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The Effect of Pressure on Gas-Condensed Phase Equilibria.

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by T.J.Webster.

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The Thesis comprises the following papers, publications and patent applications for which the author has been solely responsible.

Paper 1.	Theoretical Aspects of the Effect of Pressure on Gas-Condensed Phase Equilibria. This paper has been accepted for presentation at the Symposium of the Faraday Society in April 1953.
Paper 2.	Continuation of Paper 1. Unpublished.
Paper 3.	The Effect on Water Vapour Pressure of Superimposed Air Pressure. J.S.C.I.1950,69, p.343.
Paper 4.(a)	The Effect of Indifferent Gases on the Vapour Pressure of Carbon-dioxide. Proc. Eighth International Congress of Refrigeration(1951)-~~in the press~~. p. 201
(b)	British Patent Application No. 24989/51.
Paper 5.	The Influence of Pressure on the Equilibrium between Carbon-dioxide and Air. Proc. Roy.Soc.-A.Vol.214, pp.61-71. Aug.7th1952.
Paper 6.	A New Type of Electrical Hygrometer. Unpublished. British Patent Application No.8180/51.

Theoretical Aspects of the Effect of Pressure on Gas-Condensed Phase Equilibria

by T.J. Webster.

Paper 1.	Pages 1 to 33.	(Being presented at the Symposium of the Faraday Society, April 1953).
Paper 2.	Pages 34 to 51.	

Theoretical Aspects of the Effect of Pressure on Gas - Condensed Phase Equilibria.

by T.J.Webster

Summary

The effect of pressure on the equilibrium between an inert gas anda liquid or solid phase is to increase the vapour pressure of the condensed phase above its normal value. The theoretical increase in the vapour pressure of the condensed phase can be calculated by Poynting's Thermodynamic Relation but the vapour pressure elevation predicted by this Relation is usually much less than that found by experiment.

The results of different workers who have studied the effect of pressure on the equilibria between water and the inert gases Helium, Hydrogen, Air,Nitrogen and Carbondioxide have been examined in detail and it has been shown that the vapour pressure increase obtained with a particular gas can be related to the concentration of dissolved gas in the water. The effect of a given concentration of dissolved gas in increasing the vapour pressure of the water is shown to ~~the~~ be practically independent of pressure or temperature; the activities of different gases are not the same however but decrease in the same order as the diameters of the gas molecules.

An empirical formula has been derived which enables the vapour pressure increase produced by an ideal gas to be predicted with considerable accuracy over a wide range of temperature and pressure from the result~~s~~ of a single experimental determination of the activity coefficient of the gas.

As it is difficult to reconcile a theory based on the solution of inert gas in the condensed phase, with the known behaviour of systems in which no liquid is present it is concluded that the factor of fundamental importance in determining the extent of vapour pressure elevation is the formation of a solution in the gas phase of molecules which would otherwise condense.

Introduction

The earliest observations of the increase in the volatility of a condensed phase in the presence of a compressed gas were made by Hannay and Hogarth (1880)$^{(1)}$ who examined the solvent properties of some fluids for non-volatile solids during the passage of the solvent through the critical point. It was shown by these workers that no precipitation of solid occurred when a solution consisting of potassium iodide dissolved in alcohol was heated in an enclosed tube to a temperature above the critical temperature of the solvent. It was observed that potassium iodide crystals were precipated from the gaseous alcohol only after the pressure developed due to the evaporation of the alcohol had been released. The experiment indicated clearly that a gas under certain conditions of temperature and pressure could cause the volatilisation of an otherwise involatile solid. In studying the system cobaltous-chloride alcohol Hannay and Hogarth showed that above its critical point the solution had essentially the same absorption spectrum as in the liquid state indicating the persistance of the normal ionic condition of the salt above the critical temperature of the solution. The concentration of cobaltous chloride in the supercritical phase was far higher than could be accounted for by the normal vapour pressure of the salt.

Altschul (1897) (2) investigated the influence of temperature on the solvent power of gases. He filled a strong glass tube with a solution of potassium iodide in alcohol and heated the tube to the critical temperature of the solvent. At this temperature the potassium iodide remained in solution but on heating the tube to a higher temperature deposition of solid was observed showing that the solvent power of gas is not independent of temperature and pressure and may in fact decrease as the gas is heated at constant volume.

Between 1903 and 1910 Centnerszwer (3)(4) made a systematic quantitative study of the critical points of solutions of different salts. These experiments demonstrated that the presence of dissolved salts normally causes a rise in the critical temperature of a liquid analogous to the rise in the normal boiling point, the extent of the increase being proportional to the concentration of the salt. The importance of critical phenomena in geological processes was pointed out by Niggli in 1912 (5).

