	0·03453	0·03342	0·0$_3$219
68920	144·0	51·71	2·307	2·036	1	0·7031	0·0703	0·06804	0·0$_3$446
98060	204·8	73·56	3·281	2·896	1·422	1	0·1	0·09678	0·0$_3$635
9806×10^2	2048·0	735·6	32·81	28·96	14·22	10·00	1	0·9678	0·00635
1013×10^3	2116·0	760·0	33·90	29·92	14·70	10·33	1·033	1	0·00656
1544×10^5	3225×10^2	1158×10^2	5167	4560	2240	1574	157·4	152·4	1

---

* *See* footnote to page 42.

GRAPHS.

SECTION I.—GAS DATA.

SECTION II.—AMMONIA DATA.

SECTION III.—NITRIC ACID DATA.

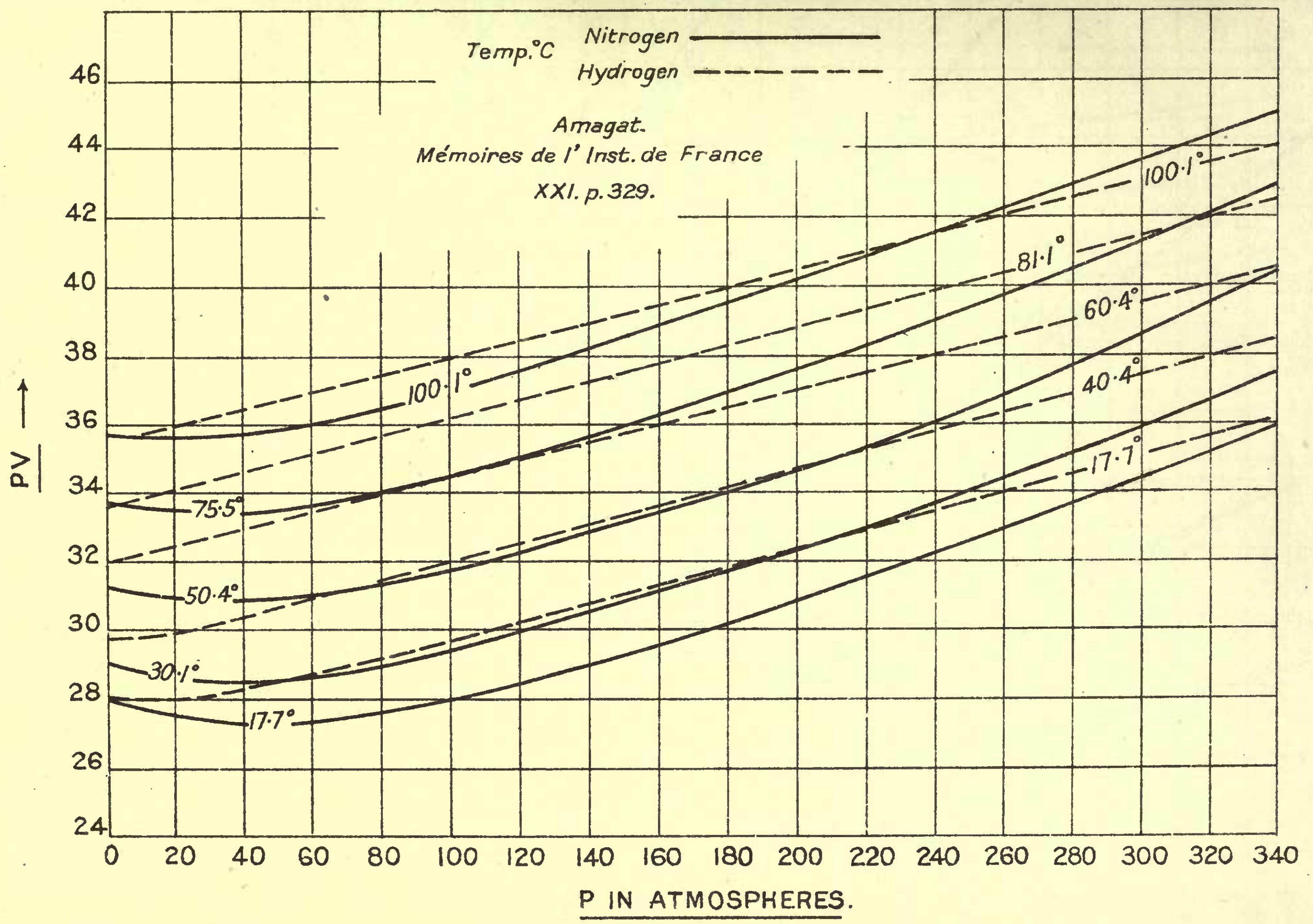
SECTION IV.—HYDROGEN PURIFICATION DATA.

SECTION V.—MISCELLANEOUS DATA.

INDEX.

FIG. I.

PV FOR NITROGEN & HYDROGEN AT DIFFERENT TEMPERATURES & PRESSURES.



Amagat.
Mémoires de l' Inst. de France
XXI. p. 329.

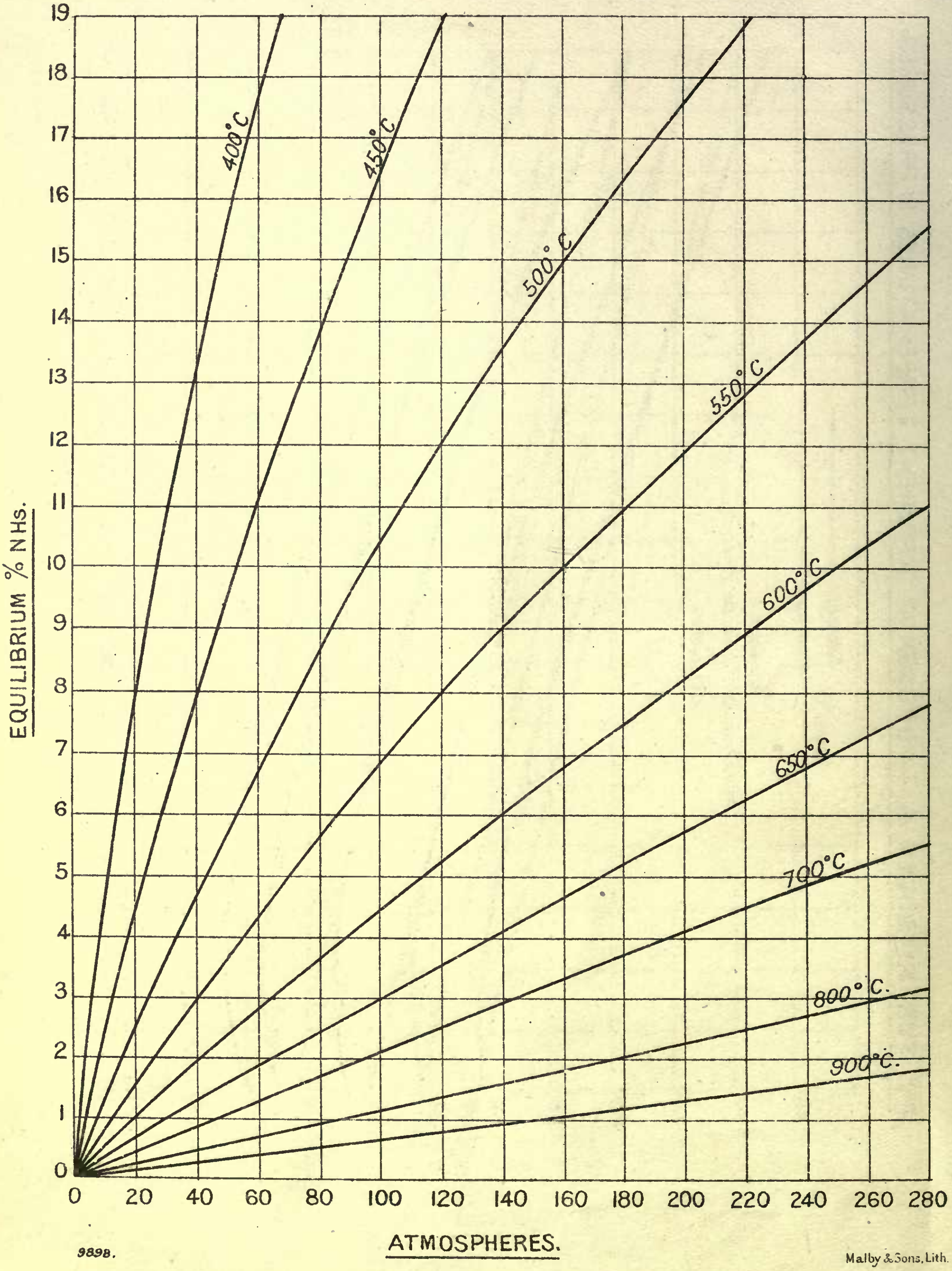
3898. 17171/153.1000.10.20.
Malby & Sons Lith.

FIG. 2.

AMMONIA EQUILIBRIUM.

% NH_3 IN EQUILIBRIUM WITH THE MIXED GASES AT DIFFERENT TEMPERATURES & PRESSURES.

FOR $N_2 + 3H_2$ + AMMONIA MIXTURE ONLY.



9898.

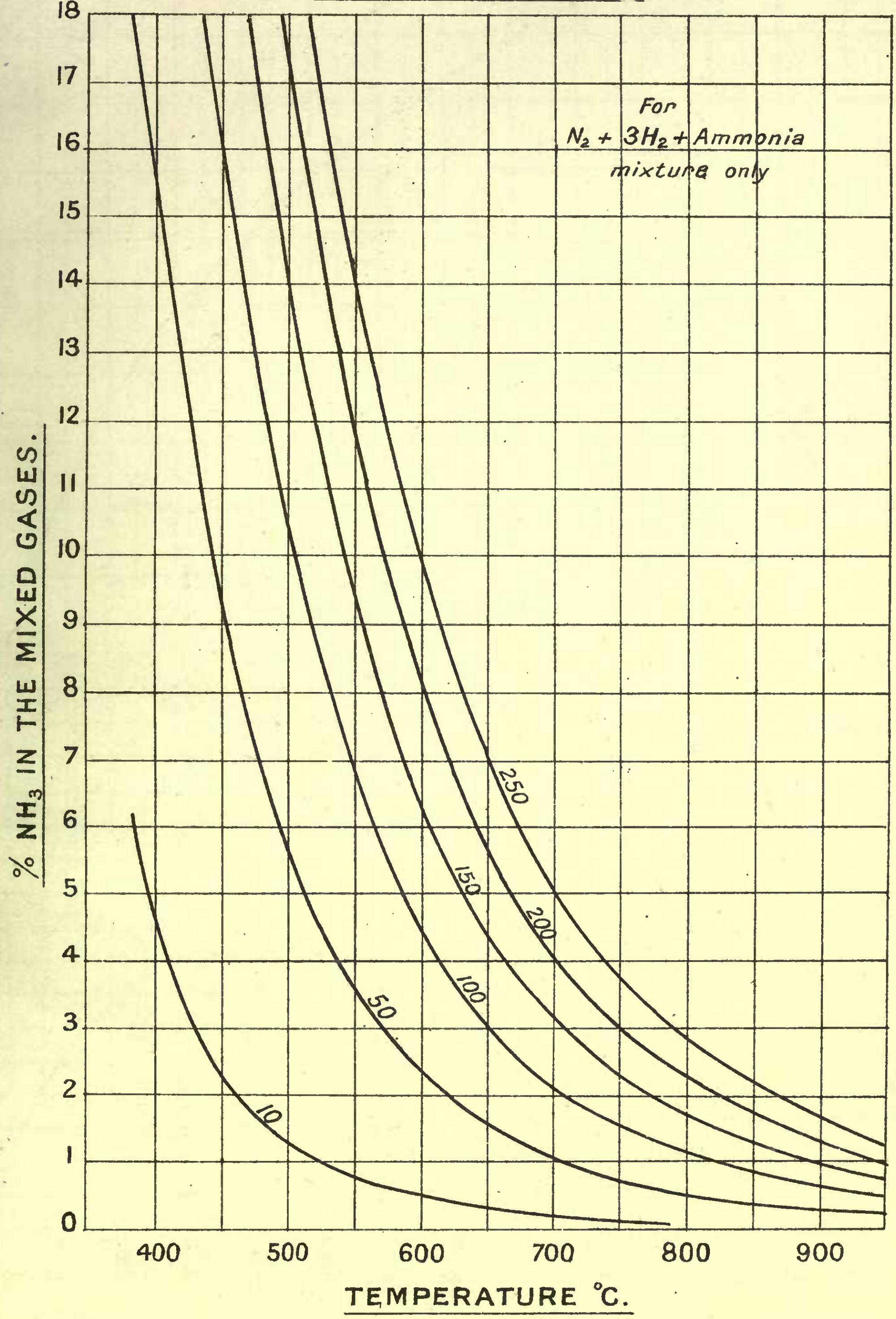
Malby & Sons, Lith.

FIG.3.

AMMONIA EQUILIBRIUM.

THE NUMBERS ON THE GRAPHS GIVE THE PRESSURE IN ATMOSPHERES.

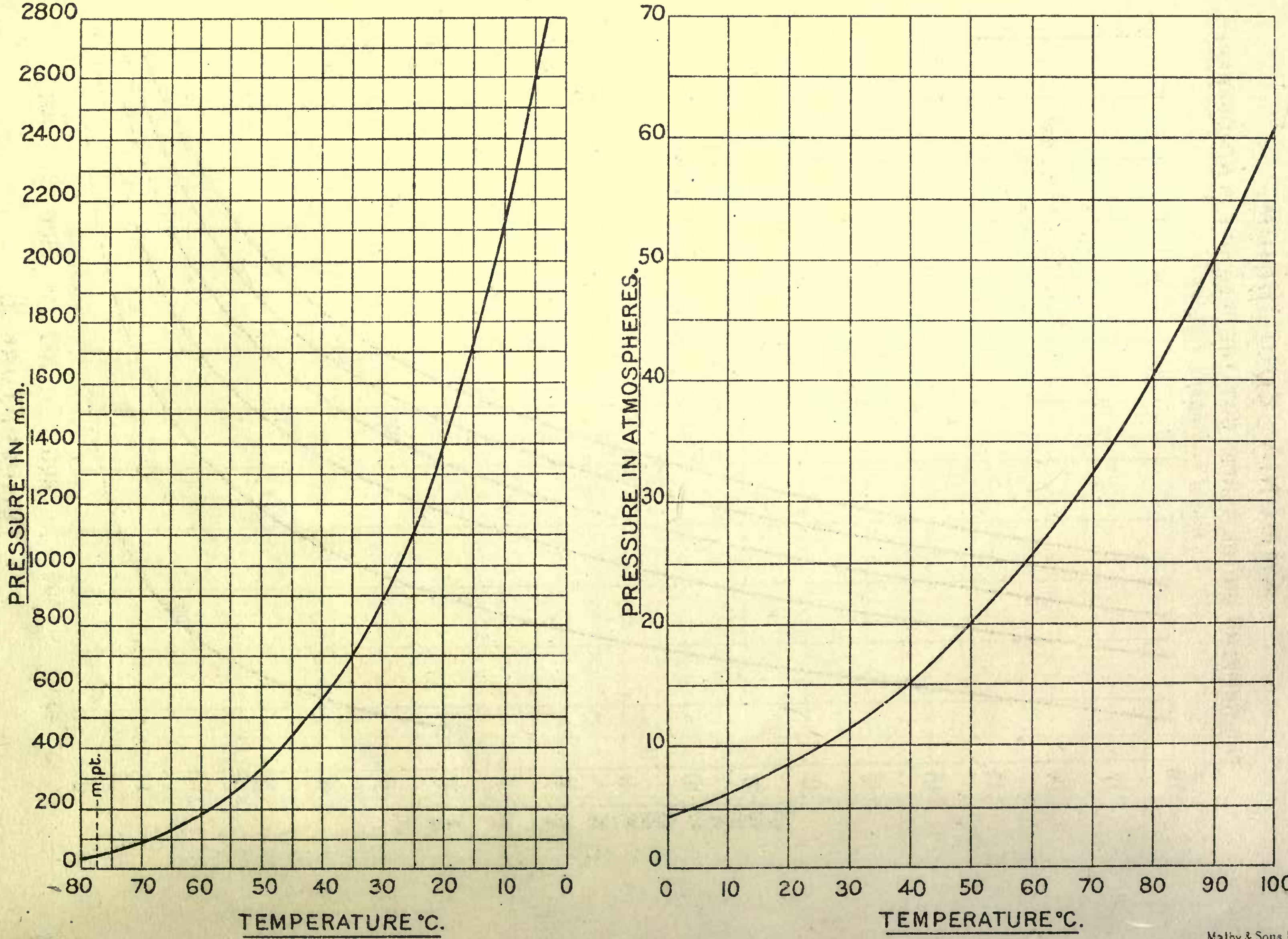
(Based on Habers Figures)



9898. 17171/153

Malby & Sons, Lith.

FIG. 4.



VAPOUR TENSION OF ANHYDROUS AMMONIA AT DIFFERENT TEMPERATURES.

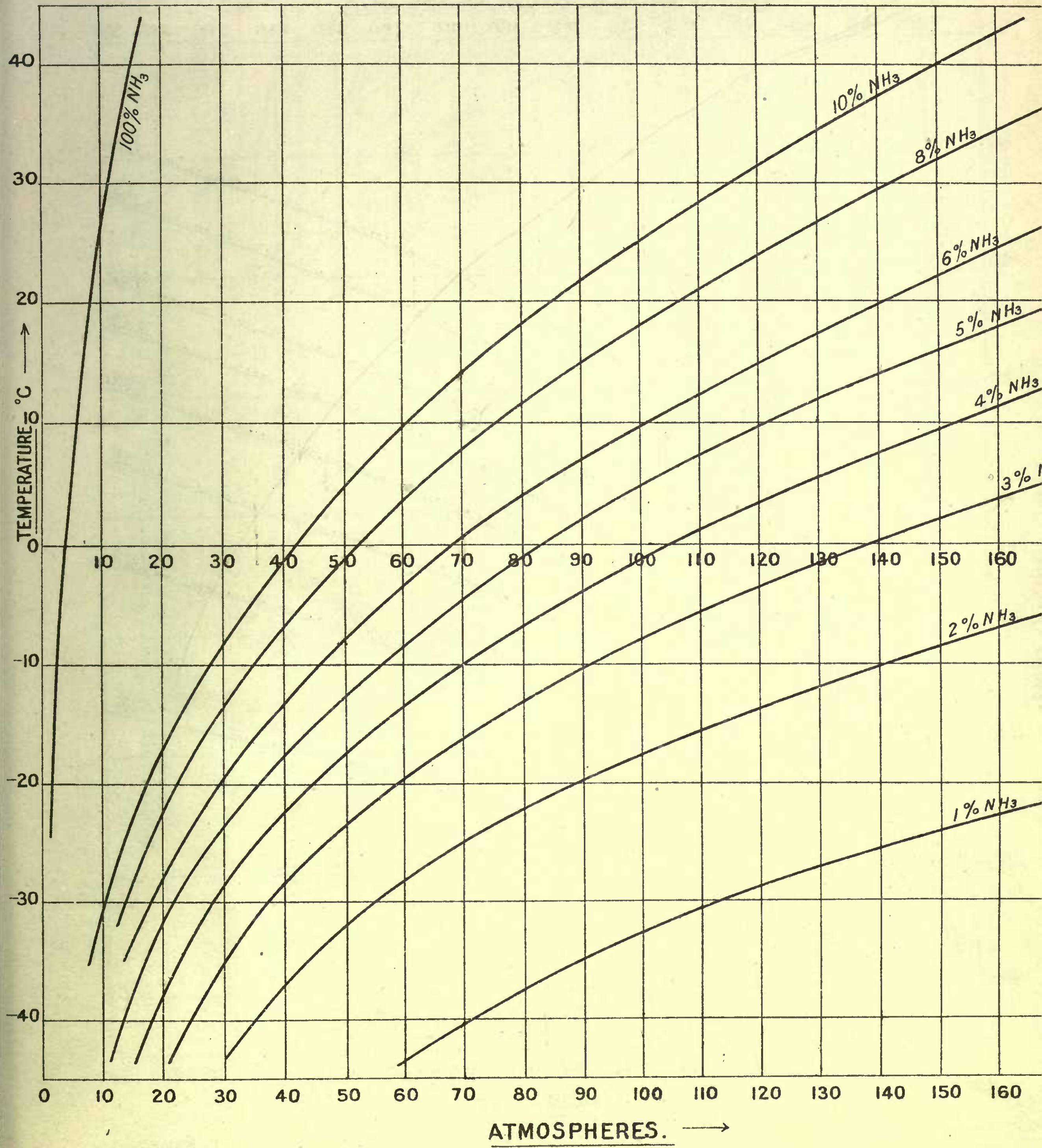
9898.

Malby & Sons. Lith.

TEMPERATURE & PRESSURE AT WHICH CONDENSATION SHOULD JUST BEGIN FOR VARIOUS PERCENTAGES (BY VOL) OF AMMONIA.