Quantitative studies of the increase in the vapour pressure of liquids and solids have been carried out by many workers. Pollitzer and Strebel (6) determined experimentally the moisture content of air, hydrogen and carbon-dioxide in equilibrium with water at 50°C and 70°C at pressures upto 200 atmospheres. Bartlett (7) who was interested in the effect of inert gas pressure on vapour pressure in connection with the manufacture of synthetic ammonia determined the equilibrium moisture content of hydrogen, nitrogen and 3:1 H_2 - N_2 mixtures between 25 and 50°C at pressures upto 1000 atmospheres. The system water - nitrogen was studied experimentally at pressures upto 300 atmospheres by Saddington and Krase (8). The solubility of different compressed gases in water was examined by Wiebe, Gaddy and Heins (9). The water content of natural gas and helium under pressure has been measured by Deaton and Frost (10). The equilibrium molar concentration of carbondioxide in air compressed upto 50 atmospheres was measured by Gratch (1945) who showed that under certain conditions the vapour pressure of carbon-dioxide is increased by a factor of ten when the solid is subjected to inert gas pressure (11). An even more remarkable result was obtained by Diepen and Scheffer (12) in studying the solubility of naphthalene in supercritical ethylene. These workers showed that at 12°C and 100 atmospheres the naphthalene concentration in the ethylene gas is over 25,000 times as great as it would be if the naphthalene exerted its normal vapour pressure.

The theoretical aspects of the change in vapour pressure when a condensed phase is subjected to pressure by an indifferent gas have been considered by Poynting (13) who derived the following thermodynamic relation expressing the magnitude of the pressure effect $\left(\frac{dp}{dP}\right)_T = \frac{V_L}{V_G}$

in which p = vapour pressure of the liquid

P = total pressure on the liquid

V_G = molal volume of the vapour

V_L = molal volume of the liquid

The formula is known as the Poynting Relation after its discoverer. The increase in vapour pressure calculated by the formula is usually much less than that determined by actual experiment. This is due to the fact that the Poynting effect is never obtained alone and is usually obscured by a solubility effect.

Derivation of Poynting Equation

The Poynting formula was derived by considering the equilibrium between two phases of a pure substance. The condition for equilibrium in any process occurring at constant temperature and pressure is defined by the equation $dF = 0$ where F = the free energy. If $P_1V_1T_1$ and $P_2V_2T_2$ are the pressures, molal volumes and molal free energies of the two phases respectively at equilibrium at constant temperature then on increasing the pressure by an amount dP_1 in one phase there will be a corresponding change in pressure dP_2 in the other and it can be shown that

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$$dP_1 = \frac{dF_1}{V_1} \quad \text{and} \quad dP_2 = \frac{dF_2}{V_2}$$

But for equilibrium $dF_1 = dF_2$

$$\text{Therefore } \frac{dP_1}{dP_2} = \frac{V_2}{V_1}$$

$$\text{or } \left(\frac{dp}{dP}\right)_T = \frac{V_L}{V_G} \quad \text{or } \left(\frac{V_s}{V_G}\right)$$

where V_L V_G and V_s = molal volumes of liquid gas and solid respectively.

The theoretical derivation is based on the assumption that a semi-permeable membrane maintains the different pressures on the two phases. The only practical means, however, of increasing the total pressure on a condensed phase in equilibrium with its vapour is to introduce an inert gas into the system. As no real gas is entirely inert it is impossible in practice to devise a method for determining the Poynting effect alone, and for this reason a discrepancy is always found between experimental results and those calculated from the thermodynamic equation.

Theoretical increase in water vapour pressure with pressure

The effect of pressure in increasing the vapour pressure of water and ice is calculated as follows from the Poynting Relation. Assuming that the vapour conforms to the perfect gas laws (i.e. $V_G = \frac{RT}{P}$) and that the molal volume of the condensed phase is unaffected by pressure the Poynting equation can be integrated to give:-

$$\frac{p}{p_s} = \frac{Vc}{RT} \quad (P - p_s)$$

in which p is the vapour pressure of the condensed phase under pressure P and p_s is the saturation vapour pressure of the condensed phase (molal volume Vc) at temperature T in the absence of indifferent gas pressure. Factors $\left(\frac{p}{p_s}\right)$ showing the relative increase in the vapour pressure of the condensed phase have been evaluated for ice and water at different temperatures and pressures; these are given in Table 1 in comparison with the practical values shown in brackets obtained from the smooth curves in Figure 4 (14) .

TABLE I

Factors $\left(\frac{p}{p_s}\right)$ calculated from Poynting Relation

Temperature oC	-35	-20	0	15	50
Pressure atmospheres gauge		Factor $\left(\frac{p}{p_s}\right)$			
50	1.05 (1.59)*	1.04(1.38)	1.04(1.25)	1.04(1.20)	1.03(1.14)
100	1.10 (2.16)	1.10(1.76)	1.08(1.50)	1.08(1.39)	1.07(1.28)
150	1.14 (2.75)	1.14(2.15)	1.13(1.75)	1.12(1.58)	1.11(1.42)
200	1.20 (3.33)	1.19(2.53)	1.17(2.00)	1.16(1.77)	1.14(1.56)

* Values in brackets have been obtained from smoothed experimental data (14)

It can be seen from the above results that the experimental factor $\left(\frac{p}{p_s}\right)$ is greater at any particular temperature and pressure than the calculated factor. In addition to the Poynting effect there is clearly another effect contributing to the total vapour pressure increase. This can be expressed mathematically as follows:-

$$p = p_s + p_p + p_x \qquad \textcircled{1}$$

in which p = the actual vapour pressure of the condensed phase at pressure P.

p_s = the normal saturation vapour pressure of the condensed phase at temperature T.

p_p = vapour pressure increase of the condensed phase due to the Poynting effect at temperature T and pressure P.

p_x = vapour pressure increase at temperature T and pressure P additional to that caused by the Poynting Effect.

From this equation it follows that

$$\frac{p}{p_s} = \left(\frac{p_s + p_p}{p_s}\right) + \frac{p_x}{p_s}$$

But $\frac{p_s + p_p}{p_s} = F_p$ where F_p is the calculated Poynting Factor.

$\therefore \; F_A - F_p = \frac{p_x}{p_s}$ where F_A is the actual Factor determined by experiment.

or $F_A - F_p = F_x$ (2) where F_x is a factor showing the relative V.P. increase caused by effects other than the Poynting Effect.

Numerical values of F_x for the system air-water at 0°, 15° and 50°C have been calculated for different pressures upto 200 atmospheres using the factors F_A and F_p given in Table 1. These are shown in Table 2.

TABLE 2

Calculated Factors (F_x) for system air-water

Temperature °C	0	15	50
Pressure atmospheres gauge	F_x ($= F_A - F_p$)		
50	.21	.16	.11
100	.42	.31	.21
150	.62	.46	.31
200	.83	.61	.42

It can be seen that the factor (F_x) varies linearly with pressure; this must of course happen as the factors F_A and F_p each vary linearly with pressure.

Correlation between Inert Gas Solubility and the Vapour Pressure Factor (F_x)

Attention has already been drawn to the fact that no real gas can be regarded as being completely inert when it is employed to increase to a relatively high value the external pressure on a liquid or a solid. The gas penetrates the condensed phase and would therefore be expected to alter the normal forces of molecular attraction within the phase thus affecting the vapour pressure of the condensed substance. In the case of a liquid the extent of the inert gas penetration will depend on the solubility of the inert gas and the increase in the vapour pressure of the liquid in the presence of the compressed inert gas would be expected to be related in some way to the gas solubility. In the case of water and air such a relationship can be shown to exist. This can be seen from the values given in Table 3 in which the solubilities at normal pressure of air in water at the temperatures 0, 15 and 50°C are compared with the factors (F_x) for the system air-water at the same temperatures and at different pressures upto 200 atmospheres. The factors (F_x) at 0, 15 and 50°C have been designated Fx0, Fx15 and Fx50 in Table 3. The following data on the solubility of air in water was obtained from the International Critical Tables (15).

Solubility at 0°C = 232×10^{-7} mols air/mol of solution (S0)
" at 15°C = 165×10^{-7} -ditto- (S15)
" at 50°C = 106×10^{-7} -ditto- (S50)

TABLE 3

Ratio of factors (Fx) and solubilities (S)

Pressure atmospheres (absolute)	Factors (Fx)			Ratio of Factors (Fx) and solubilities at 0° and 15°C		Ratio of Factors (Fx) and solubilities at 0° and ~~15°C~~ 50°C		Ratio of Factors (Fx) and solubilities at 15° and 50°C	
	Fx0	Fx15	Fx50	$\frac{Fx0}{Fx15}$	$\frac{S0}{S15}$	$\frac{Fx0}{Fx50}$	$\frac{S0}{S50}$	$\frac{Fx15}{Fx50}$	$\frac{S15}{S50}$
1.0	-	-	-	-	1.4	-	2.19	-	1.56
51.0	.21	.16	.11	1.31		1.91		1.45	
101.0	.42	.31	.21	1.35		2.00		1.48	
151.0	.62	.46	.31	1.35		2.00		1.48	
201.0	.83	.61	.42	1.36		1.98		1.45	

The above values show clearly that the ratio of the factors (Fx) at two different temperatures remain practically constant with increasing pressure and is in remarkably close numerical agreement with the ratio of the gas solubilities at the same temperatures and at atmospheric pressure. As it is indicated by the results that $Fx0 : Fx15 : Fx50 = S0 : S15 : S50$ we can express the results by the general equation

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$Fx = K.S$ where K is constant at a given pressure.