(CALCULATED FROM VAPOUR PRESSURE DATA)

FIG



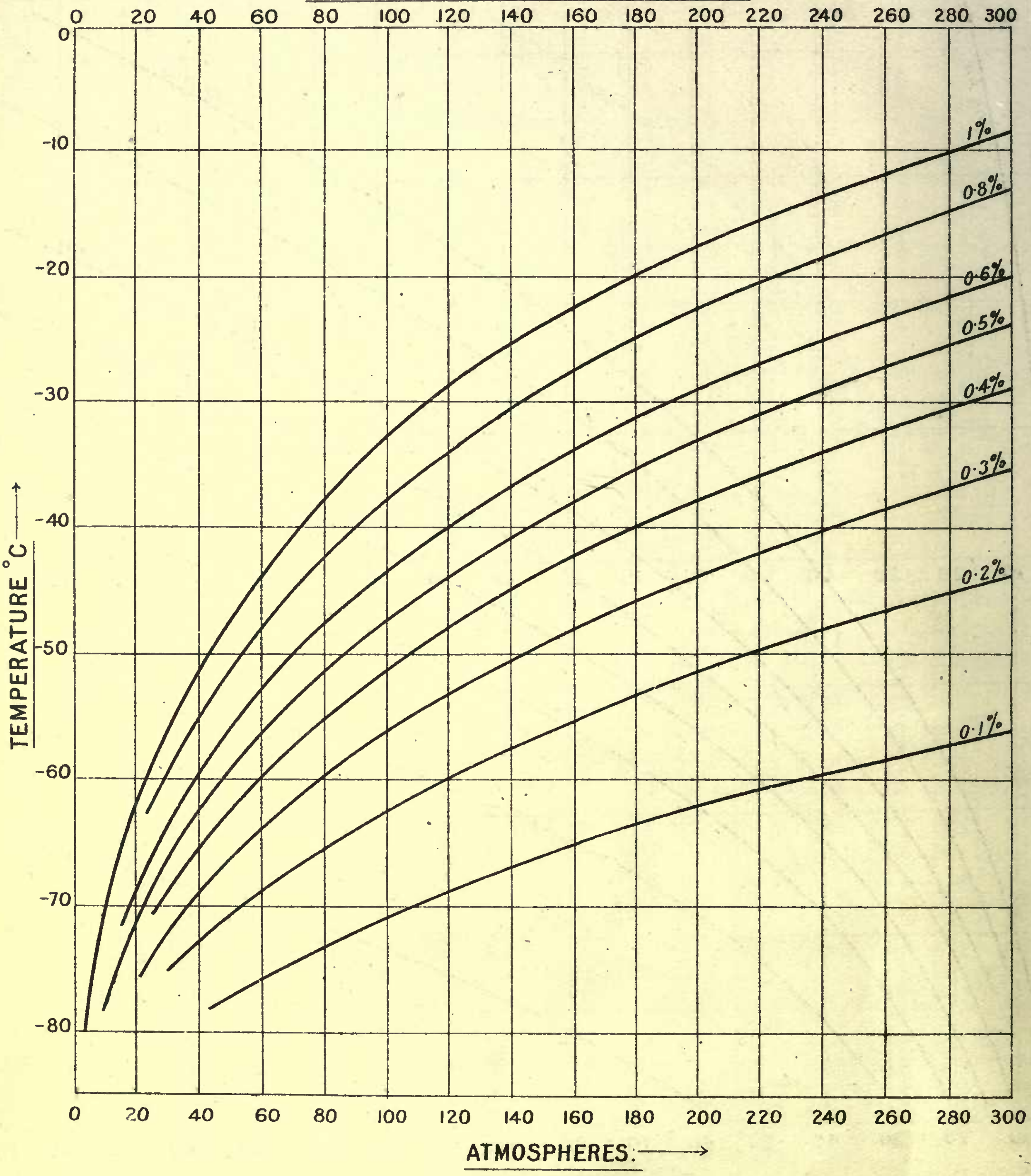
9898. 17171/153.

M

FIG.6.

TEMPERATURE & PRESSURE AT WHICH CONDENSATION SHOULD JUST BEGIN FOR PERCENTAGES OF NH_3 (BY VOL) UP TO 1·0%.

CALCULATED FROM VAPOUR PRESSURE DATA.



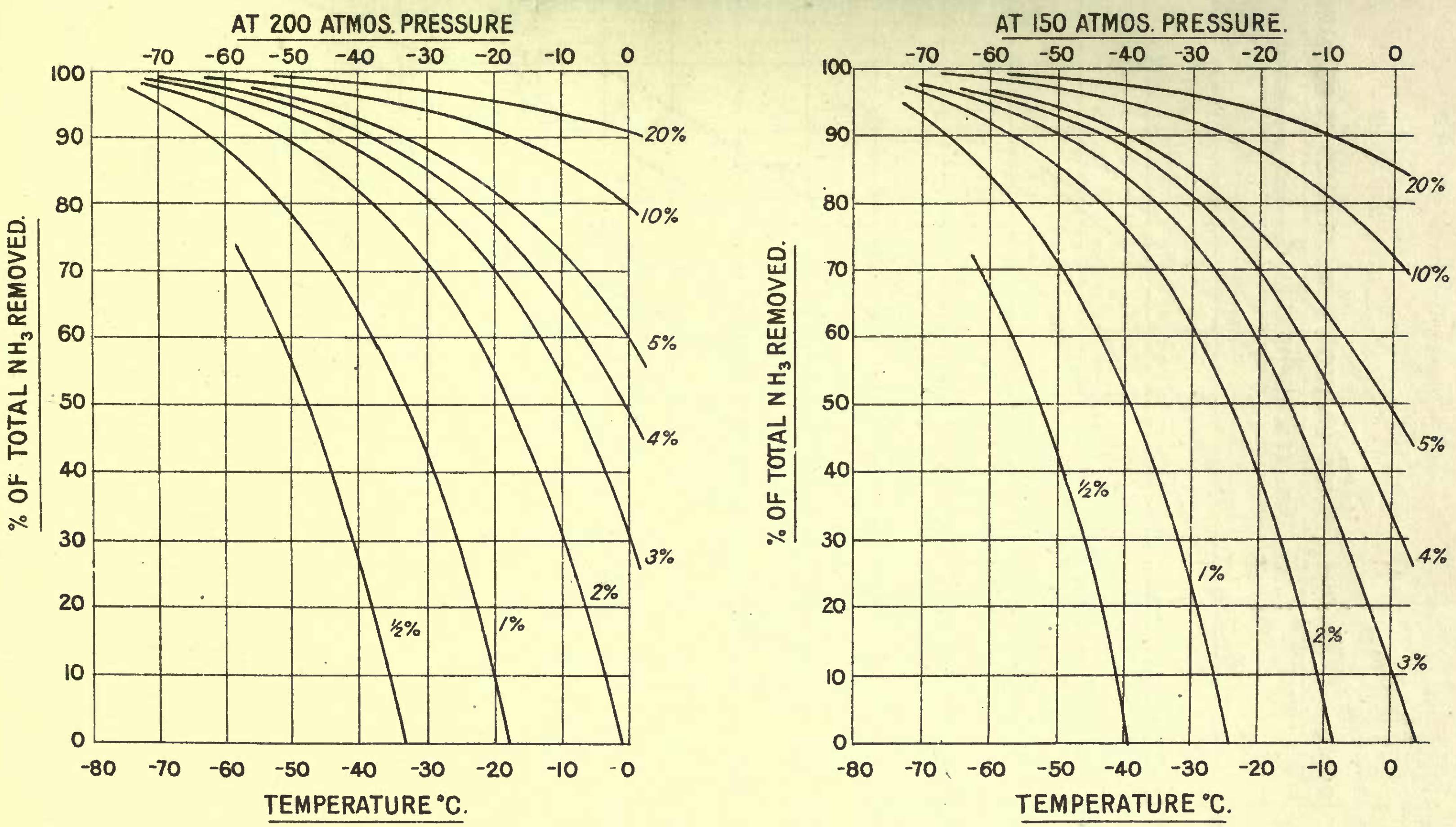
9698. 17171/153.

Malby & Sons. Lith.

FIG. 7.

REMOVAL OF NH_3 FROM GASEOUS MIXTURES BY COOLING.

(CALCULATED FROM VAPOUR PRESSURE DATA.)



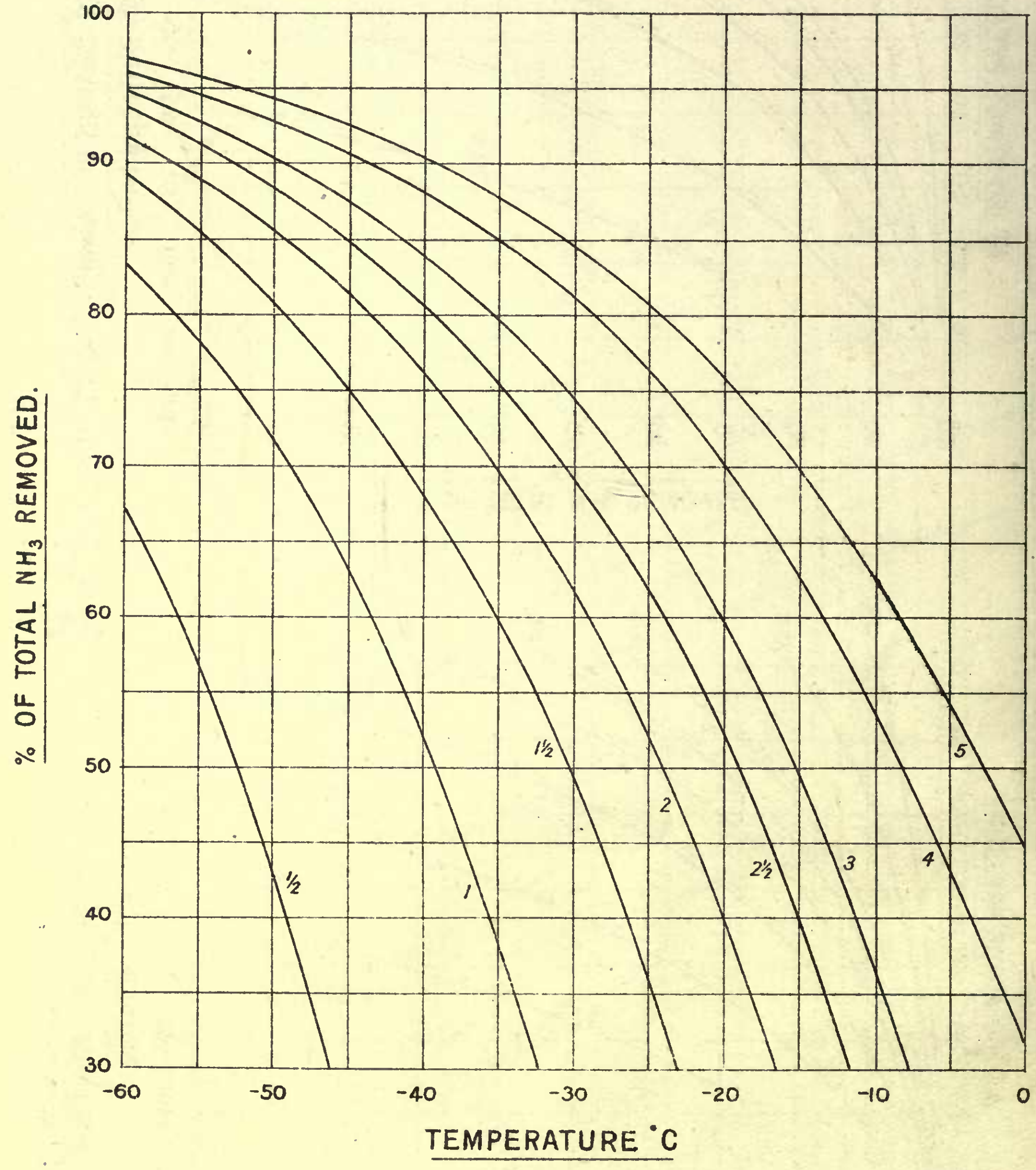
THE CONTENT OF NH_3 (% BY VOL) IN THE MIXTURE IS INDICATED ON THE CURVES. ORDINATES SHOW % OF NH_3 CONTENT REMOVED.

3698. 17171/153

Malby & Sons. Lith.

FIG.

REMOVAL OF NH_3 FROM GASEOUS MIXTURES BY COOLING AT 150 ATMOSPHERES. (*From vapour pressure data*)



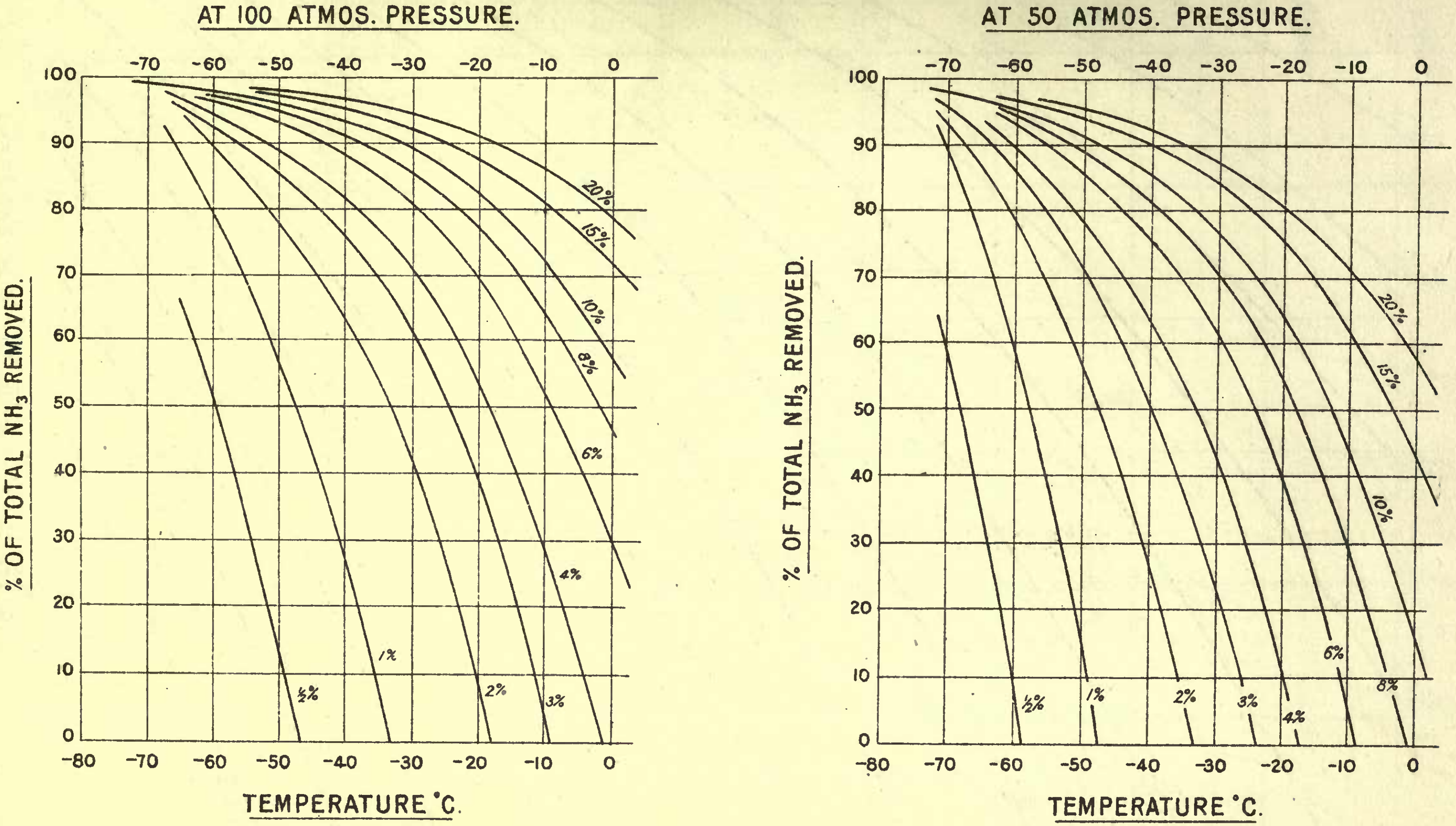
THE CONTENT OF NH_3 (% BY VOL) IS GIVEN ON THE CURVES. THE ORDINATES GIVE % OF NH_3 CONTENT REMOVED.

9898. 17171/153.
Malby & Sons, Lith.

FIG. 9.

REMOVAL OF NH$_3$ FROM GASEOUS MIXTURES BY COOLING.

(CALCULATED FROM VAPOUR PRESSURE DATA.)



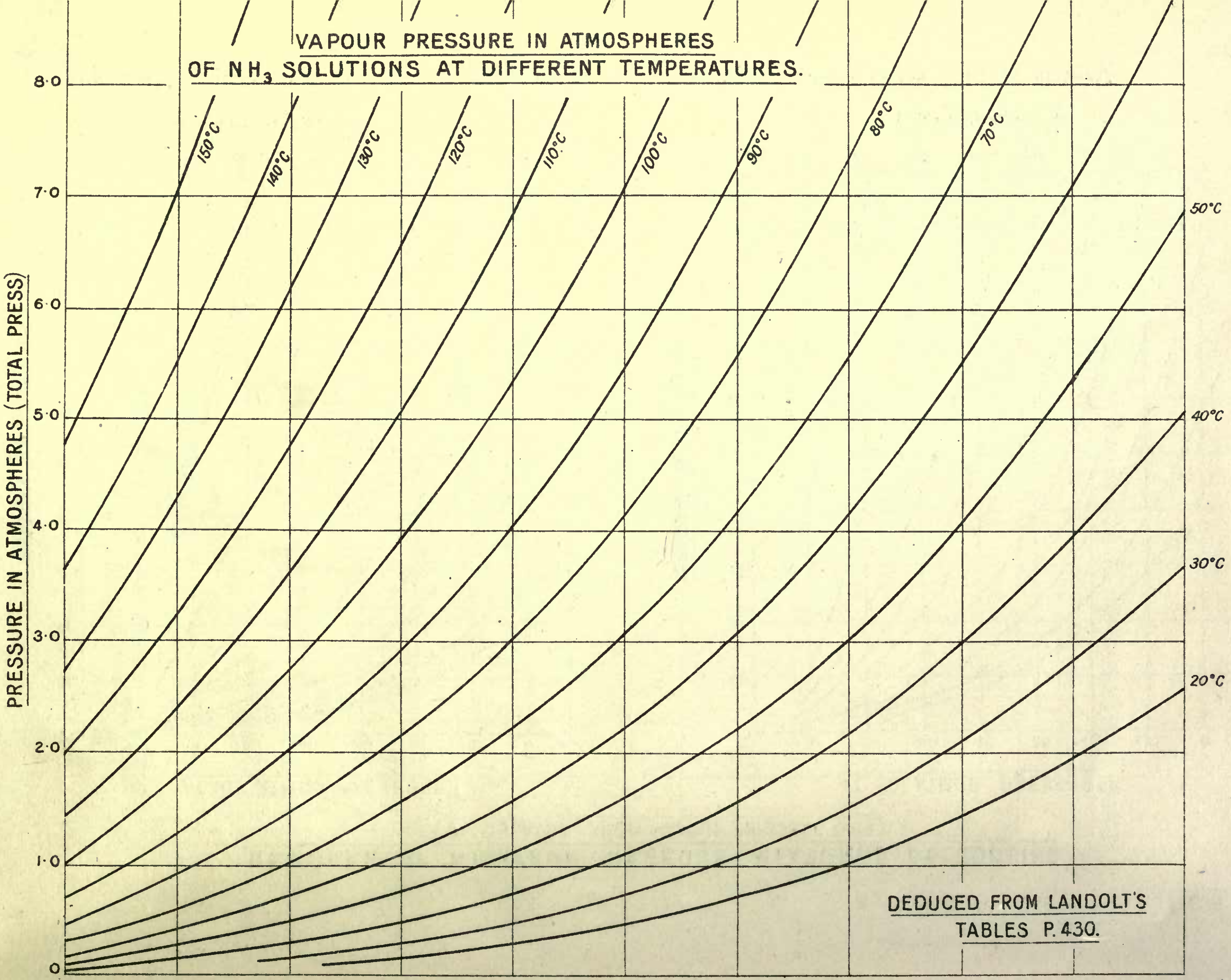
AT 100 ATMOS. PRESSURE.

AT 50 ATMOS. PRESSURE.

THE CONTENT OF NH$_3$ IN THE MIXTURE IS SHOWN ON THE CURVES. ORDINATES SHOW % OF NH$_3$ CONTENT REMOVED.

9858. 17/7/153
Malby & Sons. Lith

VAPOUR PRESSURE IN ATMOSPHERES OF NH_3 SOLUTIONS AT DIFFERENT TEMPERATURES.

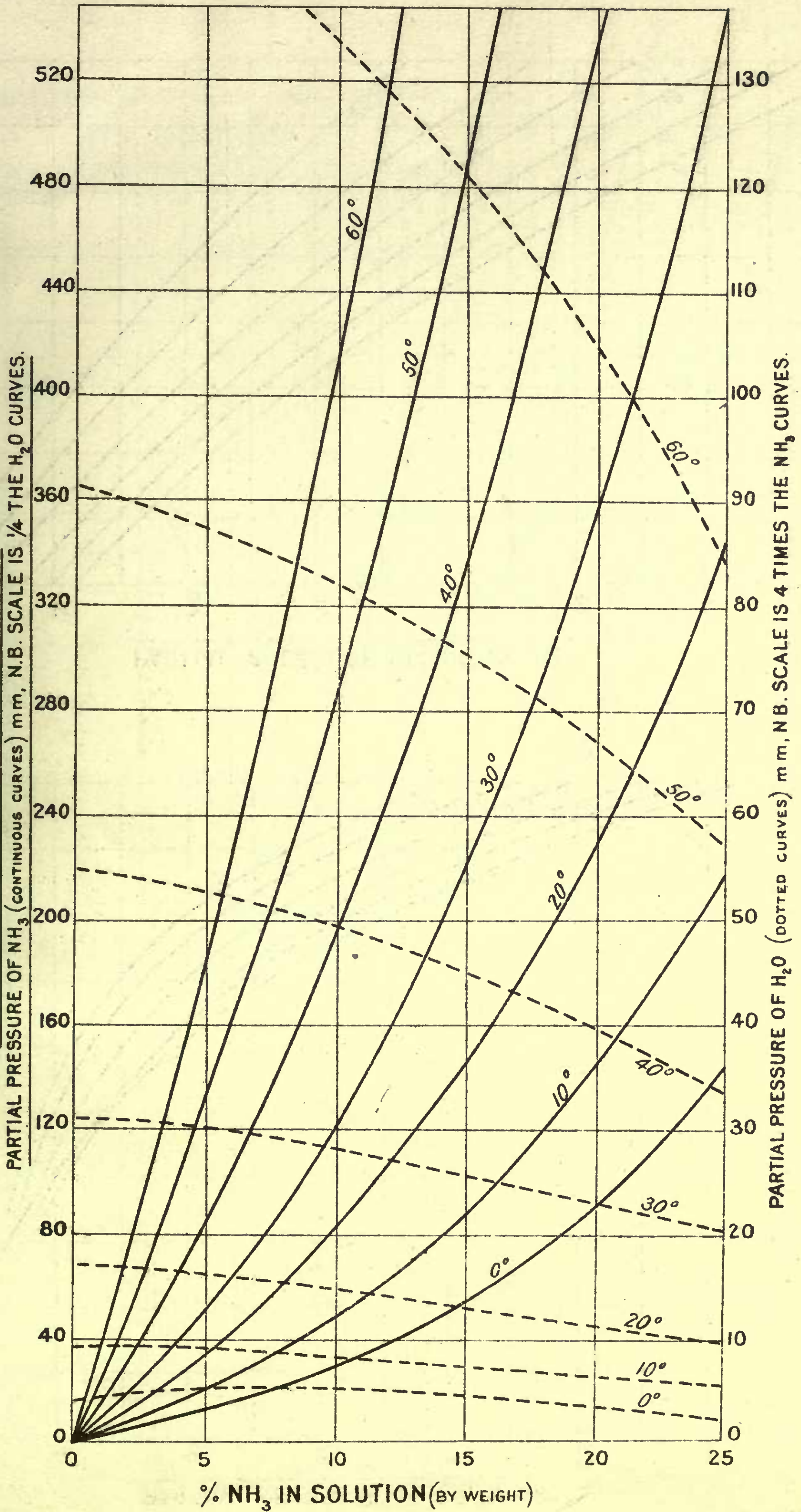


DEDUCED FROM LANDOLT'S
TABLES P. 430.

FIG. II.

PARTIAL PRESSURES AT DIFFERENT TEMPERATURES IN NH_3 SOLUTIONS.

From Perman's Figures. J. Chem. Soc. 83. 2. 1168 1903.



9898.17171/153

Malby & Sons. Lith.

FIG. 12.

PARTIAL PRESSURE OF WATER VAPOUR ABOVE AMMONIA SOLUTIONS.

NUMBERS ON THE GRAPHS GIVE % NH_3 IN THE SOLUTION.

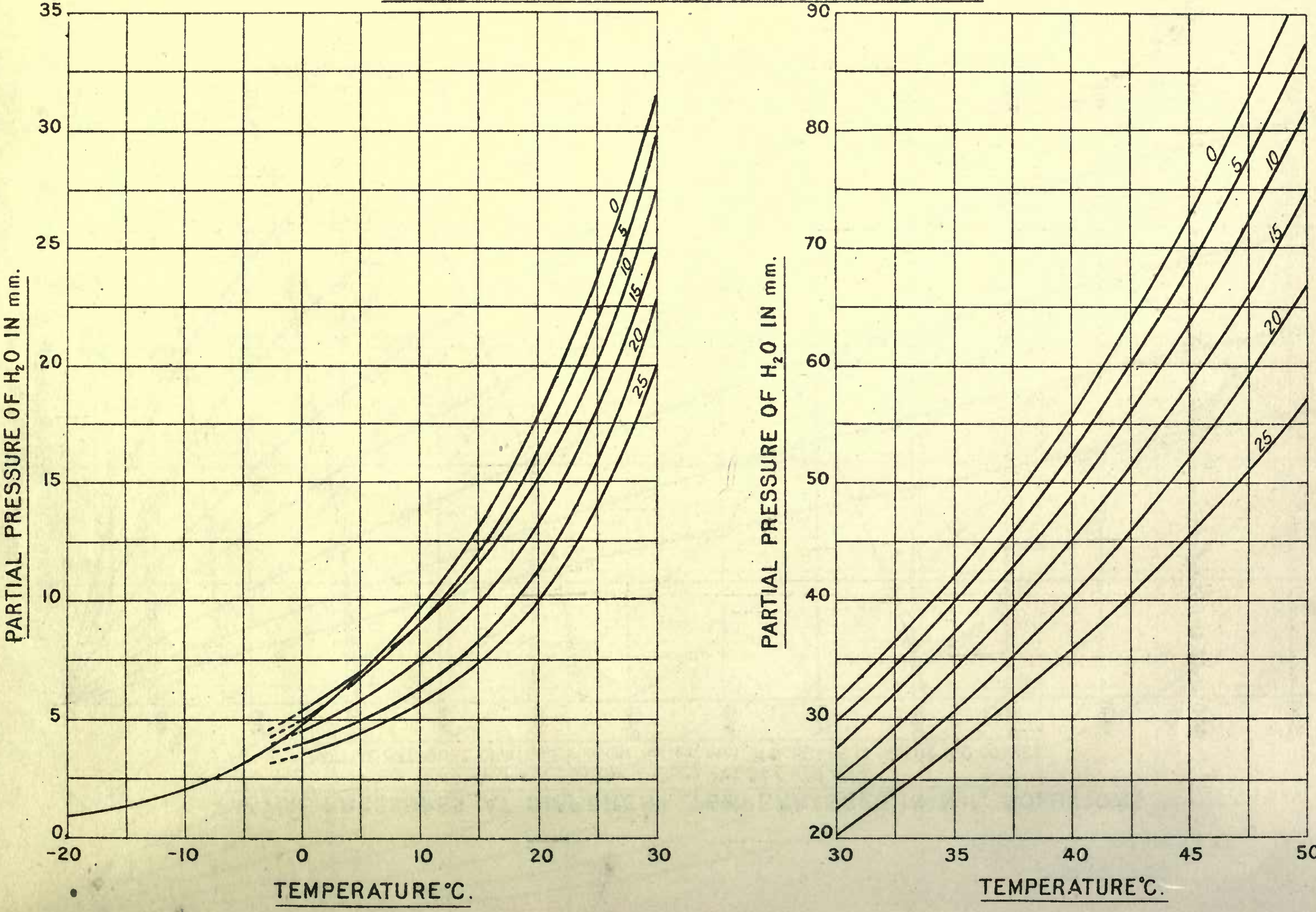
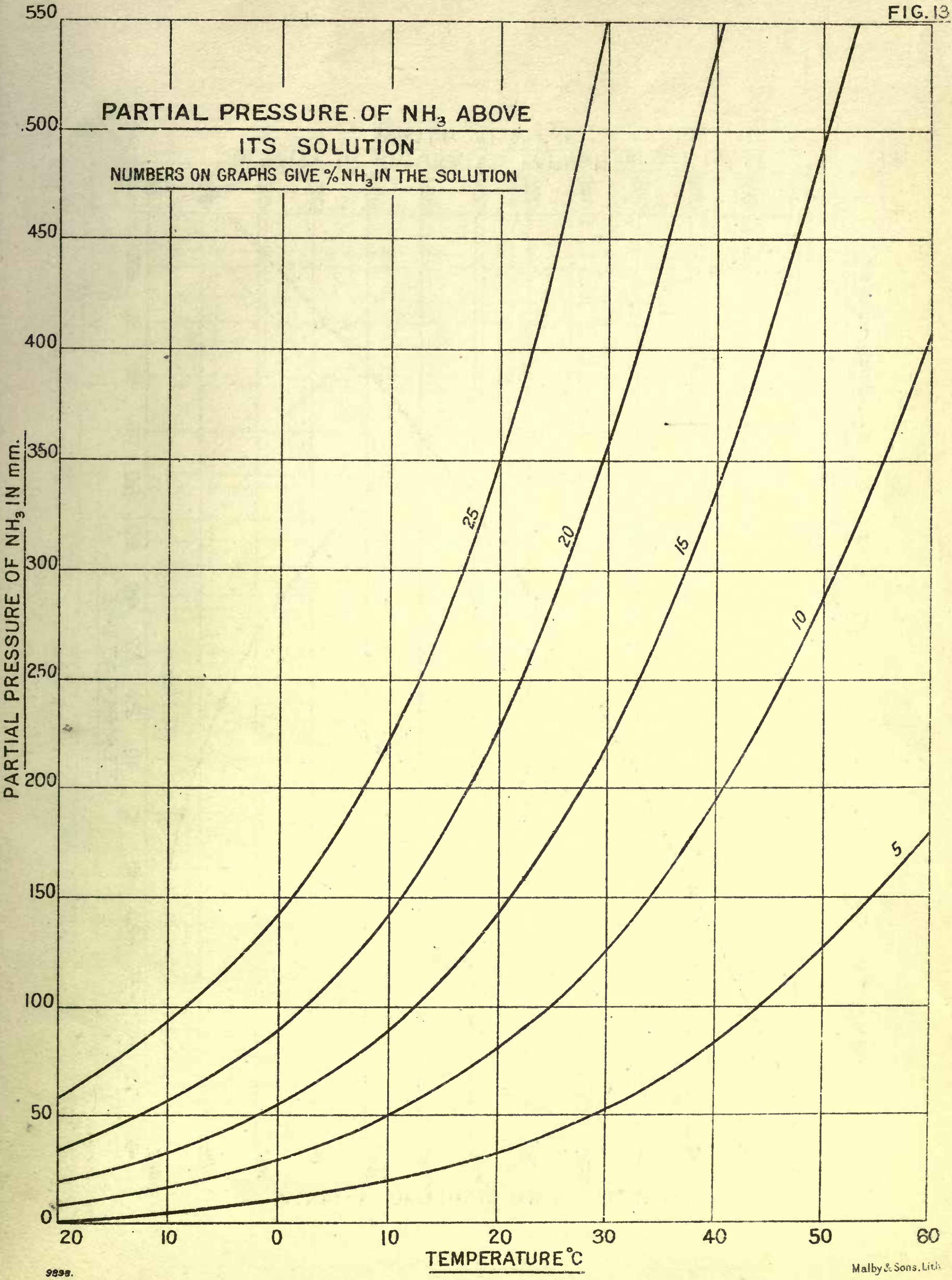


FIG. 13.



PARTIAL PRESSURE OF NH_3 ABOVE ITS SOLUTION

NUMBERS ON GRAPHS GIVE % NH_3 IN THE SOLUTION

9898.

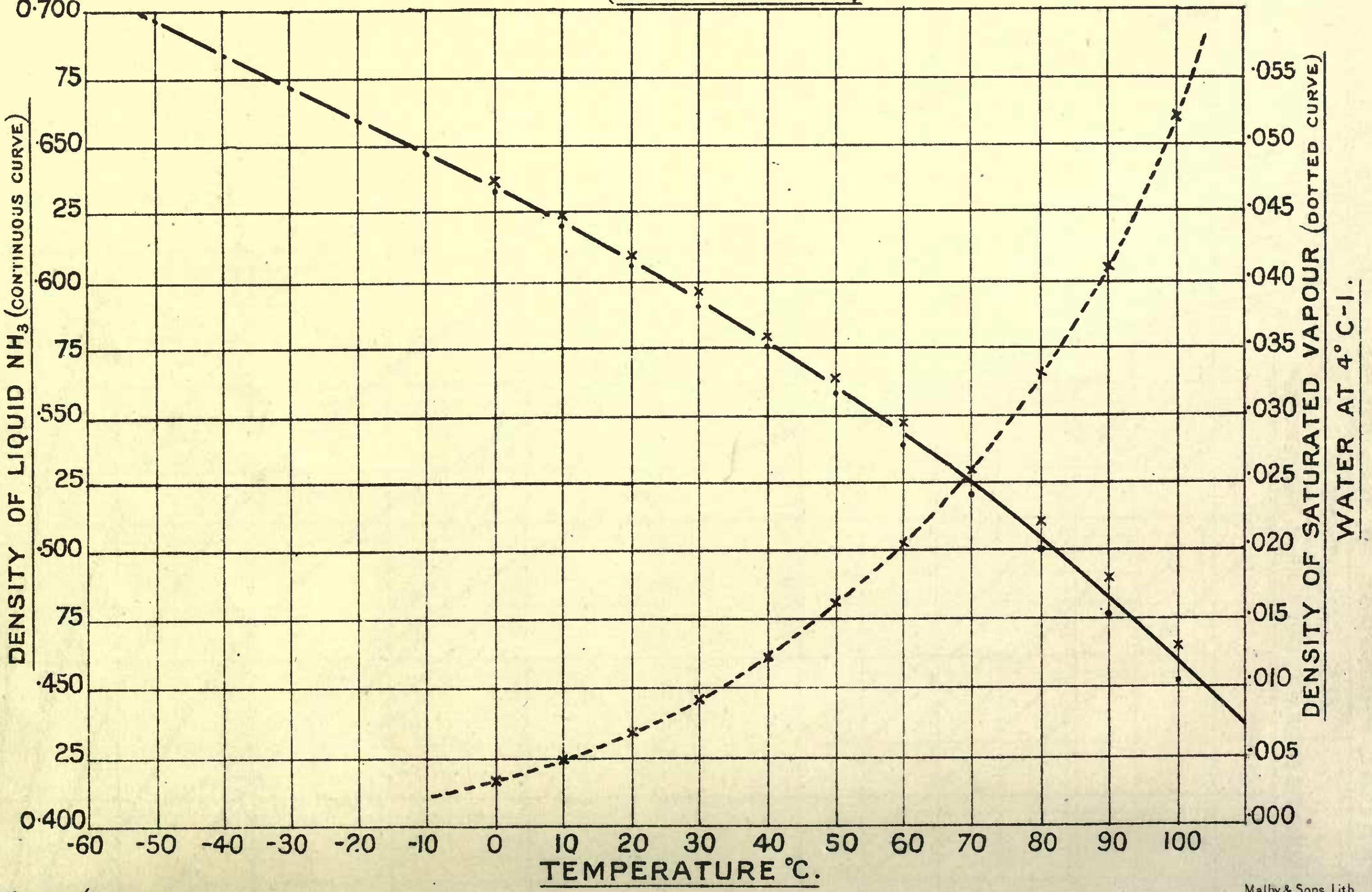
Malby & Sons, Lith.

FIG. 14.

DENSITY OF LIQUID AMMONIA AT DIFFERENT TEMPERATURES.

LANGE 1898···· DIETERICI 1904.××××

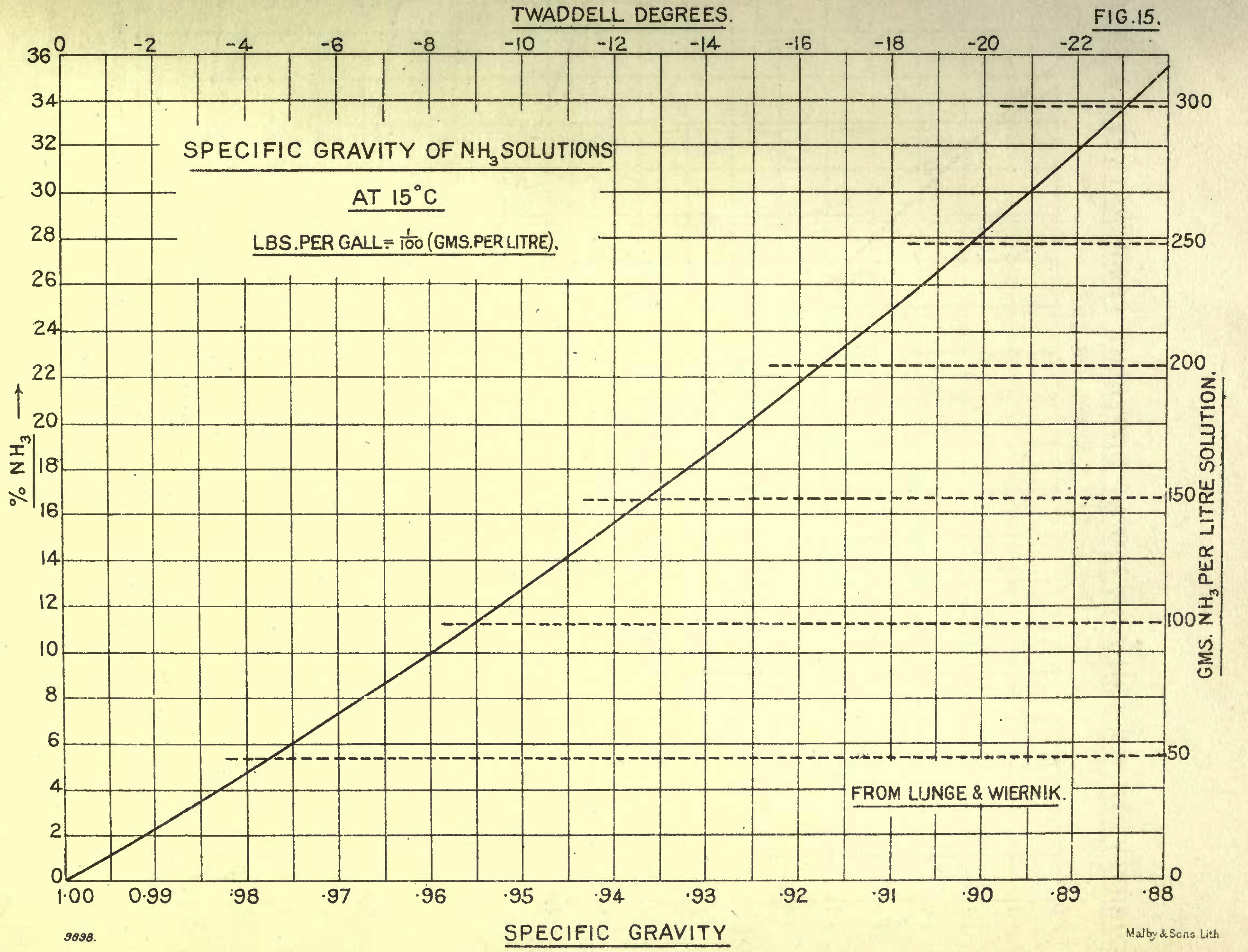
(SEE LANDOLT P. 152)



9898. 17171/153.

Malby & Sons, Lith.

FIG. 15.



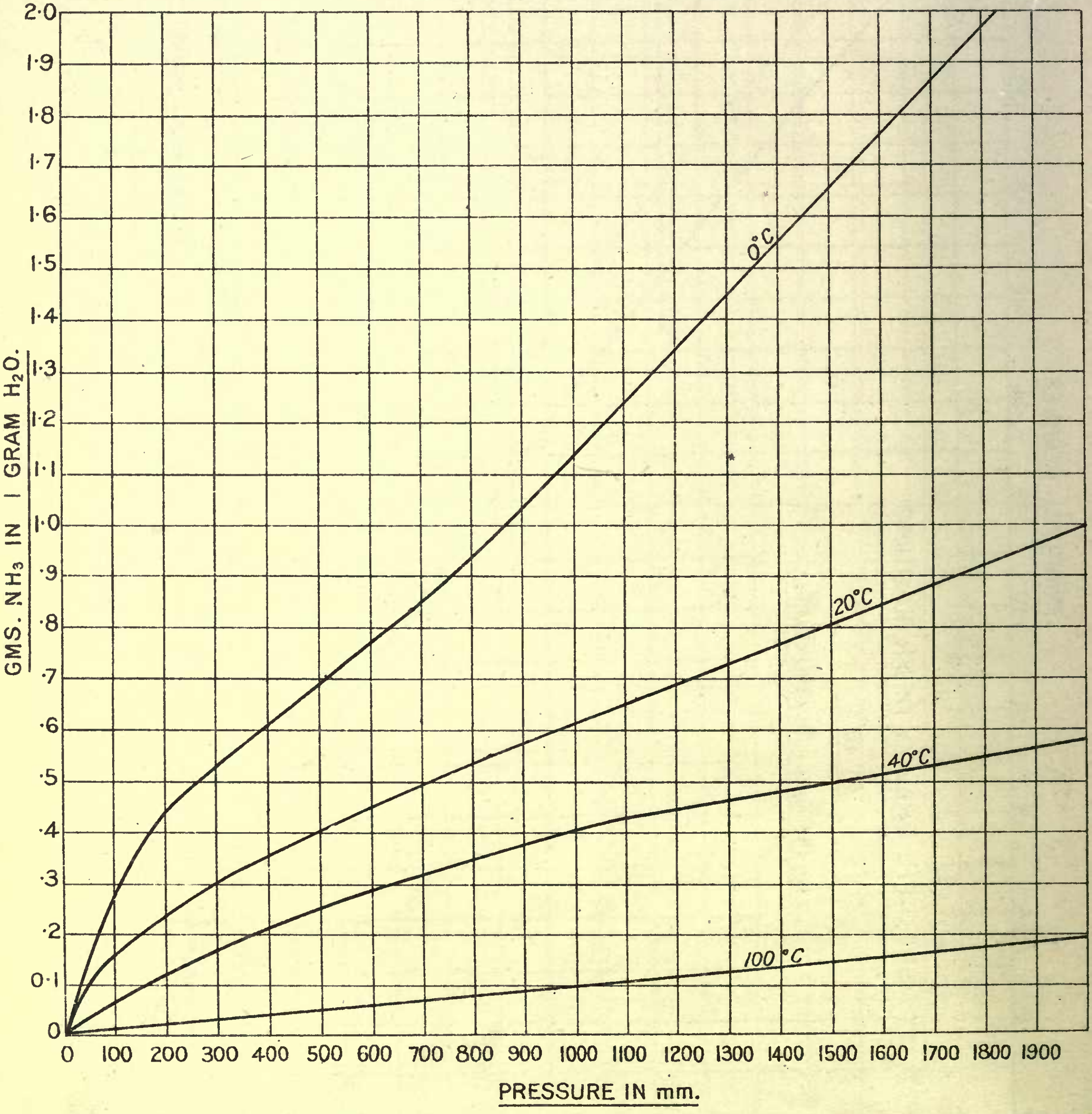
9698.

Malby & Sons Lith.