We know however that for the system air-water Fx varies linearly with pressure also that the actual solubility of the gas (SA) varies linearly with pressure if Henry's Law is obeyed (i.e. $SA = P.S$) therefore assuming that the air behaves ideally we can write:-

$$Fx = K.P.S. \quad ③$$

in which Fx = vapour pressure factor due to dissolved gas at pressure P and at temperature T

S = solubility of the gas in the liquid at atmospheric pressure and temperature

K = a constant which is independent of temperature and pressure.

Equation ③ implies that the factor (Fx) at any temperature and pressure is fixed by the molar concentration of air in the liquid and by a constant K which measures the activity of the air in elevating the vapour pressure of water. If this equation were shown to be true it would mean that in the case of a system obeying Henry's Law we could calculate from solubility data at atmospheric pressure values of Fx at any temperature ~~or~~ and pressure, having carried out a single experiment to determine the numerical value of K. The overall vapour pressure factors (FA) could then be calculated from equation ②.

For a system not obeying Henry's Law but in which the factor (Fx) is proportional to the actual solubility of the gas (SA) equation ③ becomes:-

$Fx = K.SA$ ④ where SA = the molar concentration of gas in the liquid.

Substituting ④ in equation ② we obtain

$$F_A - F_p = K.\ S_A \quad ⑤$$

If equations ④ and ⑤ were true they would enable the factors Fx and F_A to be calculated for any temperature and pressure at which the gas solubility was known after the numerical value of K had been determined by a single experiment.

To illustrate how closely equation ③ applies in the case of a system which does not deviate widely from Henry's Law, K values at different temperatures and pressures have been calculated for the system Air-Water using the known Fx values for the system and published data on the solubility of air in water at normal pressure (15). These are shown in Table 4.

TABLE 4

K values for system air-water based on solubility of air in water at 1 atmosphere

Temperature oC	Solubility at 1 atmosphere mols air/mol solution $S \times 10^7$	Pressure P atmospheres (absolute)	Fx (see Table 3)	$K = \frac{Fx}{P.S.}$
0	232	51	.21	178
15	165	51	.16	190
50	106	51	.11	204
0	232	101	.42	179
15	165	101	.31	186
50	106	101	.21	196
0	232	151	.62	177
15	165	151	.46	185
50	106	151	.31	193
0	232	201	.83	178
15	165	201	.61	184
50	106	201	.42	197

Considering the range of temperature and pressure over which they were determined the K values are in remarkably close agreement and lend considerable support to view that dissolved air is responsible for the vapour pressure increase represented by the factor (Fx). Although the results show that the numerical value of K tends to increase with increasing temperature they are nevertheless sufficiently consistent to enable the factors (Fx) and (F_A) to be calculated with reasonable accuracy for different temperatures and pressures from any particular value of K.

For instance K = 178 at 0°C and 51 atma

Using this K value to calculate the total vapour pressure factor for the system Air-Water at 201 atma and 50°C we have

$$F_A - F_p = Fx = K.P.S. \quad ② \ \& \ ③$$

$$F_A - 1.14 = 178 \times 201 \times 106 \times 10^{-7}$$

$$= .38$$

$$\therefore \quad F_A = 1.52$$

The experimental value (see Table 1) = 1.56

The fact that overall vapour pressure factors can be calculated over a wide range of pressure and temperature in this way does not necessarily mean that the ability of a given concentration of gas to increase the vapour pressure of the solvent is completely unaffected by changes of temperature or pressure. It indicates, however, that any effect of temperature or pressure on the activity of the gas is small compared with that of the concentration change accompanying the variation in temperature and pressure.

The manner in which the activity of the dissolved gas is affected by pressure and temperature can however be deduced by examining in detail the values given in Table 4. In deriving these values it was assumed that the system Air-Water obeys Henry's Law but at the high pressure for which the values were calculated this assumption is not fully justified and to obtain real K values we must consider the effect on the system of deviations from ideal behaviour. If Henry's Law is not obeyed the concentration of air in the water at a given pressure will be less than the ideal value, which means that the real K value will be greater than the ideal K value at a given pressure. Now, in general, deviations from Henry's Law increase with increasing concentration of gas in the liquid phase i.e. with increasing pressure and with reduction in temperature. It is therefore reasonable to assume that the difference between the actual and ideal K values will increase with increasing pressure and as the temperature falls. Thus whereas the ideal K values at a given temperature (Table 4) are seen to remain practically constant with increasing pressure K values based on actual solubility data would increase with increasing pressure at a particular temperature, the extent of the increase depending on the deviation of the system from Henry's Law. This suggests that the vapour pressure increase caused by a given concentration of air in water increases as the air pressure is raised. An increase in the attractive forces between the molecules in the gas phase might of course account for this effect but it is more probable that the effect is due to conditions existing in the liquid phase.

The results in Table 4 show that the ideal K value at a fixed pressure increases slightly as the temperature is raised. The corrections for the deviations from Henry's Law will, however, be greater the lower the temperature thus the actual K values at different temperatures will either be more nearly equal numerically than the ideal values or will decrease with increasing temperature. As the system under consideration does not deviate greatly from Henry's Law it is doubtful if the latter effect would be obtained; it is more probable that the actual K values increase slightly with increasing temperature. This suggests that the activity of the dissolved gas increases slightly as the temperature is raised. Normally such an effect would be completely masked in practice by the much greater effect of temperature on the gas concentration in the liquid.

It appears from these considerations that dissolved gas is capable of increasing the vapour pressure of the solvent by an amount which would account for the discrepancy between the actual and the ideal vapour pressure elevation which is usually found when a gas-liquid system is subjected to pressure. The influence of the dissolved gas is proportional to its concentration in the solvent and is practically independent of temperature or pressure although there is some evidence of a slight increase in the activity of the gas with increasing temperature and pressure.

Real K values for the System Air-Water

Reliable data on the solubility of N_2 in water at high pressure is available in the literature and we can use this information to calculate the true solubility of air in water at high pressure if it is assumed that the systems air-water, nitrogen-water deviate similarly from Henry's Law at a given temperature and pressure. The experimental values for the solubility of N_2 in water at 50°C and at different pressures which were obtained by Wiebe, Gaddy and Heins (9) are compared in Table 5 with ideal values calculated from the solubility of N_2 in water a t 50°C and at atmospheric pressure (16) . A column has been included in the table showing the percentage deviation of the system N_2 - water from ideal behaviour at different pressures.

TABLE 5

Comparison of real and ideal values for the solubility of N_2 in water at 50°C and at different pressures.

Pressure (atmospheres absolute)	Solubility of N_2 in water $S_A \times 10^6$ mols N_2/mol solution		% Deviation from Ideal Behaviour
	Experimental (9)	Ideal (16)	
? 1.0	–	8.85	–
51.0	429	451	4.9
101.0	810	895	9.5
201.0	1475	1780	17.1

If it is assumed that the systems Air-Water, Nitrogen-Water deviate similarly from Henry's Law we can estimate the real solubility of air at different pressures by applying the above corrections to the ideal solubility values for air. This has been done and the results are tabulated below.

TABLE 6

Real values for solubility of air in water at 50°C

Pressure (atmospheres absolute)	Solubility of air in water assuming that Henry's Law is obeyed mols air/mol solution $S_A \times 10^6$	% Deviation from Ideal Behaviour (see Table 5)	Real solubility of air in water $S_A \times 10^6$ mols air/mol sol^n
1.0	10.6	-	
51.0	541	4.9	514
101.0	1070	9.5	967
201.0	2130	17.1	1766

Real values of K for the system air-water have been evaluated from the data on the actual solubility of air in water and are shown in Table 7.

TABLE 7

Real K values for the system air-water at 50°C

P atm (gauge)	Factor (Fx) (see Table 4)	Solubility of air in water (Table 6) SA x 10^6 mols air/ mol solution	K $\left(= \frac{Fx}{S_A} \right)$
50	.11	514	214
100	.21	967	218
200	.42	1766	238

These results indicate the true effect of pressure on the K values for air; an attempt to derive any relationship between the K value and pressure on the basis of the results would not however be justified.

The results confirm that K values based on the true solubility of air in water increase slightly with increasing pressure.

By a method of calculation similar to that employed in deriving the results in Table 7, K values have been estimated for air at 25°C from published data on the solubility of N_2 in water at this temperature(9). The K values obtained are shown in Table 8 in comparison with the values for 50°C.

TABLE 8

Real K values for the system Air-Water at 25° and 50°C

P (atmospheres gauge)	$K \left(= \frac{Fx}{S_A} \right)$	
	25.0°C	50°C
50	174	214
100	204	218
200	230	238

The results show that the K values at a given pressure increase as the temperature is raised indicating that the activity of the dissolved gas increases slightly with increasing temperature. In practice any increased activity of the gas with temperature elevation is completely masked by the reduction in gas solubility with the result that the vapour pressure factor (Fx) decreases as the temperature is raised.

K values for the system Nitrogen-Water

K values for the system Nitrogen-Water have been calculated from the smoothed experimental vapour pressure data of Bartlett (7) and Saddington and Krase (8). These are shown in Table 9 below.