FI

SOLUBILITY OF AMMONIA IN H_2O AT DIFFERENT TEMPERATURES & PRESS

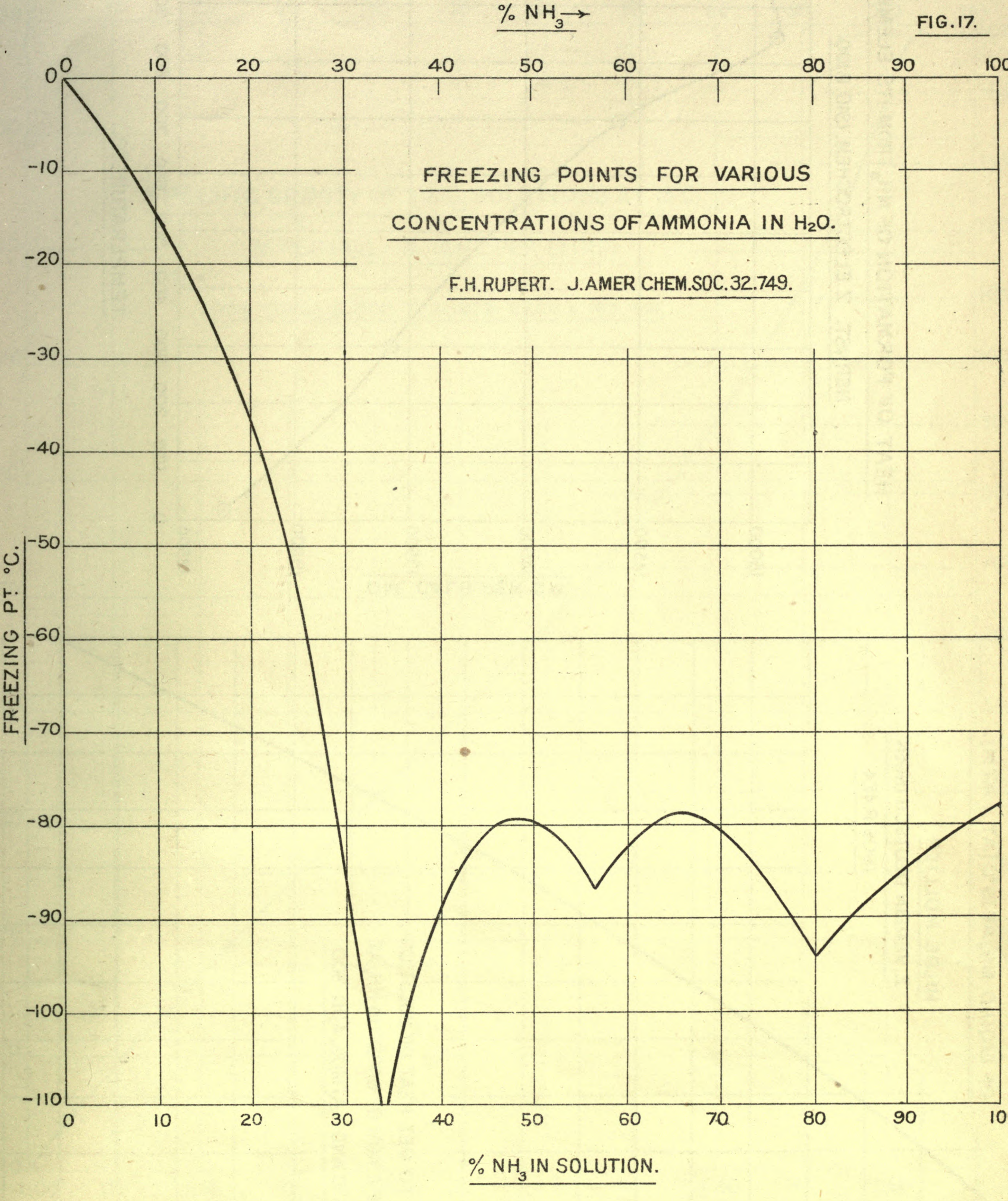
(*See Castell – Evans, II p. 1002*)



989A.

Malby & Sons, Lit

FIG. 17.

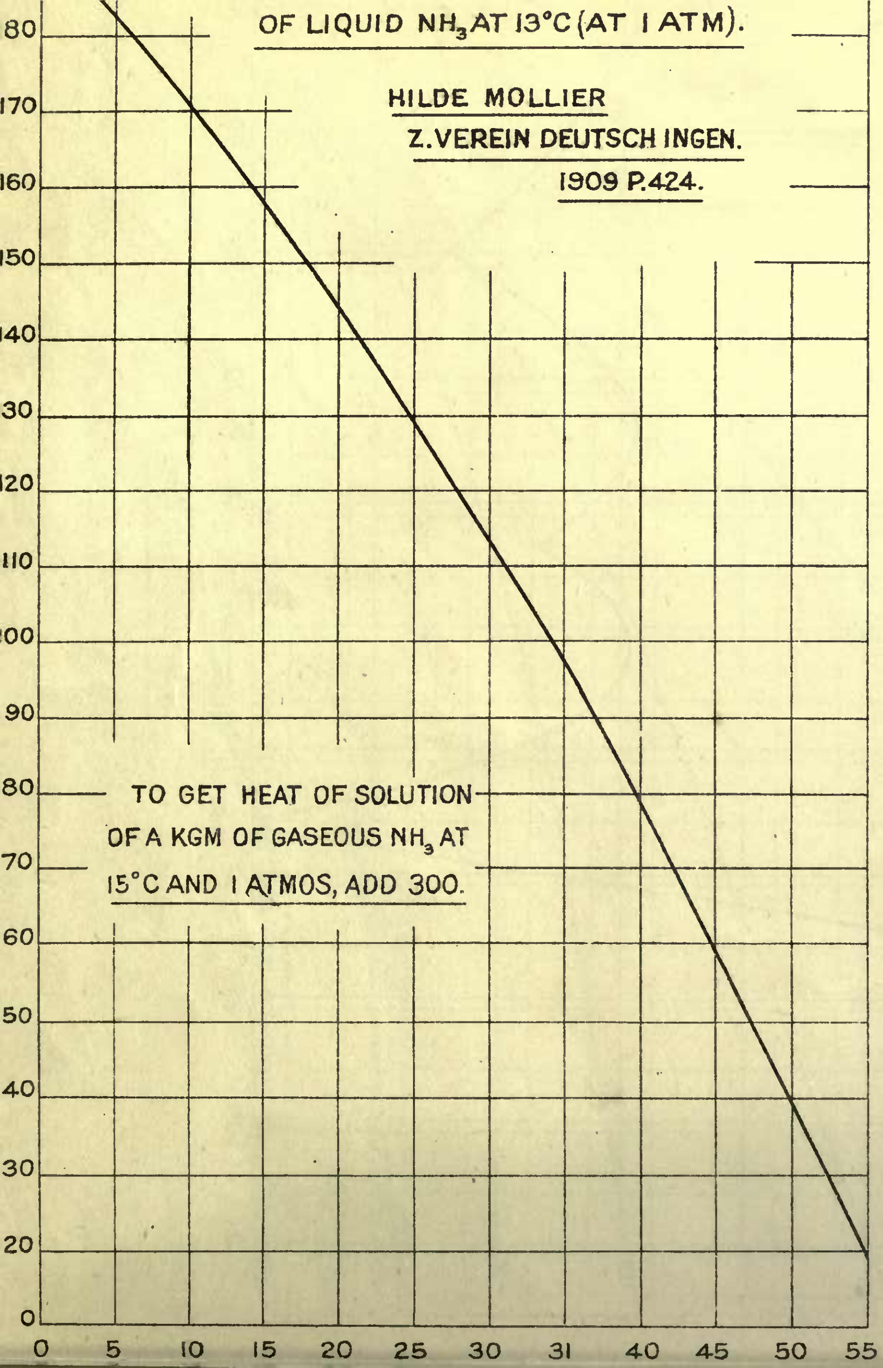


FREEZING POINTS FOR VARIOUS CONCENTRATIONS OF AMMONIA IN H_2O.

F.H. RUPERT. J. AMER CHEM. SOC. 32.749.

9898

Malby & Sons. Lith.



OF LIQUID NH_3 AT 13°C (AT 1 ATM).

HILDE MOLLIER

Z. VEREIN DEUTSCH INGEN.

1909 P. 424.

TO GET HEAT OF SOLUTION OF A KGM OF GASEOUS NH_3 AT 15°C AND 1 ATMOS, ADD 300.

HEAT OF FORMATION OF NH_3 FROM ITS ELEMENTS.

NERNST. Z. ELECTROCHEM. 1910. P. 100.

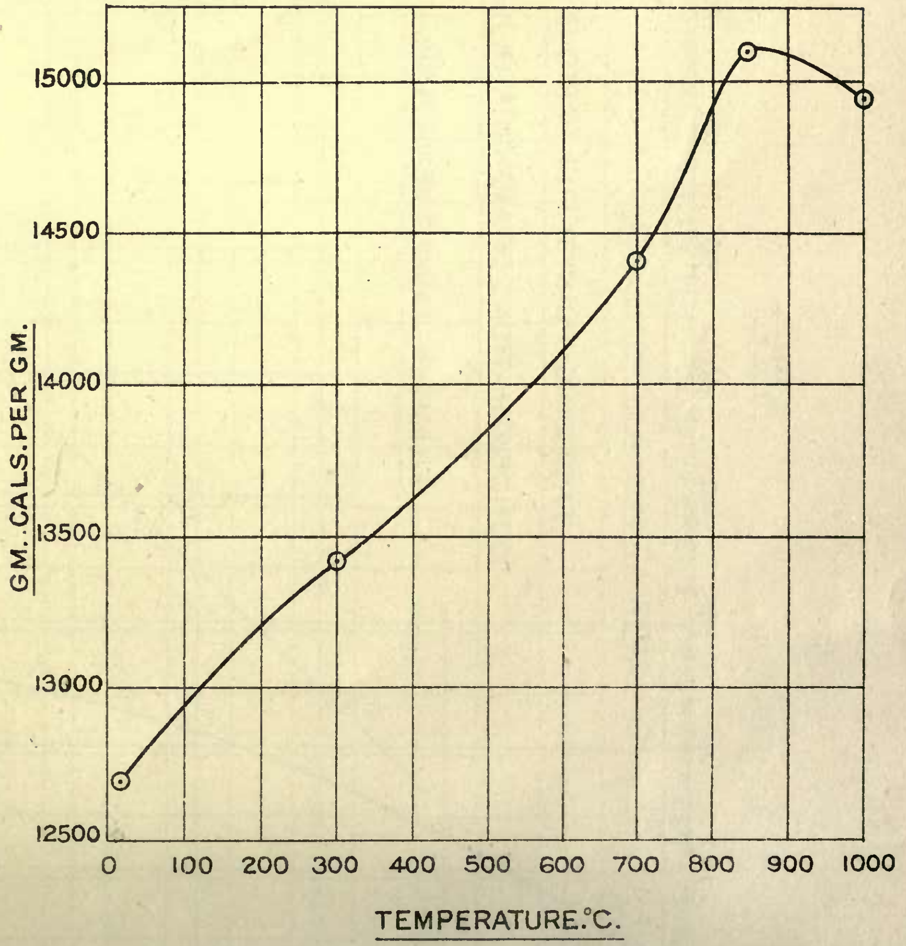
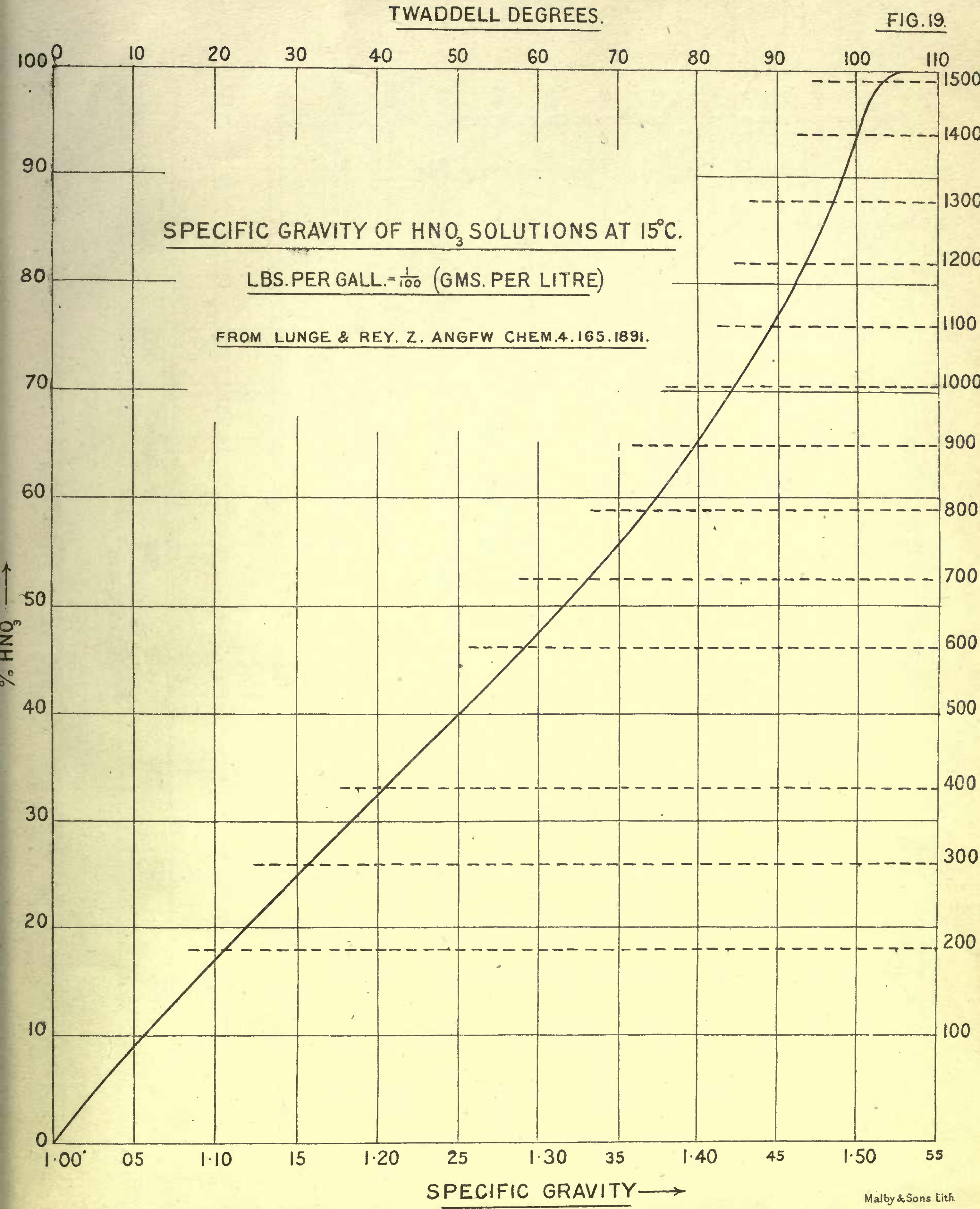


FIG. 19.



SPECIFIC GRAVITY OF HNO_3 SOLUTIONS AT 15°C.

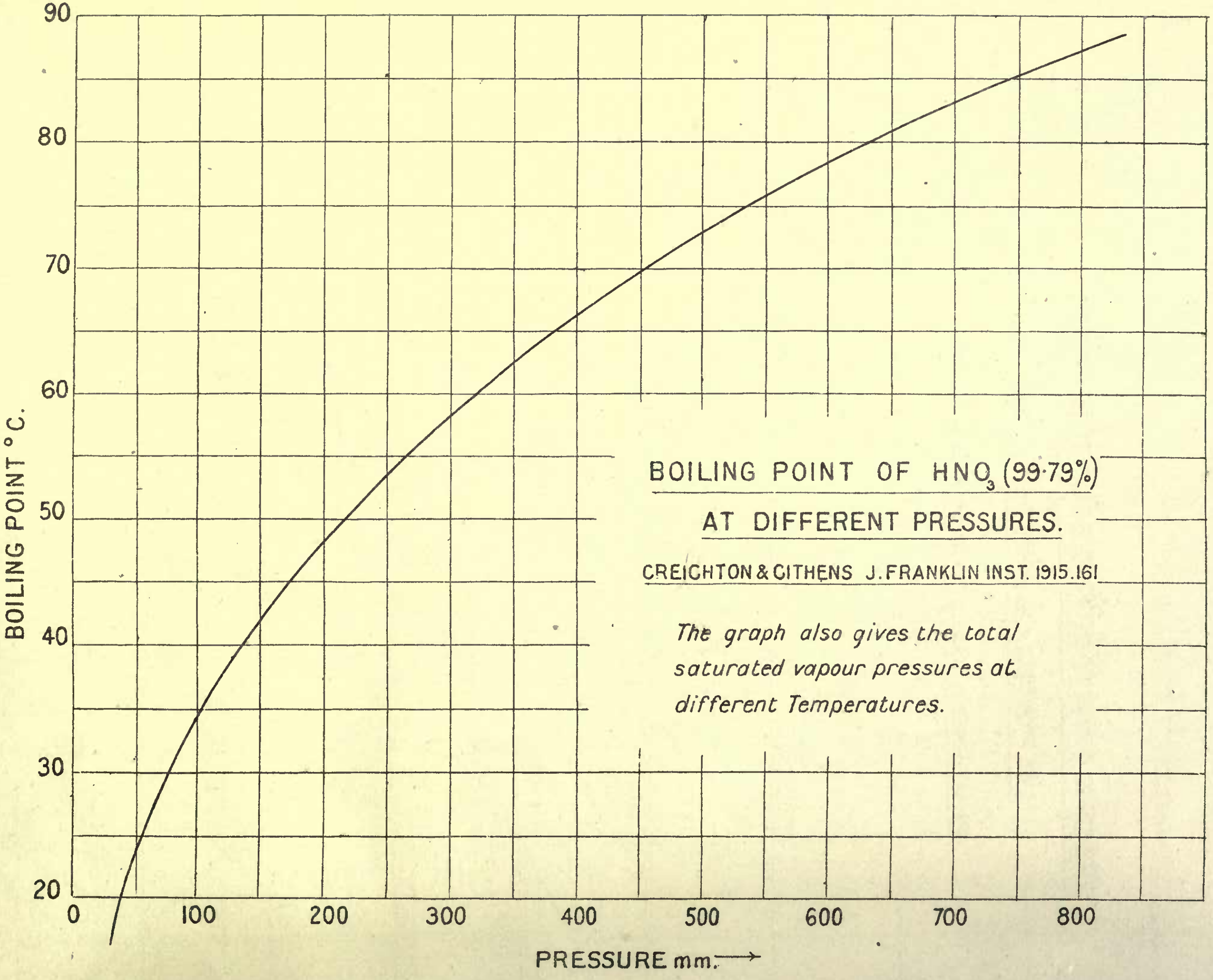
LBS. PER GALL. = $\frac{1}{100}$ (GMS. PER LITRE)

FROM LUNGE & REY. Z. ANGFW CHEM. 4. 165. 1891.

Malby & Sons. Lith.

3898.

FIG. 20.



BOILING POINT OF HNO_3 (99·79%)
AT DIFFERENT PRESSURES.

CREICHTON & CITHENS J. FRANKLIN INST. 1915. 161

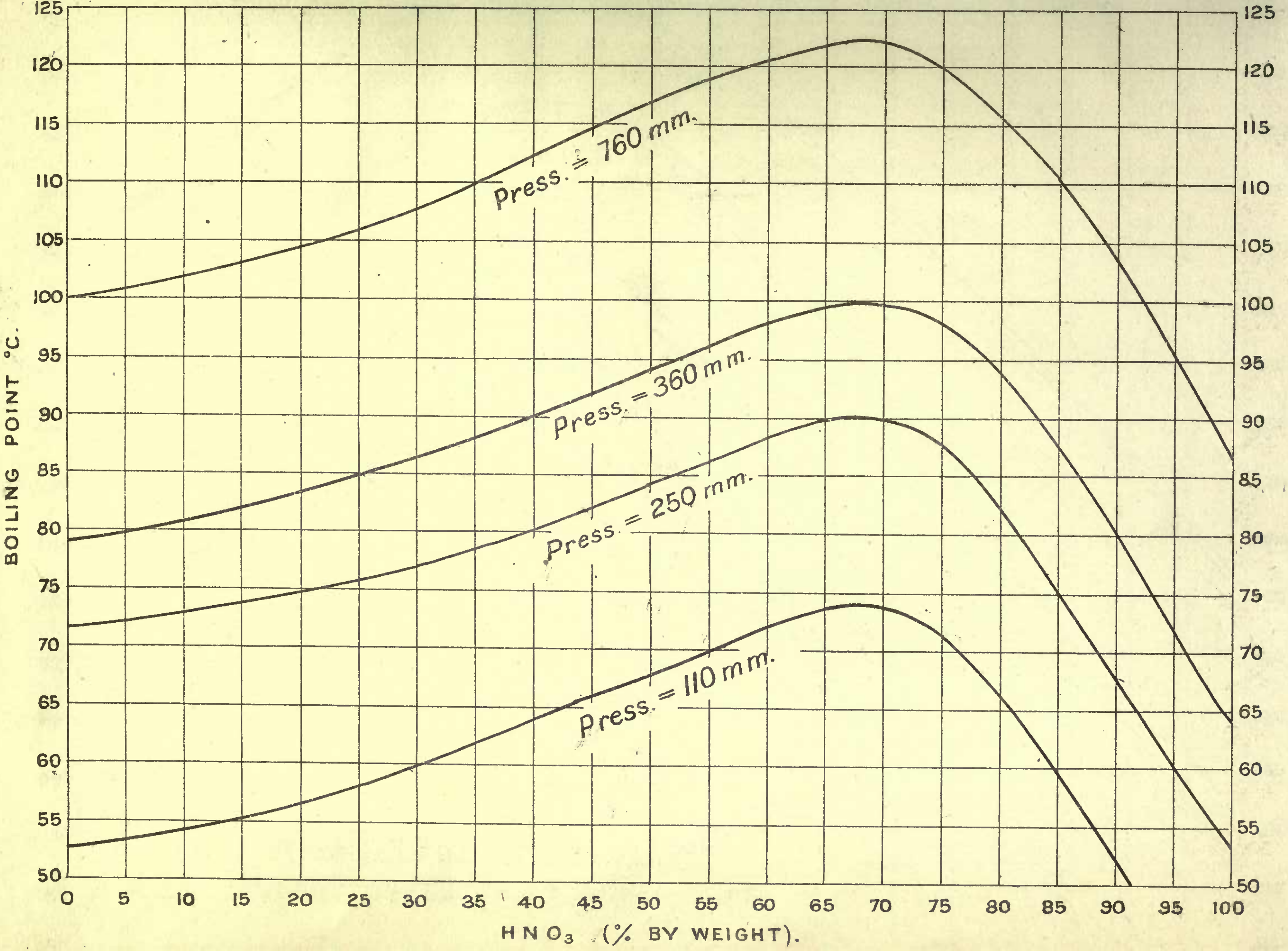
The graph also gives the total saturated vapour pressures at different Temperatures.