TABLE 9

K values for system Nitrogen-Water at 50°C based on experimental data for solubility of Nitrogen in water(9)

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Pressure (atm)	F_p	F_A		$F_x (= F_A - F_p)$			$K\left(=\frac{F_x}{S_A}\right)$		K Averag
		Bartlett	Sadd. & Krase	Bartlett	Sadd & Krase	Solubility $S_A \times 10^6$ mols N_2/ mol Soln	Bart-lett	S&K S&K	
50	1.03	1.15	1.21	.12	.18	429	280	420	350
100	1.07	1.29	1.43	.22	.36	810	272	445	358
200	1.14	1.55	1.81	.41	.67	1470	279	455	367
300	1.22	1.77	2.29	.55	1.07	2040	269	525	397

The experimental factors obtained by Bartlett are consistently lower than those obtained by Saddington and Krase thus the K values calculated from the two sources are not in numerical agreement. As air contains 79% Nitrogen the behaviour of the system Nitrogen-Water would not be expected to differ greatly from that of the system air-water. We should therefore expect the K values for N_2 to increase slightly with increasing pressure. It can be seen that the K values calculated from Bartlett's data become lower with increasing pressure and that those calculated from the data of Saddington and Krase show a relatively sharp increase with increasing pressure particularly between 200-300 ats. Now any inaccuracy inherent in a particular experimental method of determining vapour pressure factors usually becomes accentuated as the pressure is raised and it would appear therefore that Bartlett's results are low and those of Saddington and Krase are high, the deviation from reality being in each case greater at the higher pressures. If this is so then K values obtained by averaging the results from the two sources should give a more accurate picture of the influence of pressure on the K values than the K values from either source. Average K values assessed in this way are shown in Table 9. These conform with the values obtained for the system Air-Water in showing that K increases slightly with increasing pressure. It is interesting to note that the numerical value of K is greater in the case of N_2 than for air. This indicates that the activity of dissolved N_2 is greater than that of dissolved air. If we assume that the average K values shown in Table 9 represent the true values for the system N_2-water it follows that there is remarkably little change in K value with pressure up to 300 atmospheres. This means that factors F_A for N_2 could be calculated with considerable accuracy at pressures up to 300 atmospheres from the equation

$$F_A - F_p = K\ S_A$$

using the K value derived from a single experiment carried out at some intermediate pressure.

K Value and Inert Gas Composition

Consideration of the systems Air-Water and Air-Nitrogen has shown that there is a marked correlation between the vapour pressure increase of the water and the gas solubility. To establish whether or not the solubility effect is independent of the composition of the inert gas it is necessary to determine K values for systems in which water is subjected to pressure by different inert gases. Fortunately this can be done for the effect of pressure on the equilibria between water and the gases Helium, Hydrogen, Nitrogen, CO_2 and Air has been studied by different workers. Although the published results display many discrepancies they are consistent in showing that the vapour pressure increase of water in the presence of these gases rise~~d~~s in the order of He, H_2, Air, N_2 and CO_2. The overall vapour pressure factors (F_A) obtained with these gases at 50°C and at 50 atmospheres pressure are shown in Table 10 in comparison with the solubilities of the gases at 50°C and at atmospheric pressure.

TABLE 10

Factors (F_A) for different gases at 50°C and 50 atmospheres.

Gas	F_A	Solubility in water at 50°C and 1 atm. $S \times 10^7$ mols gas/mol solution
He	1.0 [x~~x~~]	73 (20)
H_2	1.04 [xx]	131 (16)
Air	1.14	106
N_2	1.15	88.5
CO_2	2.20 [xxx]	3540

Assuming that at 50 atmospheres the gases are soluble in the same order as at 1 atmosphere it follows from the values tabulated above that there is no fundamental relation between the activities and solubilities of different gases. Clearly it is not only solubility which determines the vapour pressure

[x] Deaton and Frost at 40 atmospheres
[xx] Bartlett
[xxx] Pollitzer and Strebel

elevation produced by a particular gas but also the activity of the gas, which according to the data given in Table 10 varies with the nature of the gas. It is not surprising to find that activity varies with the nature of the gas for if as has been supposed dissolved gas is responsible for increasing the vapour pressure of the liquid we should expect the magnitude of the vapour pressure increase to depend not only on the concentration of the gas but also on certain fundamental properties of the gas and liquid. The size of the gas molecule in relation to the space available for molecular motion within the liquid is a factor which would be expected to influence the activity and it can in fact be shown that a relationship exists between the size of the gas molecules and activity.

K value and size of Inert Gas Molecule

It has been shown that the K values for the systems Air-Water and N_2-Water change little with variation in temperature or pressure. This indicates that the numerical value of K is determined chiefly by some property of the gas which is unaffected by temperature or pressure, and suggests that the K value may be a function of the size of the gas molecules. We can examine this possibility by comparing the K values for different gases with the diameters of the gas molecules. This has been done using vapour pressure factors and solubilities for the gases He, H_2, Air, N_2 and

CO_2 and the results are shown in Table II.