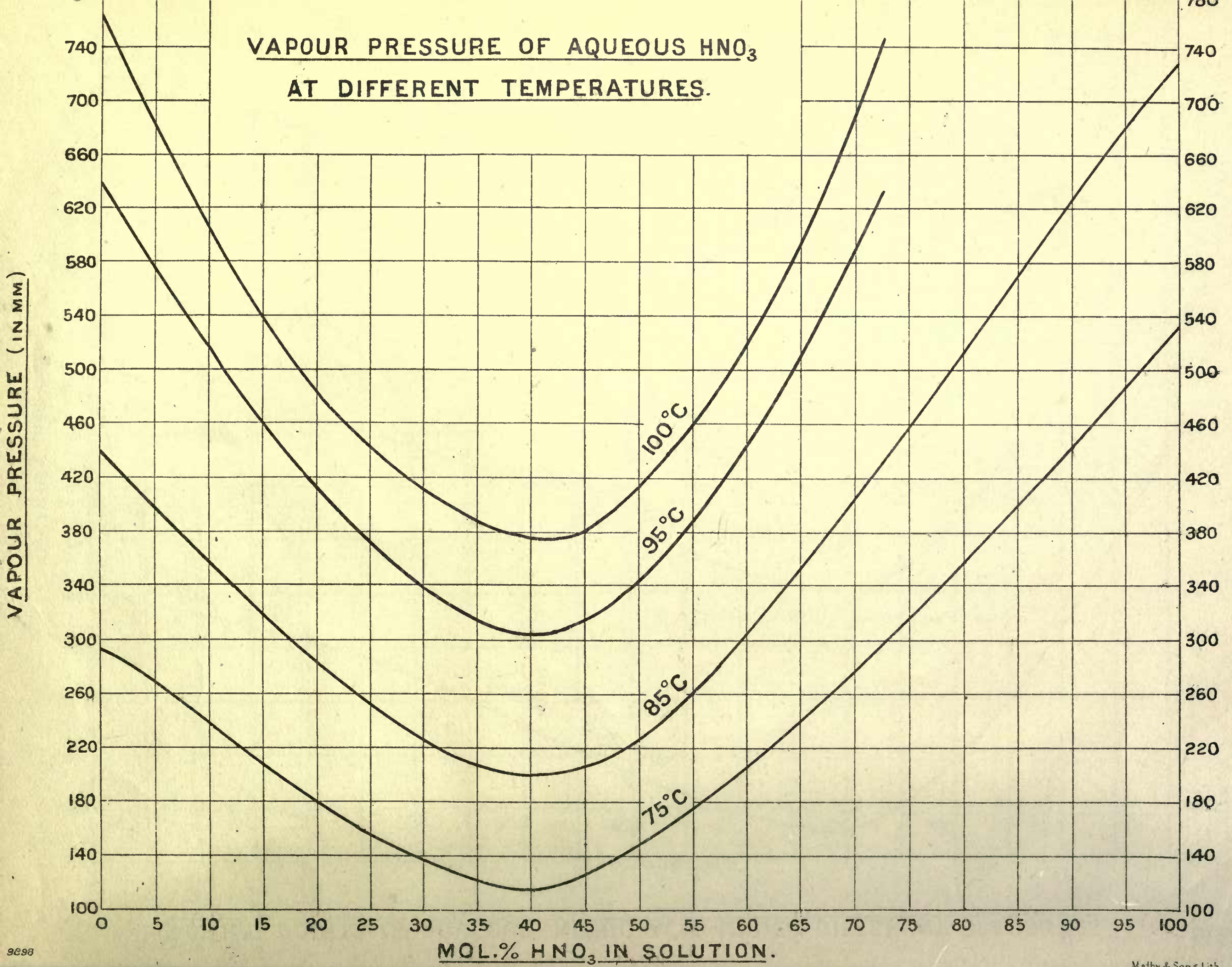
9838.

Malby & Sons. Lith.

FIG. 21.

BOILING POINTS OF AQUEOUS NITRIC ACID UNDER DIFFERENT PRESSURES.





VAPOUR PRESSURE OF AQUEOUS HNO_3 AT DIFFERENT TEMPERATURES.

9898

Malby & Sons Lith.

VAPOUR TENSION OF AQUEOUS SOLUTIONS OF HNO_3 AT DIFFERENT TEMPERATURES.

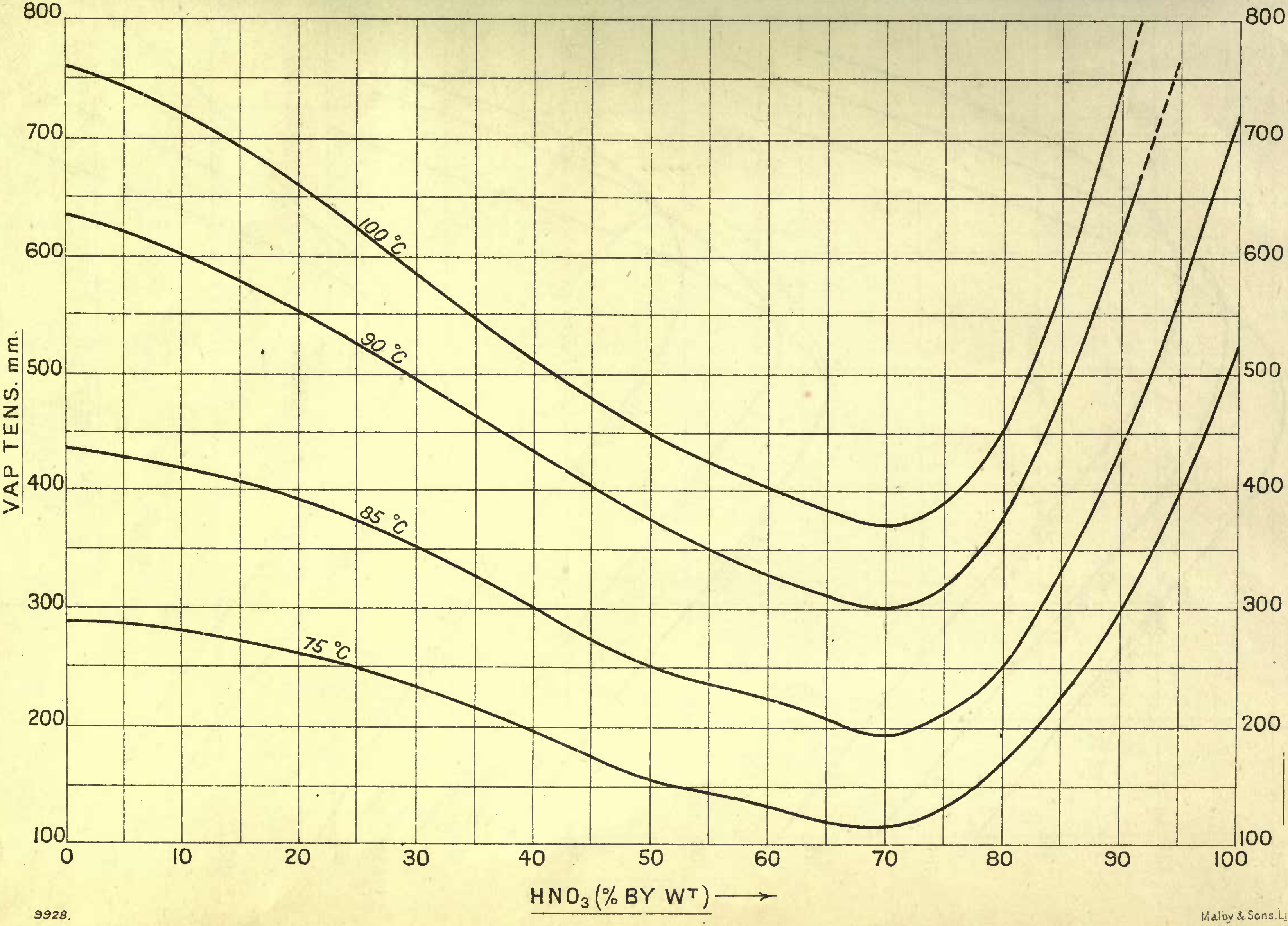


FIG. 23.

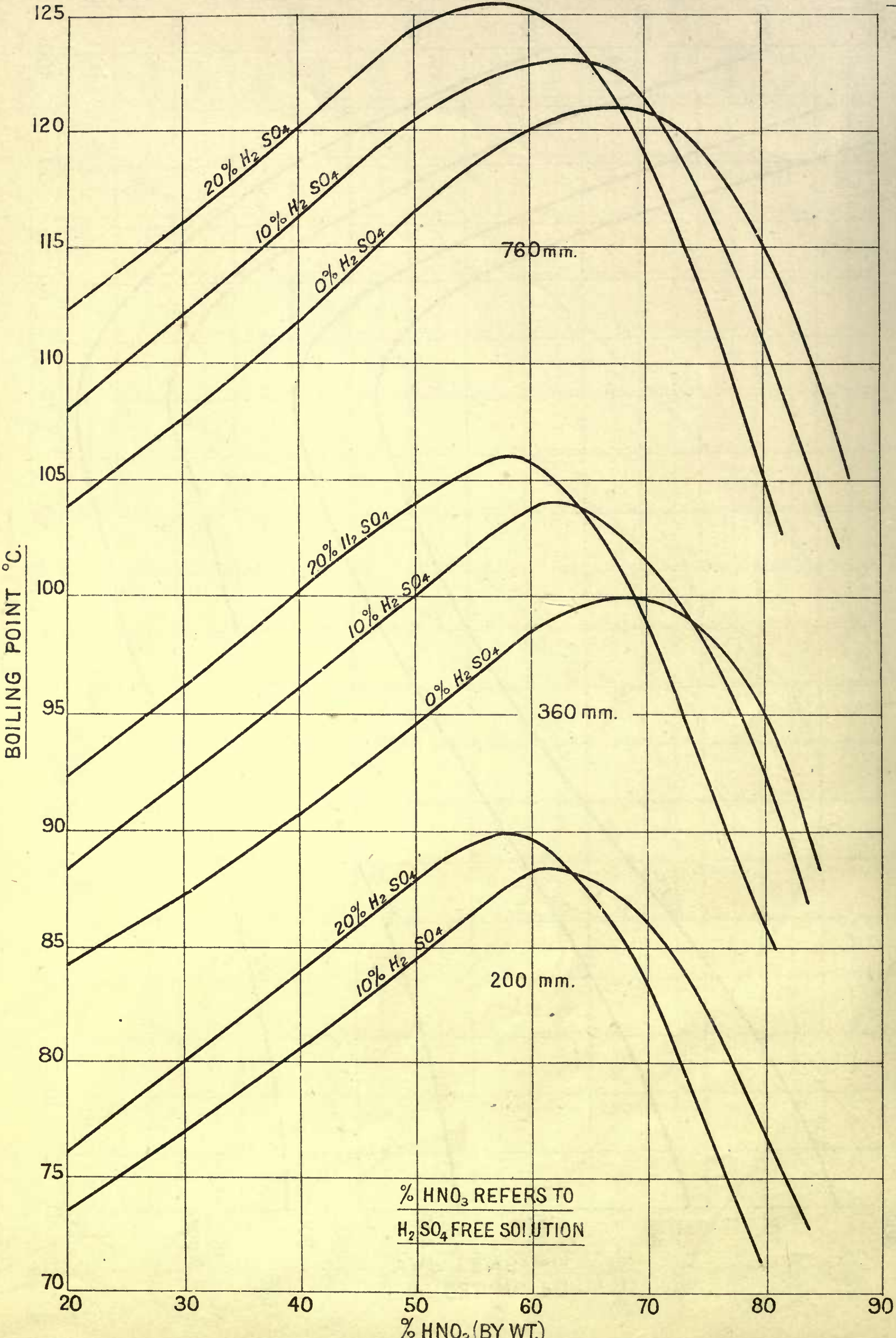
9928.

Malby & Sons. Lith.

INFLUENCE OF H_2SO_4 ON THE BOILING POINTS OF AQUFOUS HNO_3

CREIGHTON & SMITH J. FRANKLIN INST. 1915 P. 706.

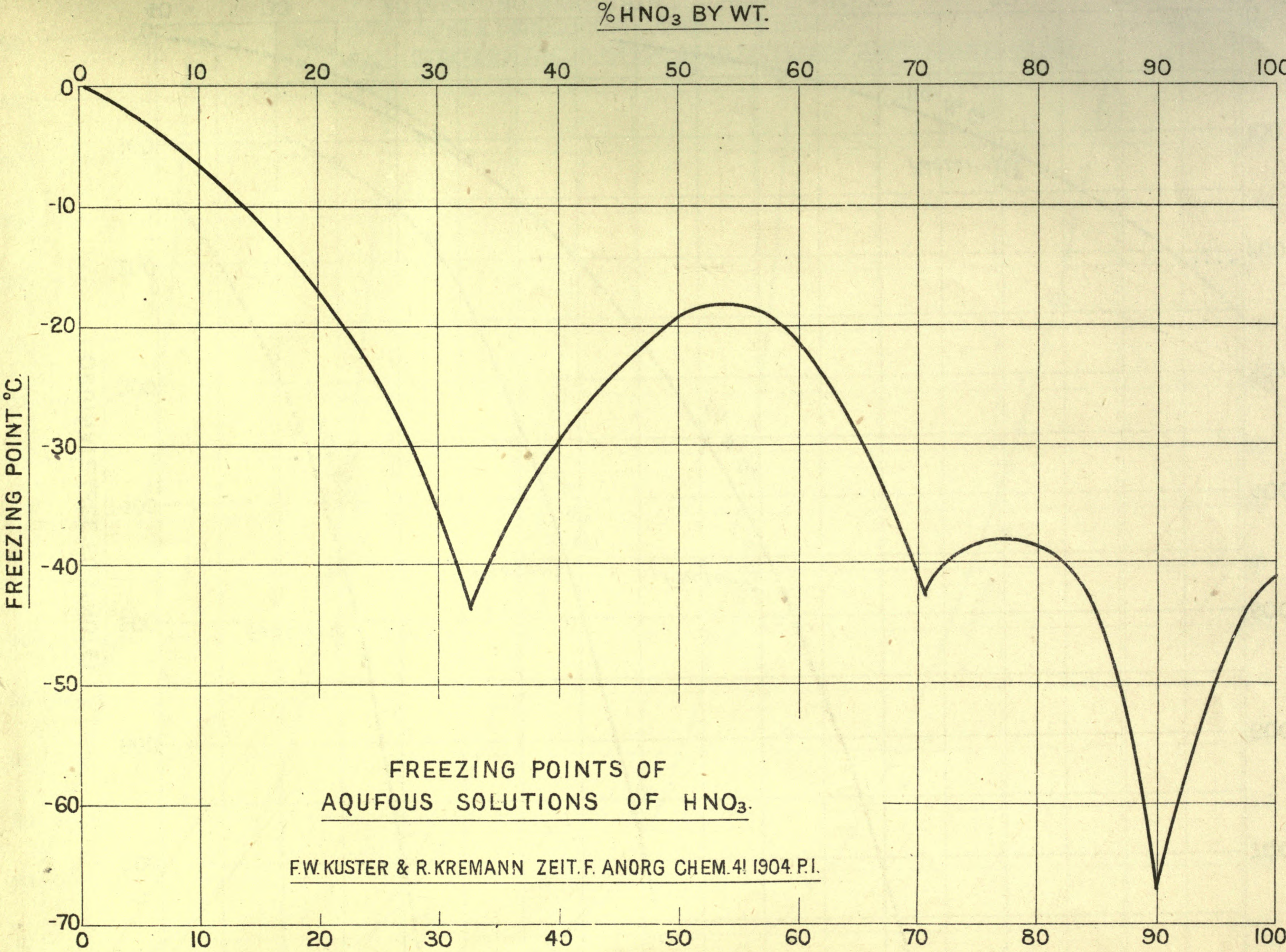
FIG. 24.



% HNO_3 REFERS TO H_2SO_4 FREE SOLUTION

9928

FIG. 25.



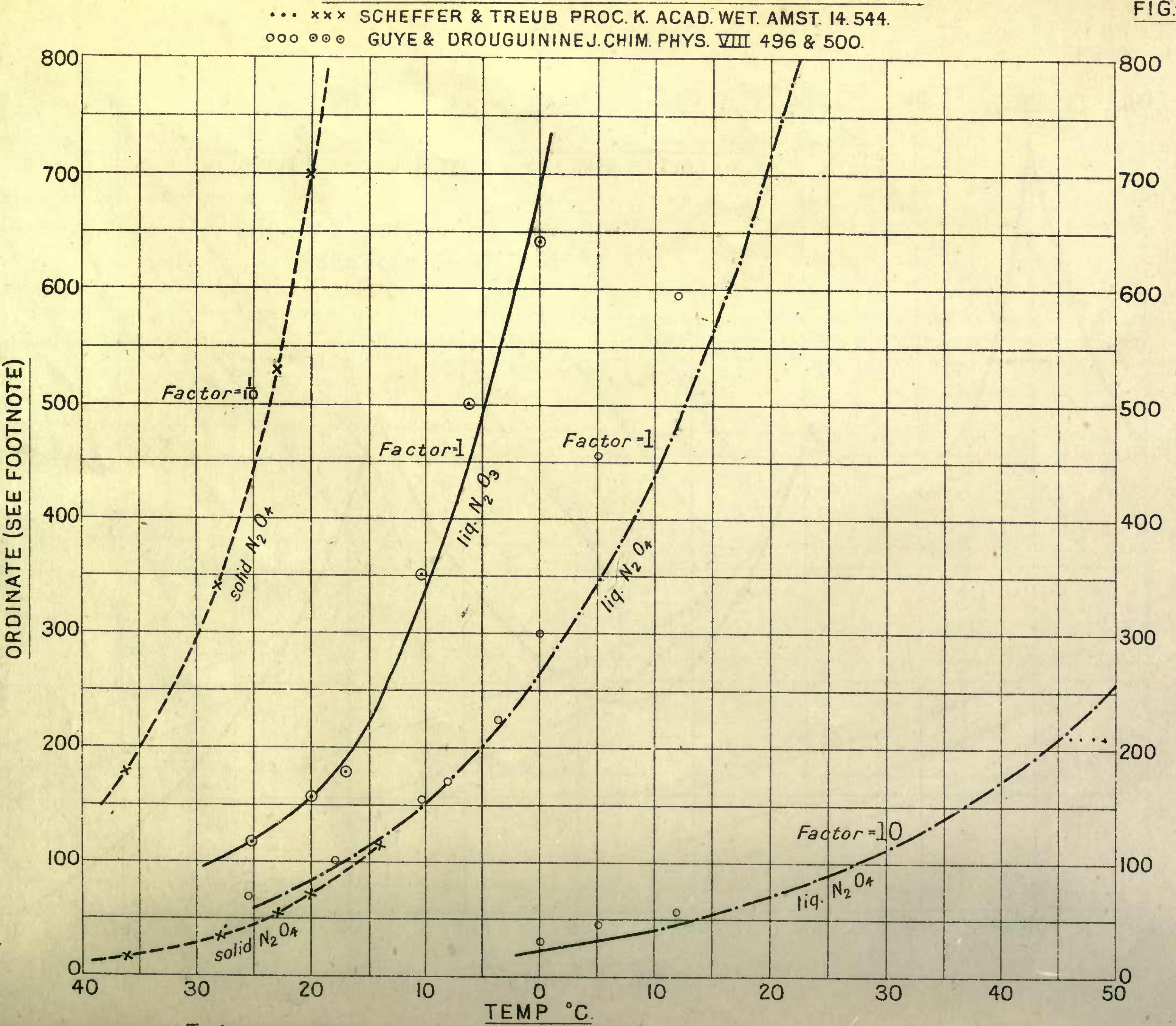
FREEZING POINTS OF AQUFOUS SOLUTIONS OF HNO_3.

F.W. KUSTER & R. KREMANN ZEIT. F. ANORG CHEM. 41 1904. P.1.

9928.

Malby & Sons. Lith.

FIG: 26.


••• ××× SCHEFFER & TREUB PROC. K. ACAD. WET. AMST. 14. 544.
ooo ⊙⊙⊙ GUYE & DROUGUININE J. CHIM. PHYS. VIII 496 & 500.
ORDINATE (SEE FOOTNOTE)
800
700
600
500
400
300
200
100
0
40
30
20
10
0
10
20
30
40
50
TEMP °C.
Factor = 1/10
solid N_2O_4
Factor 1
liq. N_2O_3
Factor = 1
liq. N_2O_4
Factor = 10
liq. N_2O_4
solid N_2O_4

VAPOUR PRESSURE OF SOLID N_2O_4

FIG. 27.

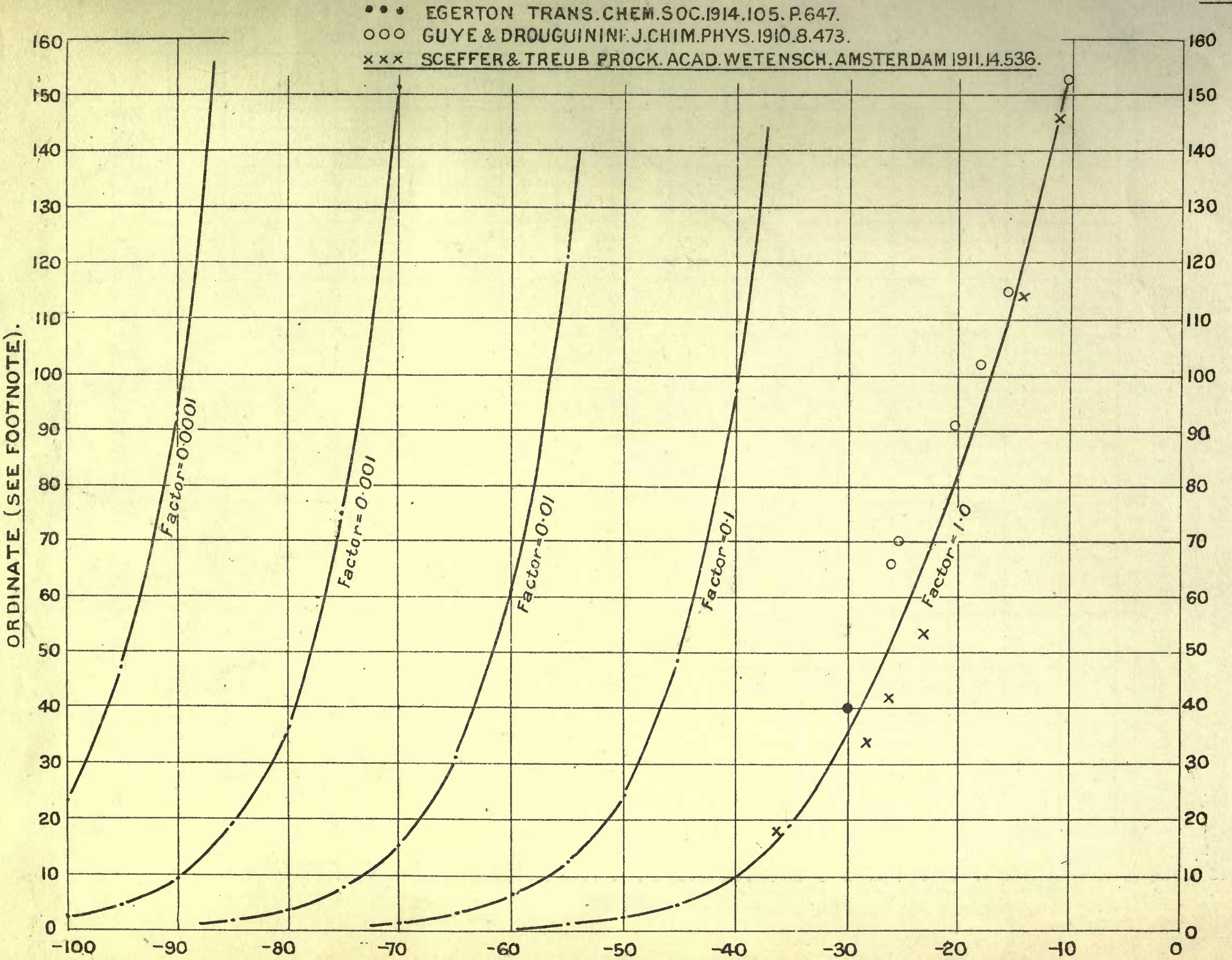
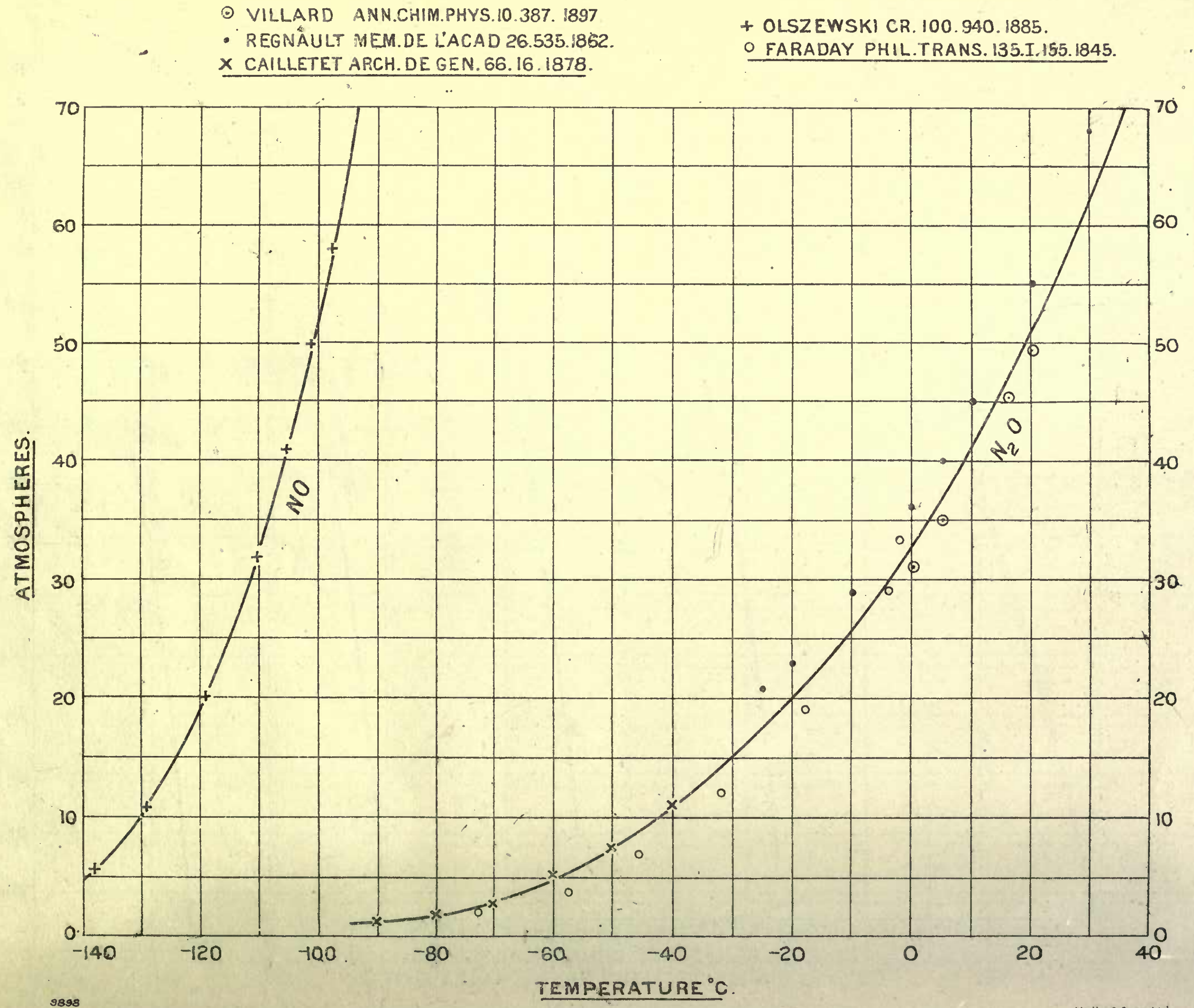


FIG. 28.



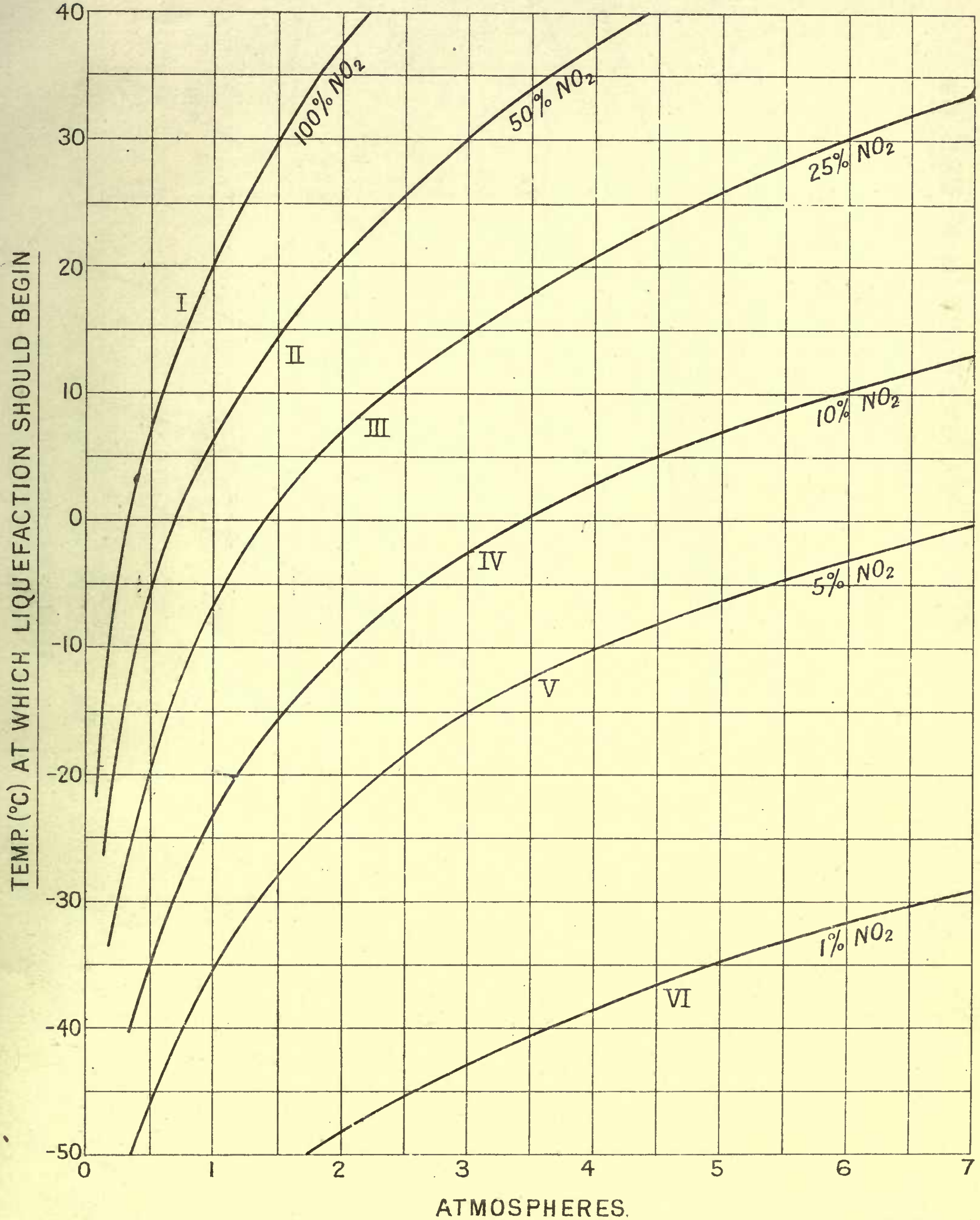
9898

Malby & Sons, Lith.

FIG. 29.

LIQUEFACTION OF NITROGEN PEROXIDE.

(IN THE PRESENCE OF GASES OF VERY LOW BOILING POINT)
FROM VAPOUR PRESSURE DATA THE % NO_2 (BY VOL).
PRESENT IN THE GAS IS SHOWN ON THE CURVES



9898.

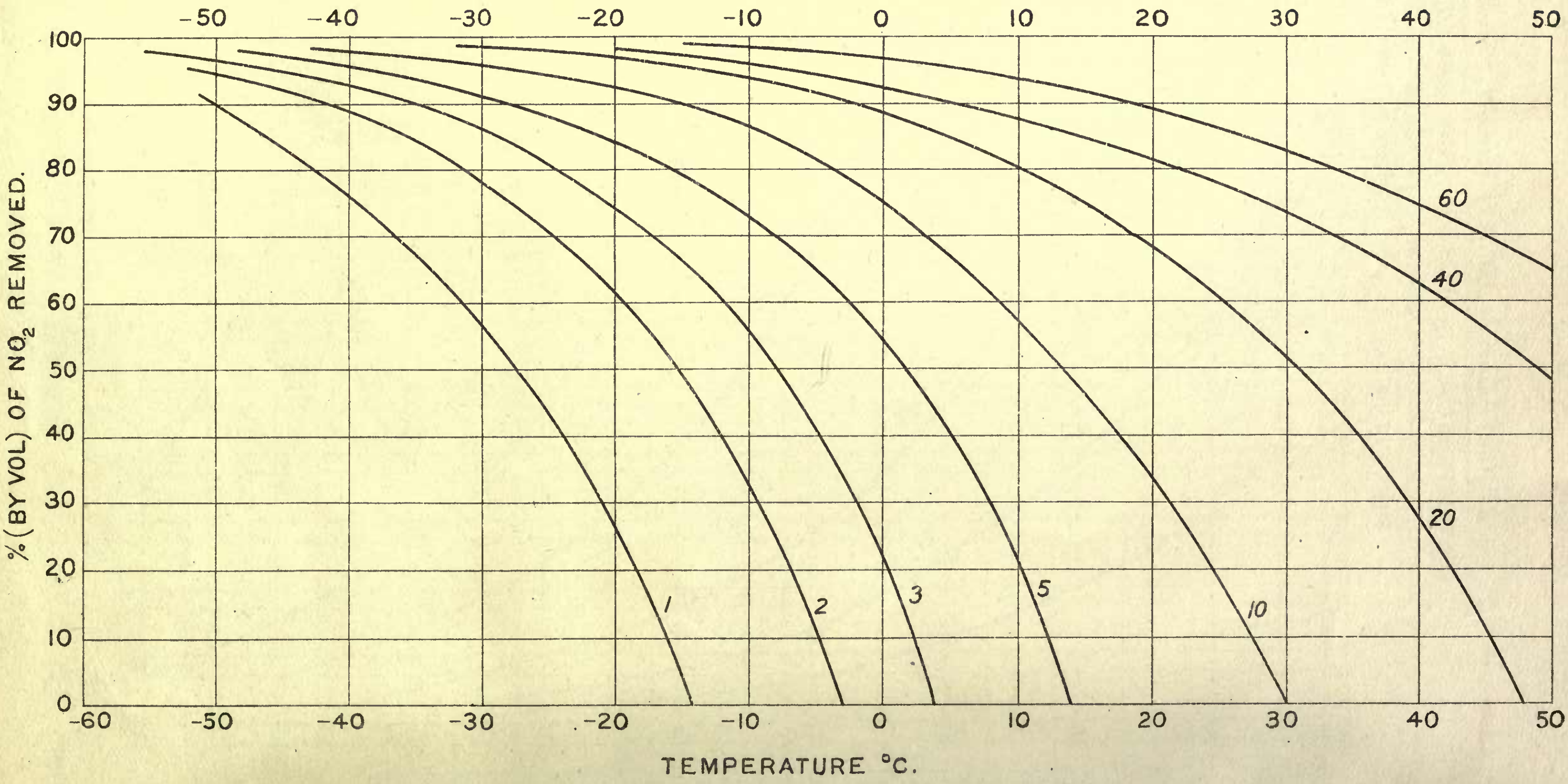
Malby & Sons. Lith.

FIG 30.

REMOVAL OF NO_2 FROM A 15% GASEOUS MIXTURE BY
COOLING AND PRESSURE.

(Calculated from Vapour Pressure data).

The numbers on the curves give the pressure in atmospheres



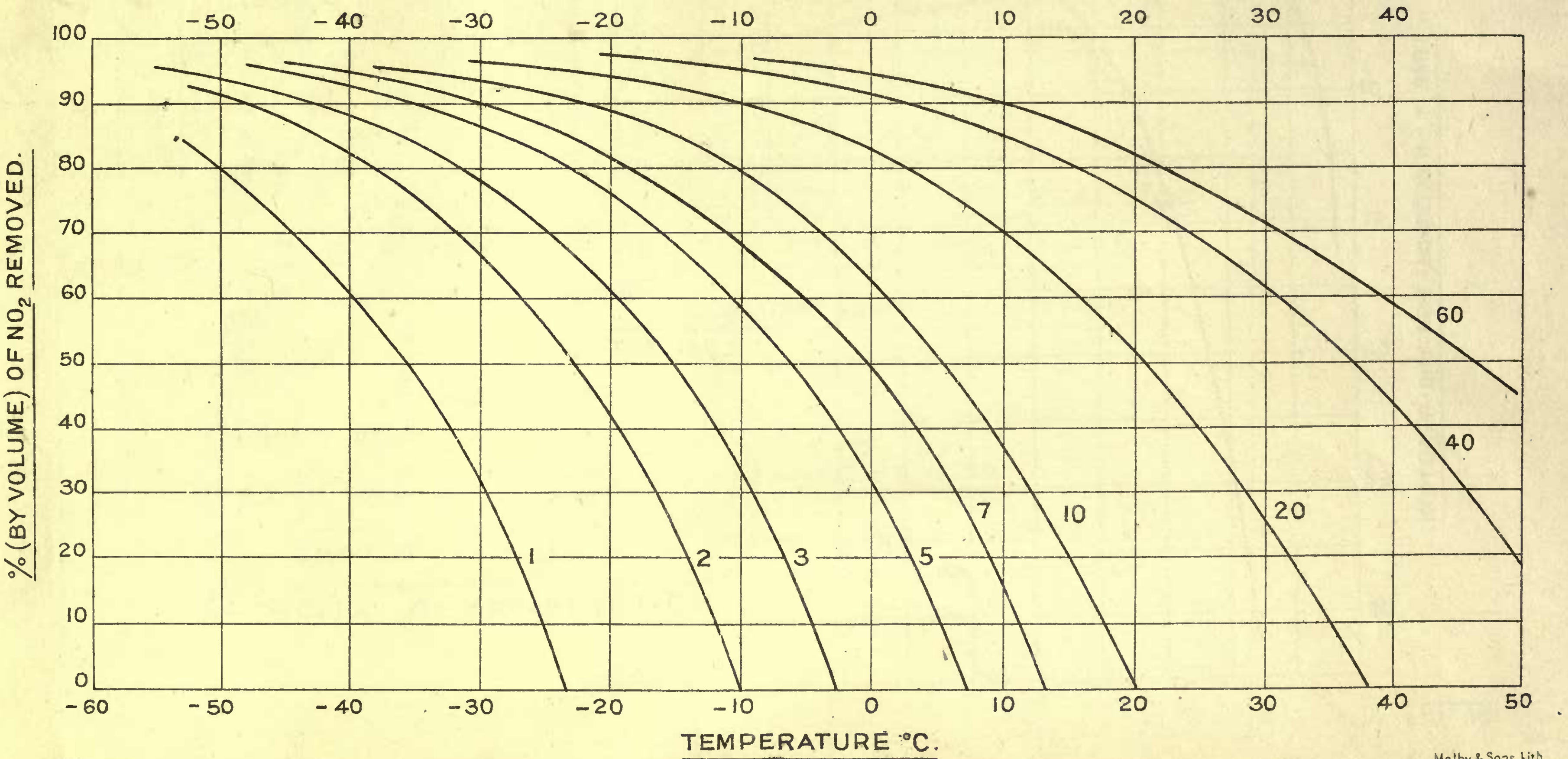
9898.

FIG. 31.

REMOVAL OF NO_2 FROM A 10% GASEOUS MIXTURE BY COOLING AND PRESSURE.

(CALCULATED FROM VAPOUR PRESSURE DATA.)

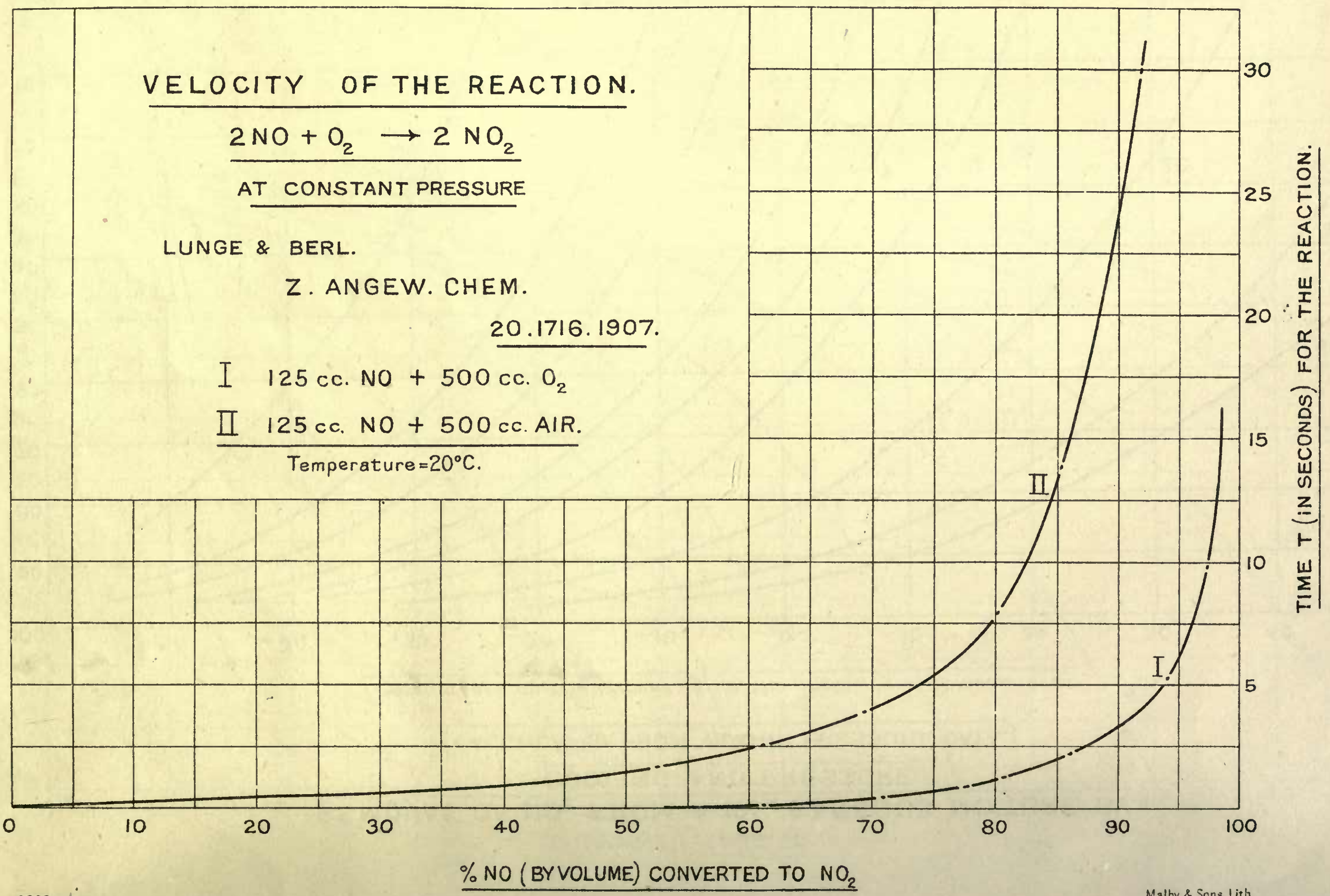
The numbers on the curves give the pressure in atmospheres.



9898.