TABLE II

K values for different gases at 50°C and 50 atmospheres pressure

Gas	F_A	Fp	Fx	Solubility at 50°C and 50 ats $S_A \times 10^6$ mols gas/ mol solution	$K\left(= \frac{Fx}{S_A} \right)$	Molecular Dia (18) cms x 10^8
He	1.0	1.03	–	354^{x}	< 1.7	1.9
H_2	1.04	1.03	.01	605 (9)	1.7	2.4
Air	1.14	1.03	.11	514	214	3.1
N_2	1.15	1.03	.12	429 (9)	280	3.15
CO_2	2.20	1.03	.17	14000	12	3.34

x Calculated from solubility at 1 atmosphere assuming 4.9% deviation from Henry's Law at 50 ats.

In general the results show that the K values for the different gases vary in the same order as the diameters of the gas molecules, CO_2 being the only gas to display exceptional behaviour. The low K value for CO_2 in relation to the diameter of the CO_2 molecule can be explained by the fact that this gas is not inert but actually combines chemically with the water. This will have the effect of reducing the vapour pressure increase to a value lower than would be obtained if CO_2 were entirely inert towards water, and the K value for the gas will therefore be abnormally low. The results in Table II support the view that the size of the molecule is an important factor in determining the vapour pressure increase due to dissolved gas.

Unfortunately the results must be looked upon as providing a qualitative rather than a quantitative picture of the relation between molecular dimension and vapour pressure increase for although the experimental values of different workers are consistent in placing the activities of the gases in the order shown in Table II there are many instances when the actual experimental values are in considerable disagreement.

Discussion

A detailed examination has been made of experimental results obtained by several workers who have studied the effect of pressure on the equilibrium between water and the inert gases Air, H_2, He, N_2 and CO_2 and it has been shown that each of these gases with the exception of Helium increases the V.P. of water by an amount which is greater than would be expected theoretically. It has been shown that the difference between the actual and the theoretical V.P. increase when a particular system is under pressure is directly related to the concentration of gas in the condensed phase. This suggests that in addition to the vapour pressure increase due to the Poynting effect there is further vapour pressure increase for which dissolved gas is responsible, the magnitude of the latter increase varying linearly with the concentration of the dissolved gas. It has been shown that the activity of the dissolved gas varies with the nature of the gas but is little affected by change of either temperature or pressure; an increase in either of these variables has the effect of slightly increasing the activity. The activities of different gases decrease in the order of decreasing gas molecule diameters.

The following empirical equation has been derived relating the actual vapour pressure increase obtained when a liquid is in the presence of inert gas under pressure and the solubility of the gas in the liquid

$$F_A - F_p = K. S_A$$

in which

F_A is the relative increase in V.P. of the liquid

F_p is the " " " " of the liquid due to the Poynting effect.

S_A is the molar concentration of the gas in the liquid

K is a constant determined by the activity of the gas in solution.

For the system Air-Water at temperatures from 0°C to 50°C and at pressures up to 200 atmospheres and for the system N_2 - water at 50°C and at pressures up to 300 ats this equation gives values of F_A which are in close agreement with published data. The published data for the system H_2 - water is insufficiently consistent to justify any attempt to determine accurately the activity coefficient K for this gas although it will clearly have a value numerically lower than that for Air or N_2. The workers Deaton and Frost found no increase in the V.P. of water in the presence of He compressed to 40 ats. As it is doubtful whether any inert gas would fail to produce a vapour pressure elevation due to the Poynting effect even if there were no additional vapour pressure increase due to dissolved gas it is probable that the method used by Deaton & Frost was insufficiently sensitive to detect the effect of compressed He on the liquid phase vapour pressure. The fact that Deaton and Frost were unable to observe any vapour pressure increase with He suggests that dissolved He increases the vapour pressure of water by only a very small amount if at all: in fact it is reasonable to assume that the activity coefficient for He has a numerical value lower than that for H_2. If this is so, the behaviour of He is in conformity with that of the gases H_2, N_2 and Air in showing that activity decreases with reduction in gas molecule diameter. A gas such as ethylene which has a relatively large molecule would be expected to have a marked effect in increasing the vapour pressure of a liquid phase and it is interesting to note that this is borne out by the results of Diepen and Scheffer (12) who found that the vapour pressure of acetylene is increased to 25,000 times its normal value at 12.0°C in the presence of ethylene gas compressed to 100 atmospheres. The activity of a particular

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gas will of course depend not on the properties of the gas but also on the properties of the liquid in which it is dissolved. We would expect the activity coefficient to vary according to the forces of cohesion and the mean free path in the liquid or solid subjected to inert gas pressure. This could explain why air at pressures up to 200 atmospheres shows a much greater effect in increasing the vapour pressure of CO_2 (17)(19)(11)than of water (14) for the forces of cohesion in water are very high.