Malby & Sons. Lith

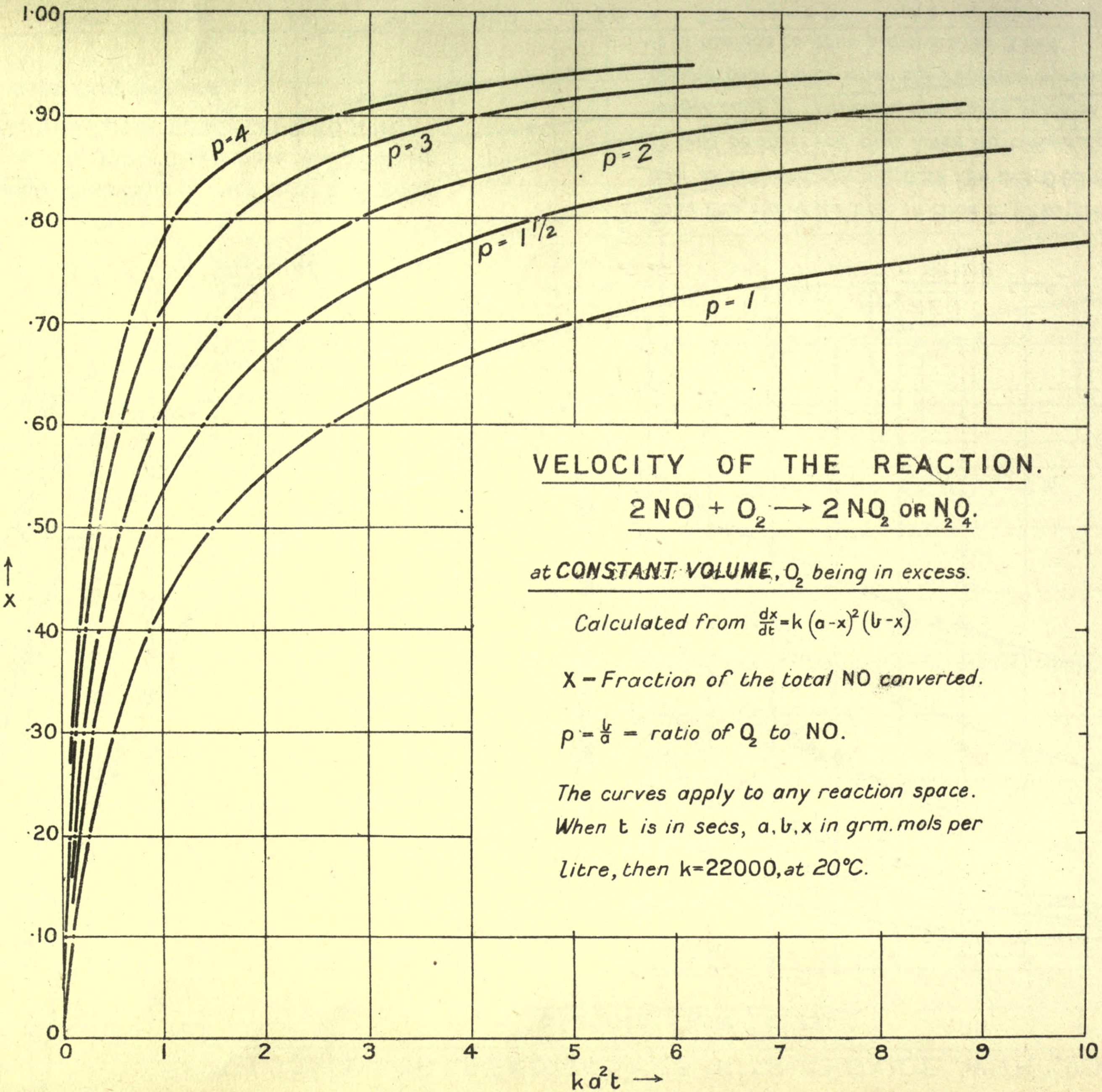
FIG. 32.



9898.

Malby & Sons. Lith.

FIG. 33.



VELOCITY OF THE REACTION.

$2NO + O_2 \longrightarrow 2NO_2$ OR N_2O_4.

at CONSTANT VOLUME, O_2 being in excess.

Calculated from $\frac{dx}{dt} = k(a-x)^2(b-x)$

X – Fraction of the total NO converted.

$p = \frac{b}{a}$ = ratio of O_2 to NO.

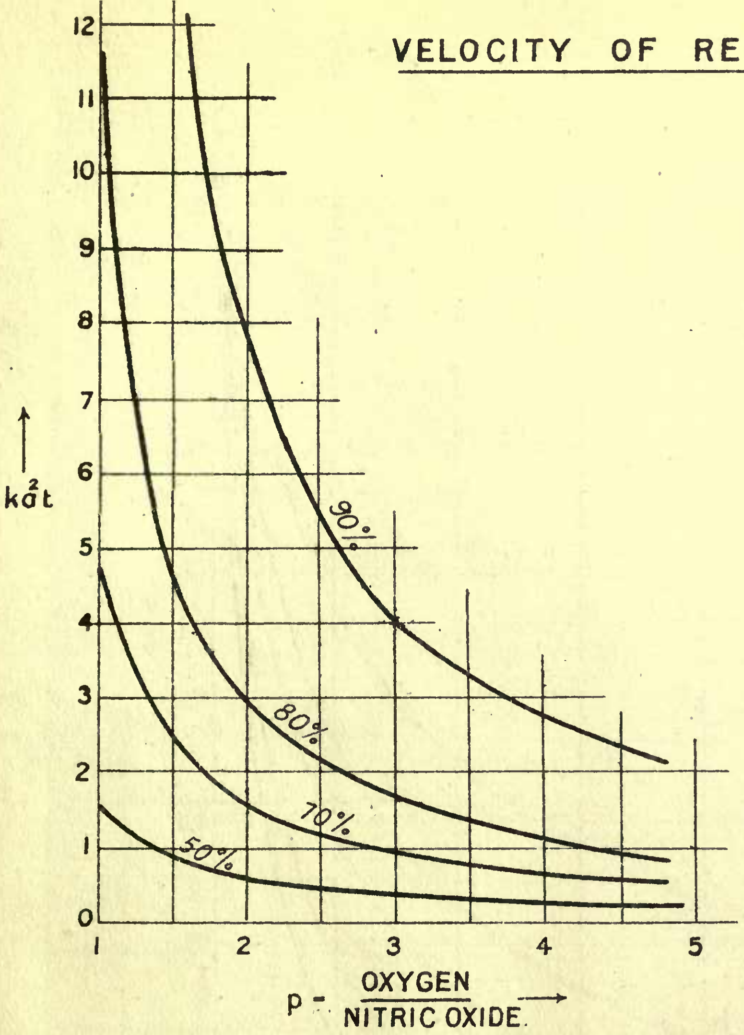
The curves apply to any reaction space. When t is in secs, a, b, x in grm. mols per litre, then k=22000, at 20°C.

Malby & Sons, Lith.

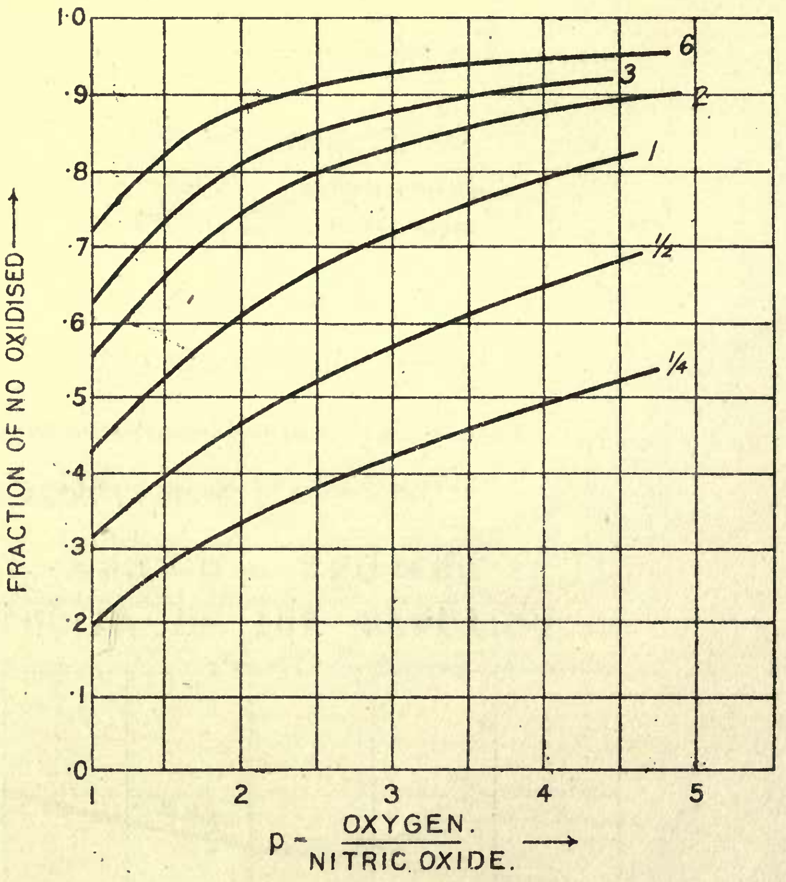
FIG. 34.

VELOCITY OF REACTION OF NITRIC OXIDE WITH OXYGEN.

DEDUCED FROM FIG. 33.



Example. Suppose $p = 3$ Then in the time given by $ka^2t = 4$, 90% NO will have been oxidised; in the time given by $ka^2t = 1{\cdot}7$, 80% NO will have been oxidised.

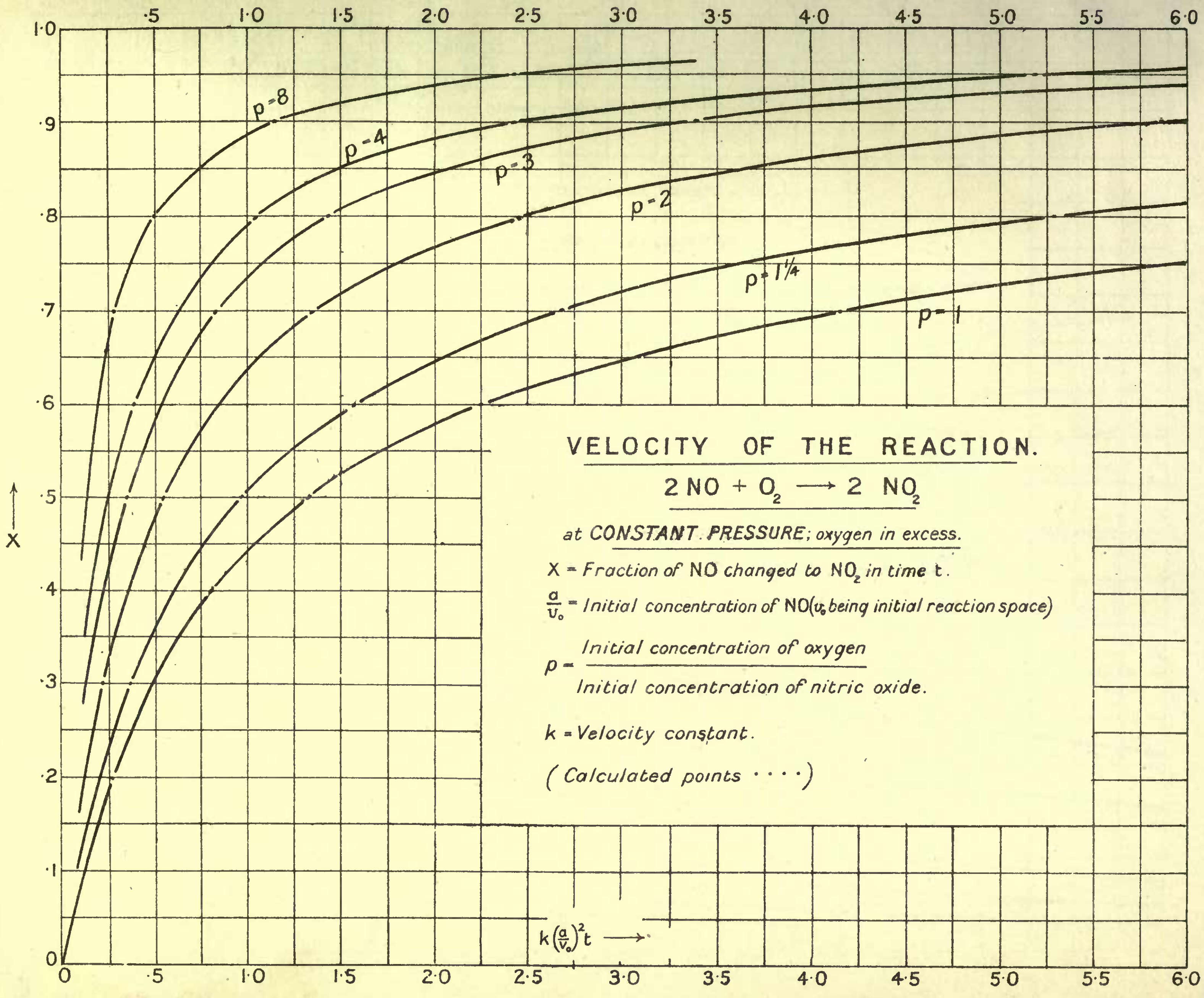


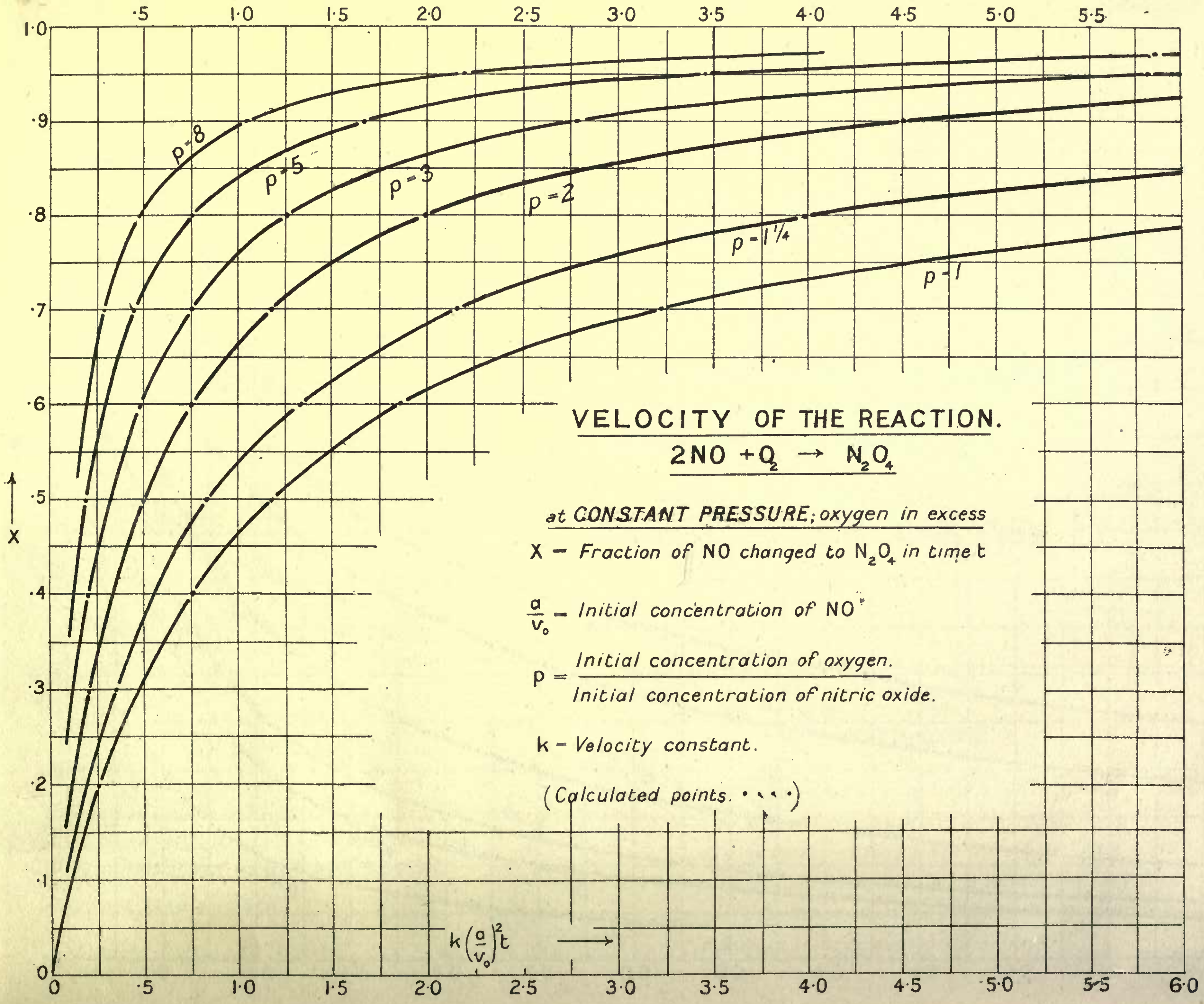
Take the curve $ka^2t = \frac{1}{2}$. In time $t = 1/2ka^2$; 0·46 of the NO will be oxidised for $p = 2$; 0·57 for $p = 3$; 0·65 for $p = 4$

It will be observed that when $ka^2t = 6$, ie, for a much longer time of reaction, the curve becomes very flat beyond $p = 3$. Hence when the reaction times are great it is useless to have p more than 3 or 4.

Malby & Sons. Lith.

FIG.35.


VELOCITY OF THE REACTION.
$2NO + O_2 \longrightarrow 2NO_2$
at CONSTANT PRESSURE; oxygen in excess.
X = Fraction of NO changed to NO_2 in time t.
$\frac{a}{v_0}$ = Initial concentration of NO (v_0 being initial reaction space)
$p = \frac{\text{Initial concentration of oxygen}}{\text{Initial concentration of nitric oxide.}}$
k = Velocity constant.
(Calculated points · · · ·)
p = 8
p = 4
p = 3
p = 2
p = 1¼
p = 1
X
$k\left(\frac{a}{v_0}\right)^2 t$
0
·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0
·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0
5·5
6·0



VELOCITY OF THE REACTION.

$2NO + O_2 \rightarrow N_2O_4$

at CONSTANT PRESSURE; oxygen in excess

X – Fraction of NO changed to N_2O_4 in time t

$\frac{a}{v_0}$ – *Initial concentration of NO*

$p = \frac{\text{Initial concentration of oxygen.}}{\text{Initial concentration of nitric oxide.}}$

k – Velocity constant.

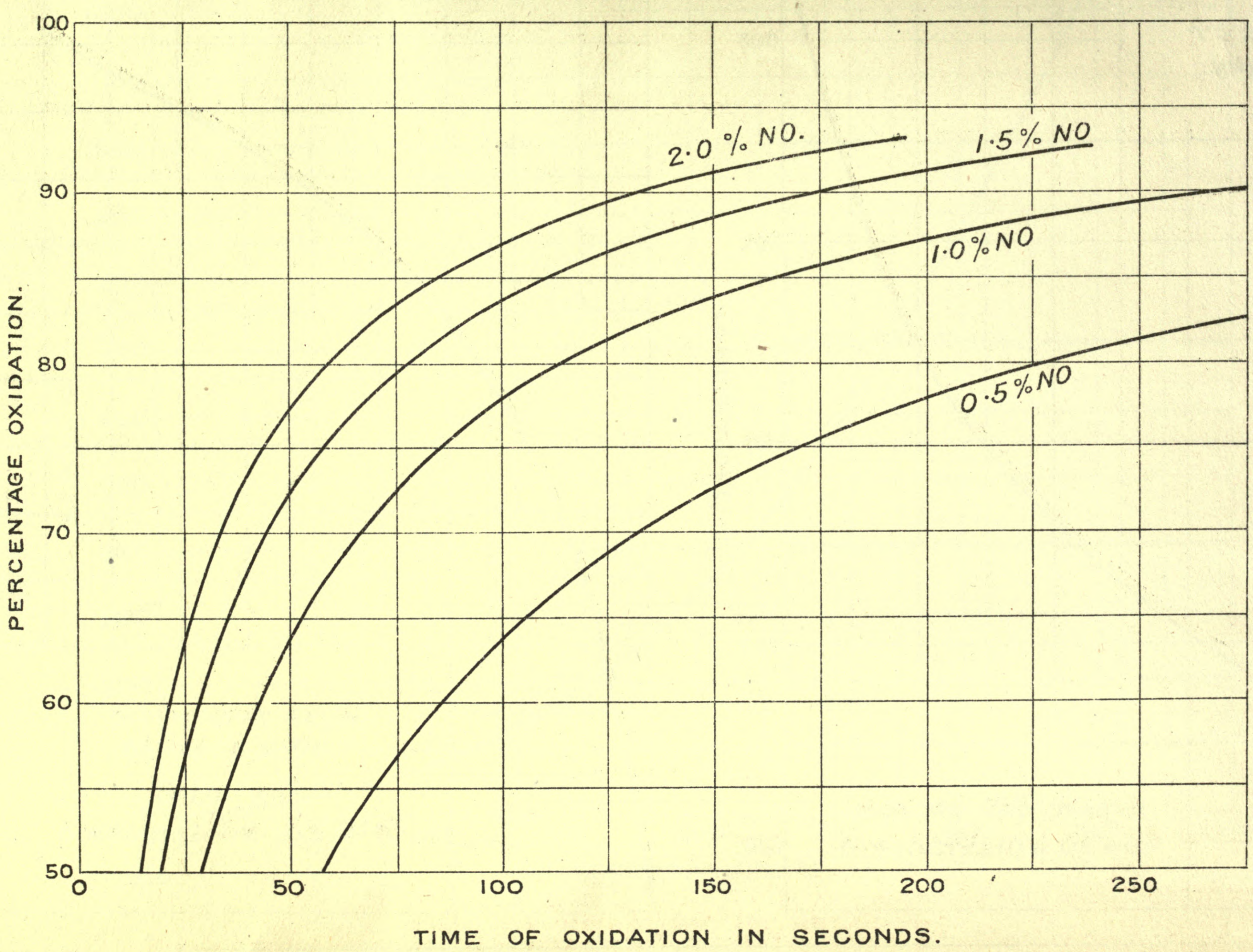
(Calculated points. • • • •)

Malby & Sons. Lith.

FIG. 37.

TIME OF OXIDATION OF NO TO NO_2 IN AIR MIXTURES CONTAINING A SMALL PERCENTAGE (BY VOL) OF NO.

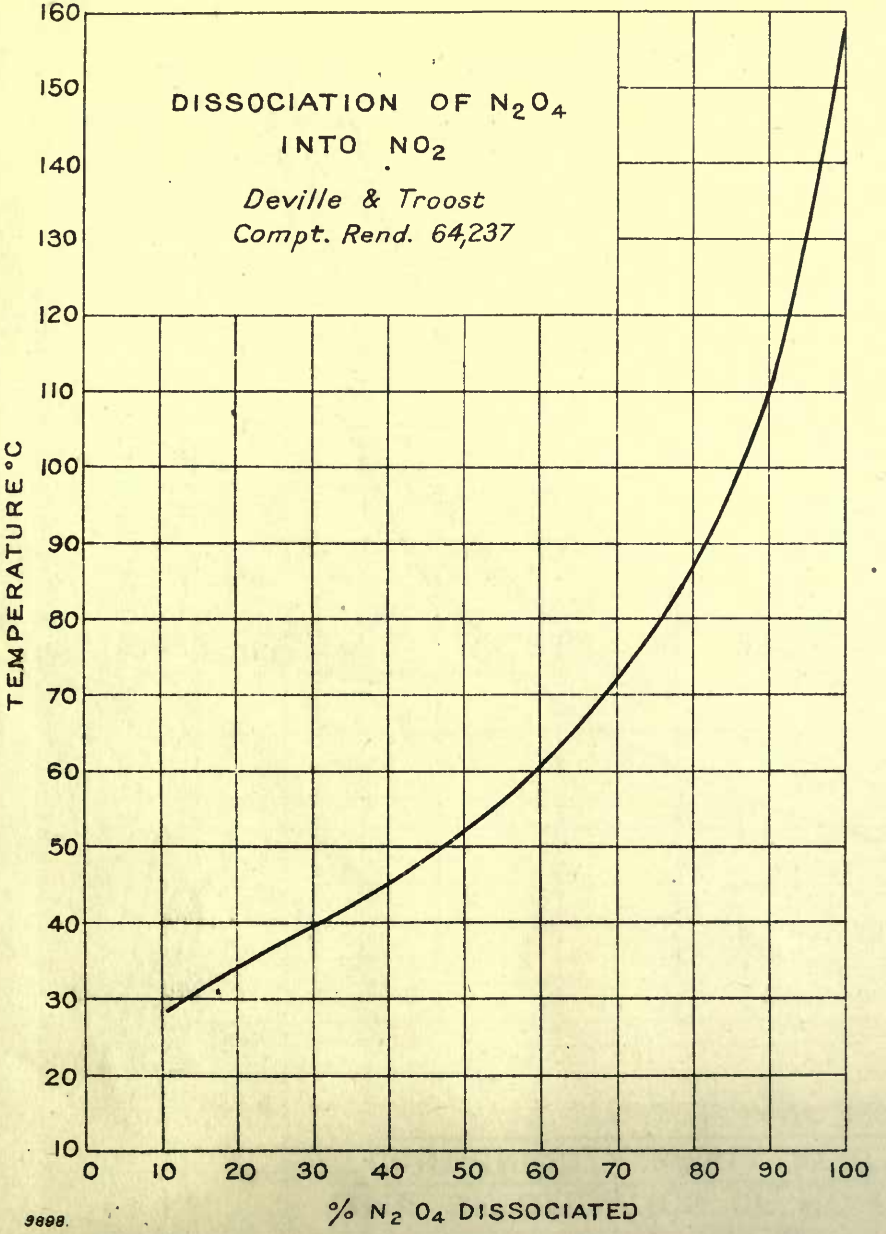
(Temperature of Reaction = 20° C.)

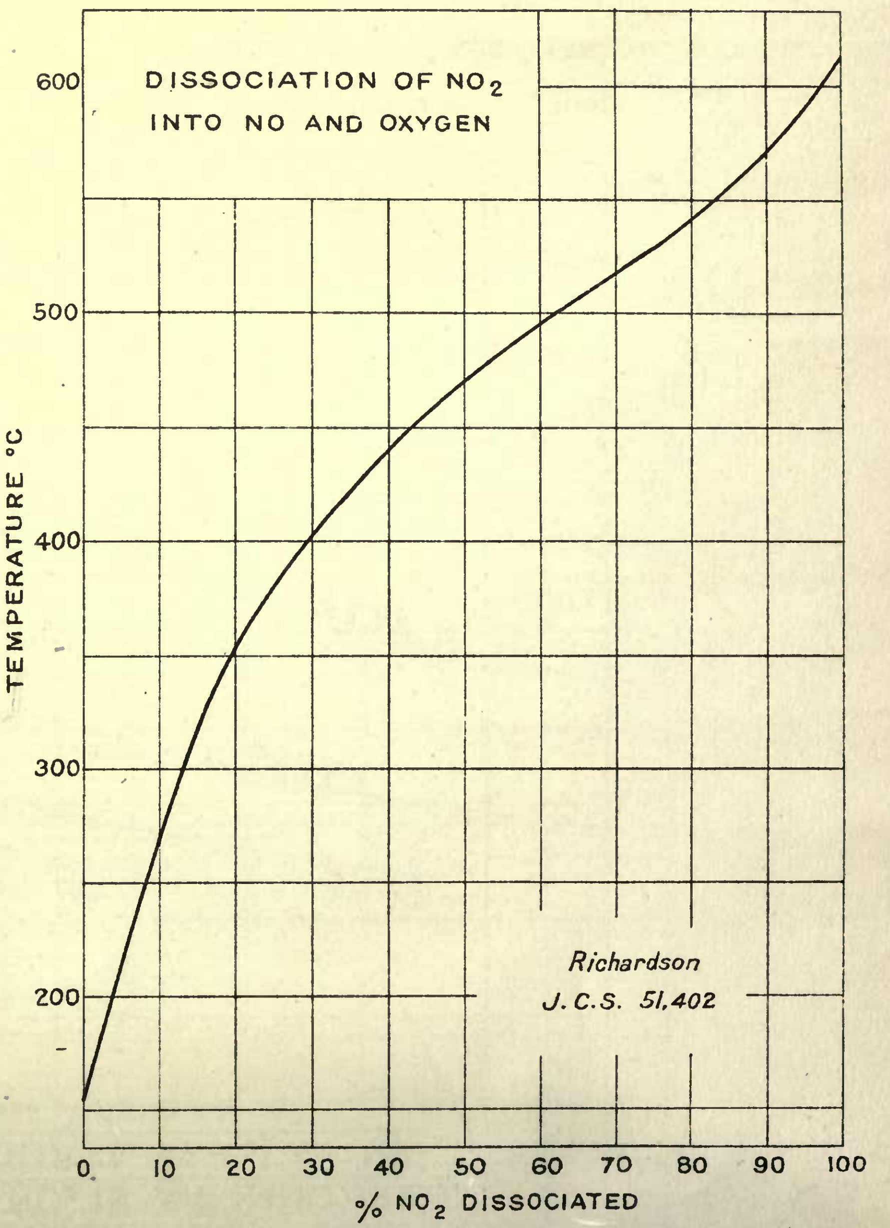


9898.

Malby & Sons. Lith.

DISSOCIATION OF NITRIC PEROXIDE (AT ONE ATMOSPHERE PRESSURE)



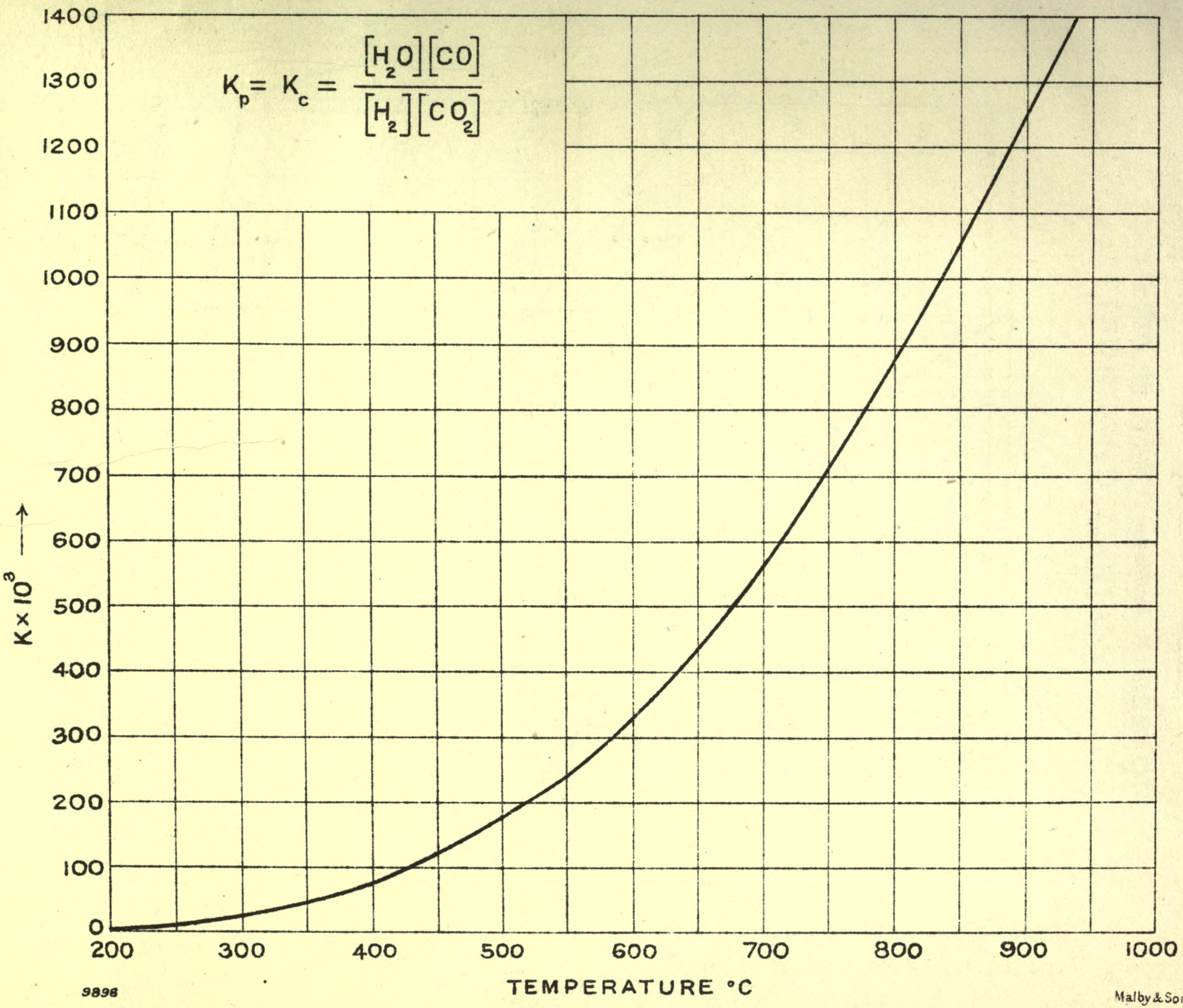


9888.

Malby & Sons. Lith

FIG. 39.

WATER-GAS EQUILIBRIUM.



9898

Malby & Sons. Lith.

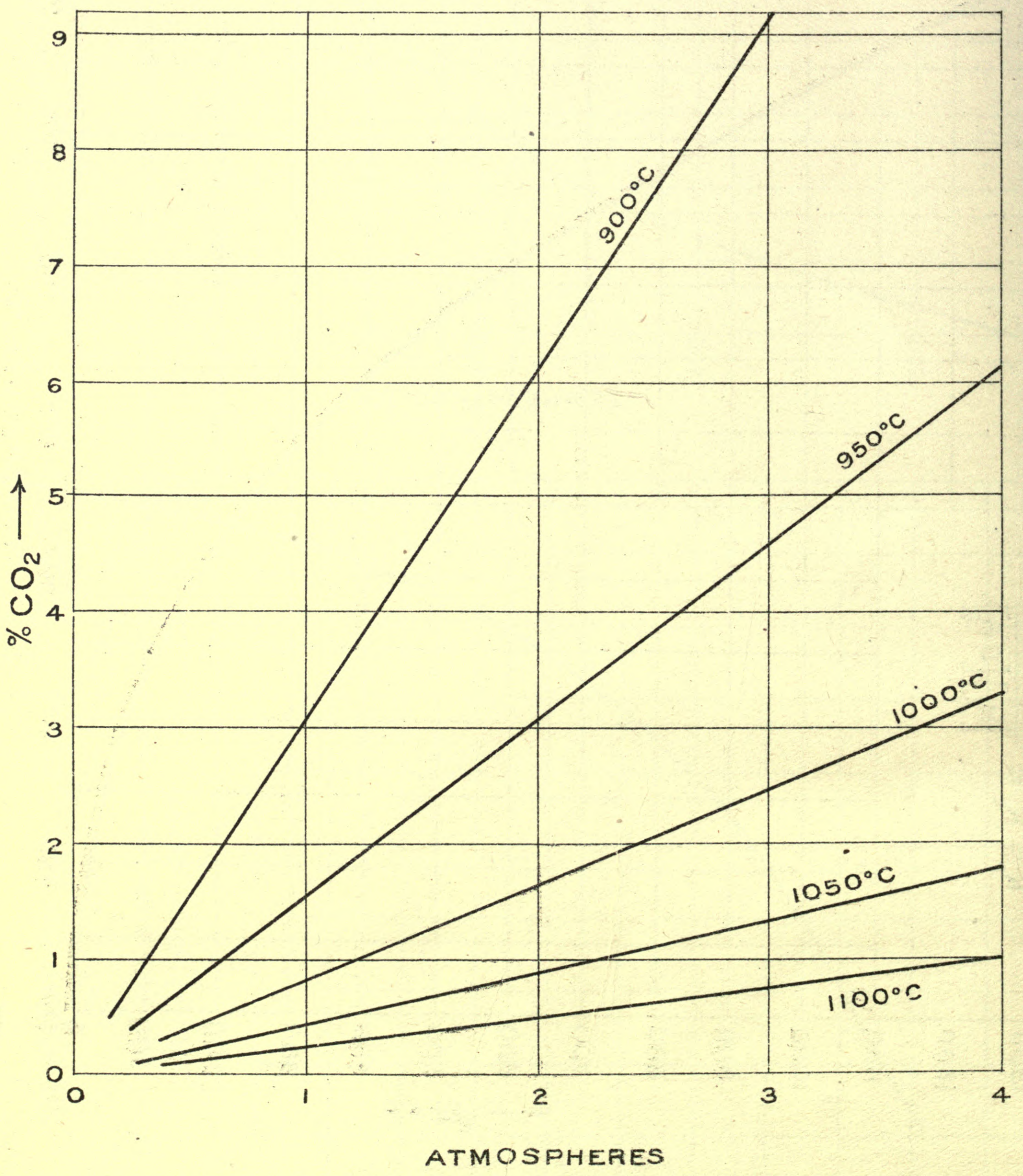
FIG. 40.

DISSOCIATION OF CARBON MONOXIDE

(at temperatures indicated)

$$2CO \rightleftharpoons CO_2 + C.$$

Rhead & Wheeler. J.C.S. 99. 1151.



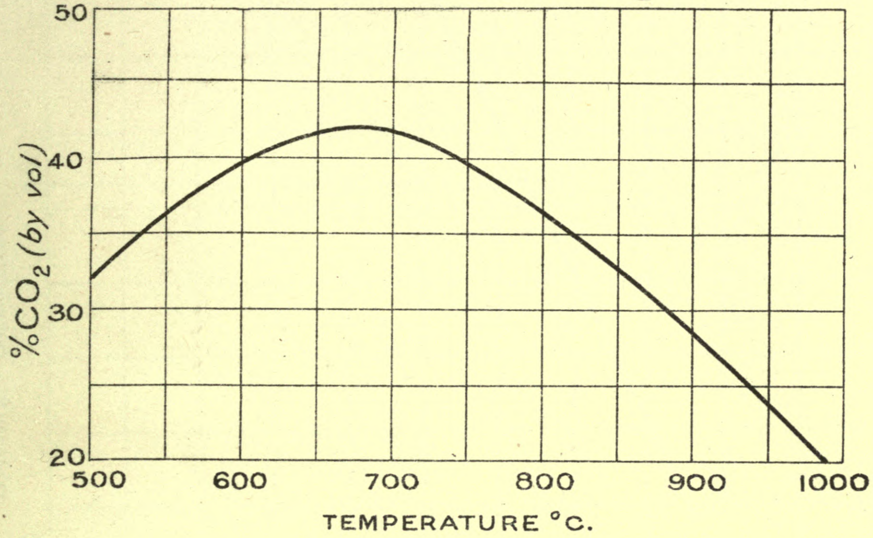
·9898.

Malby & Sons, Lith.

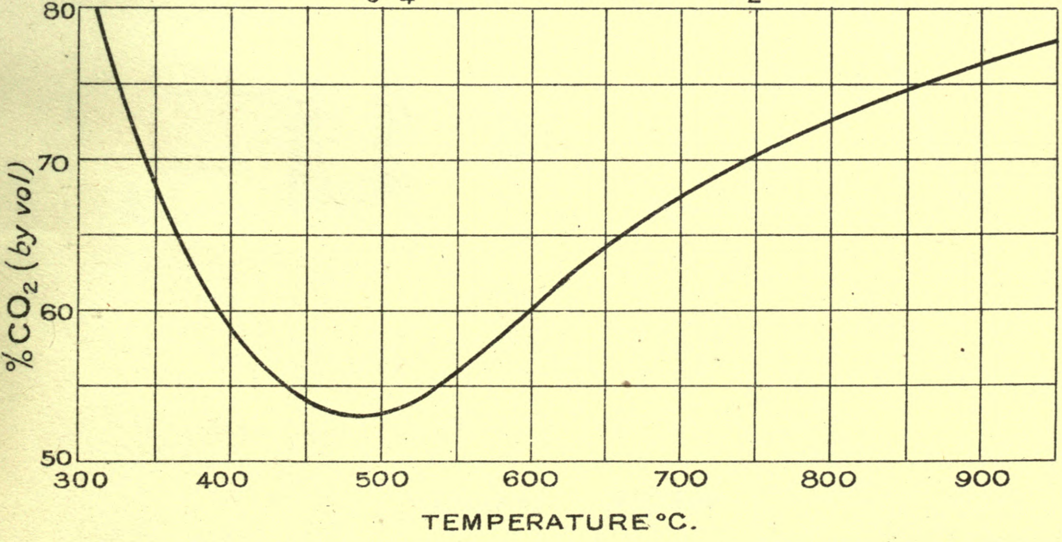
FIG. 41.

EQUILIBRIA BETWEEN OXIDES OF IRON AND CARBON.

$FeO + CO \rightleftharpoons Fe + CO_2$

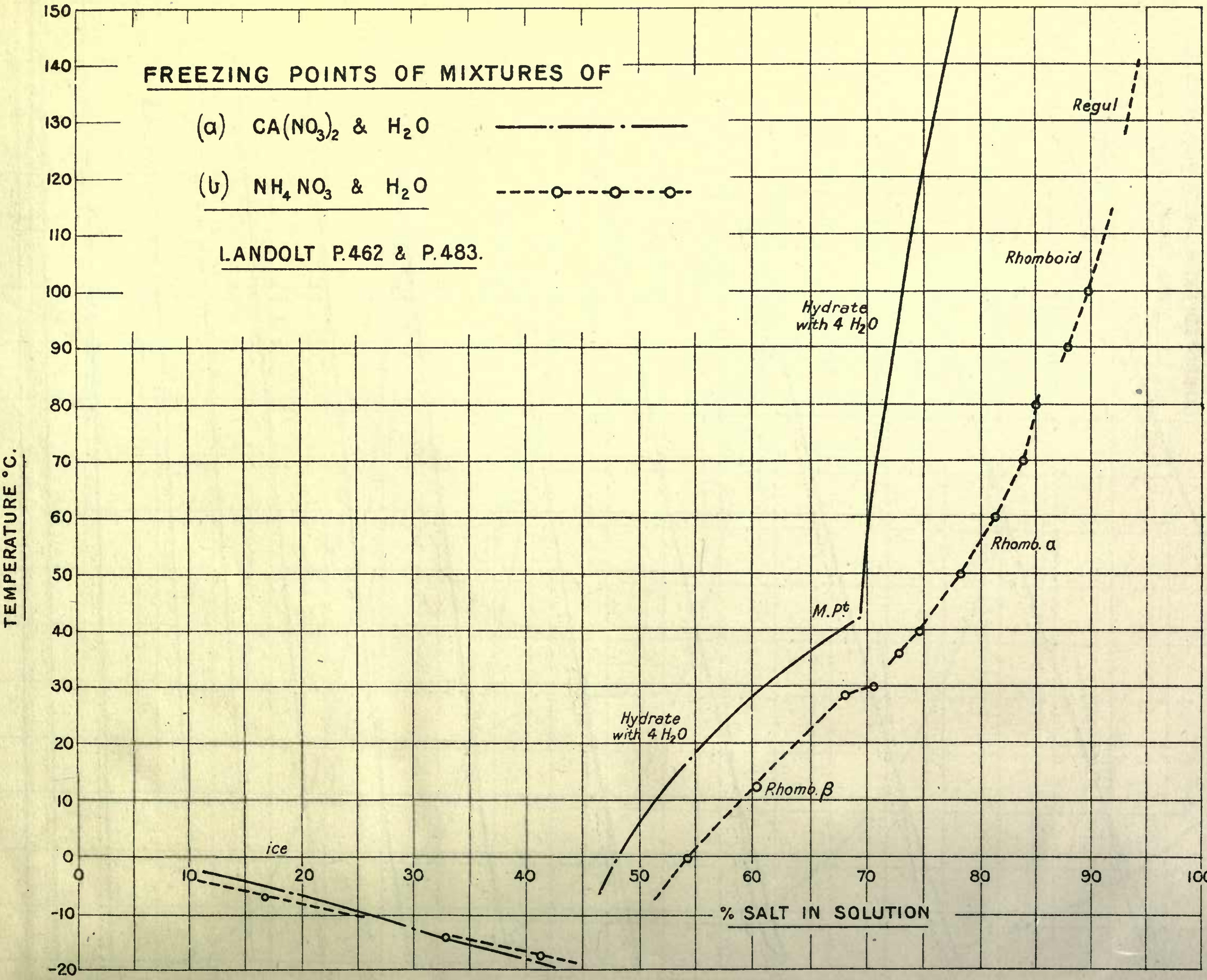


$Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2$



Malby & Sons, Lith.

9898.



FREEZING POINTS OF MIXTURES OF

9838.

Malby & Sons, Lith.