Conclusion

Although an interesting relation has been established between dissolved inert gas and the elevation in solvent vapour pressure in a two phase system under pressure there are several objections to viewing gas solubility as the fundamental impulse causing vapour pressure elevation. It is for instance impossible to formulate a theory based on the solution of inert gas if consideration is given to a system in which no liquid phase is present. High pressure air containing a known concentration of water vapour represents such a system. If we cool such a system at constant pressure the effect of pressure on the vapour pressure of water manifests itself as a lowering of the condensation temperature of the water vapour below the value calculated using normal vapour pressure data. As an increase in vapour pressure can in this way be obtained in the absence of liquid, circumstances clearly exist in which vapour pressure elevation cannot be **explained** by the influence of dissolved gas. A further difficulty arises in the consideration of solid-gas equilibra for one cannot readily accept the solution of the gas in the solid which the dissolved gas theory requires.

In view of these considerations we can only attach secondary importance to the relationship between inert gas solubility and vapour pressure elevation which has been revealed in the present study. There is little doubt that solubility in the gas phase is the factor fundamentally responsible for vapour pressure elevation. The available experimental results are now being examined from this point of view and it is hoped to publish soon a detailed account of this study.

Part 2 - Solubility Effects in the Vapour Phase

It has been shown in the paper comprising the first part of this study that a theory based on the solution of inert gas in the condensed phase cannot explain all the phenomena associated with the systems which have been considered. This does not render valueless the results which have so far been obtained for although they must be looked upon as representing only a secondary effect,it is reasonable to assume from their consistency that a solubility effect is in fact responsible for the observed vapour pressure elevation and this suggests that the primary effect is the formation of a solution of condensed phase molecules in the inert gas. If this is the case it would appear from the observations made in Part 1 of this study that the solvent power of an inert gas and its ability to dissolve in a liquid are similarly affected by pressure and temperature.

In a two phase system comprising gas and liquid the concentration of gas in the liquid varies directly as the pressure,if Henry's Law is obeyed. In other words, as the gas becomes more dense its solubility increases. As it has shown that the vapour pressure elevation of a liquid varies directly as the inert gas solubility in the liquid it is not unreasonable to anticipate that the concentration of condensed phase molecules in the gas phase will also increase with inert gas density. In considering gas-solid equilibria according to this theory it would no longer be necessary to postulate the existence of a gas-solid solution to account for the elevation in the vapour of the solid, for this would occur as a direct result of the increased solvent power of the inert gas at higher pressures. A liquid-gas system we can regard as a system having conjugate solutions i.e. a solution of component A in component B in equilibrium with a solution of component B in component A. The components A and B would in this case comprise the gas and liquid phases respectively. Any physical change in conditions affecting the solubility of the gas in the liquid would be expected to effect similarly the solubility of liquid molecules in the gas. This would explain why it is possible to relate inert gas solubility and vapour pressure elevation. As fundamental importance can only be attached to changes occurring in the gas phase, further consideration will now be given to the experimental results obtained in investigating the systems air-water and air-carbondioxide in order to establish any relationships which may exist.

System Air-Water

As it is an object of this investigation to examine the factors governing the solubility of water vapour in air under pressure we must distinguish clearly between water vapour that can be looked upon as being dissolved in the air and water vapour which is present in the air as a result of of the vapour pressure of the liquid or solid. If no such distinction is made then the solubility of water vapour in the air at a particular temperature at atmospheric pressure will be relatively high, while we are looking for an effect which is realised only at higher pressures. As shown previously the factors Fx provide a measure of the solubility effect. Factors Fx between -35° and $50^{\circ}C$ have been calculated from the data given in Table I and are tabulated below in Table 12.

TABLE 12

Calculated factors Fx for system air-water/ice

Temperature °C	-35	-20	0	15	50
Pressure atmospheres gauge	$Fx \ (= F_A - F_p)$				
50	.54	.34	.21	.16	.11
100	1.06	.66	.42	.31	.21
150	1.61	1.01	.62	.46	.31
200	2.13	1.34	.83	.61	.42

We can employ the above factors to calculate the actual concentration of water in the air at different temperatures and pressures due to the solvent effect of the air.

Thus if Ws = mgms/litre of water in saturated vapour in the absence of air pressure.

Wx = mgms water/litre of compressed air at T°C due to the solubility effect

Then Wx = Fx.Ws.

Calculated Values for Wx at different temperatures and pressures are given below.

TABLE 13

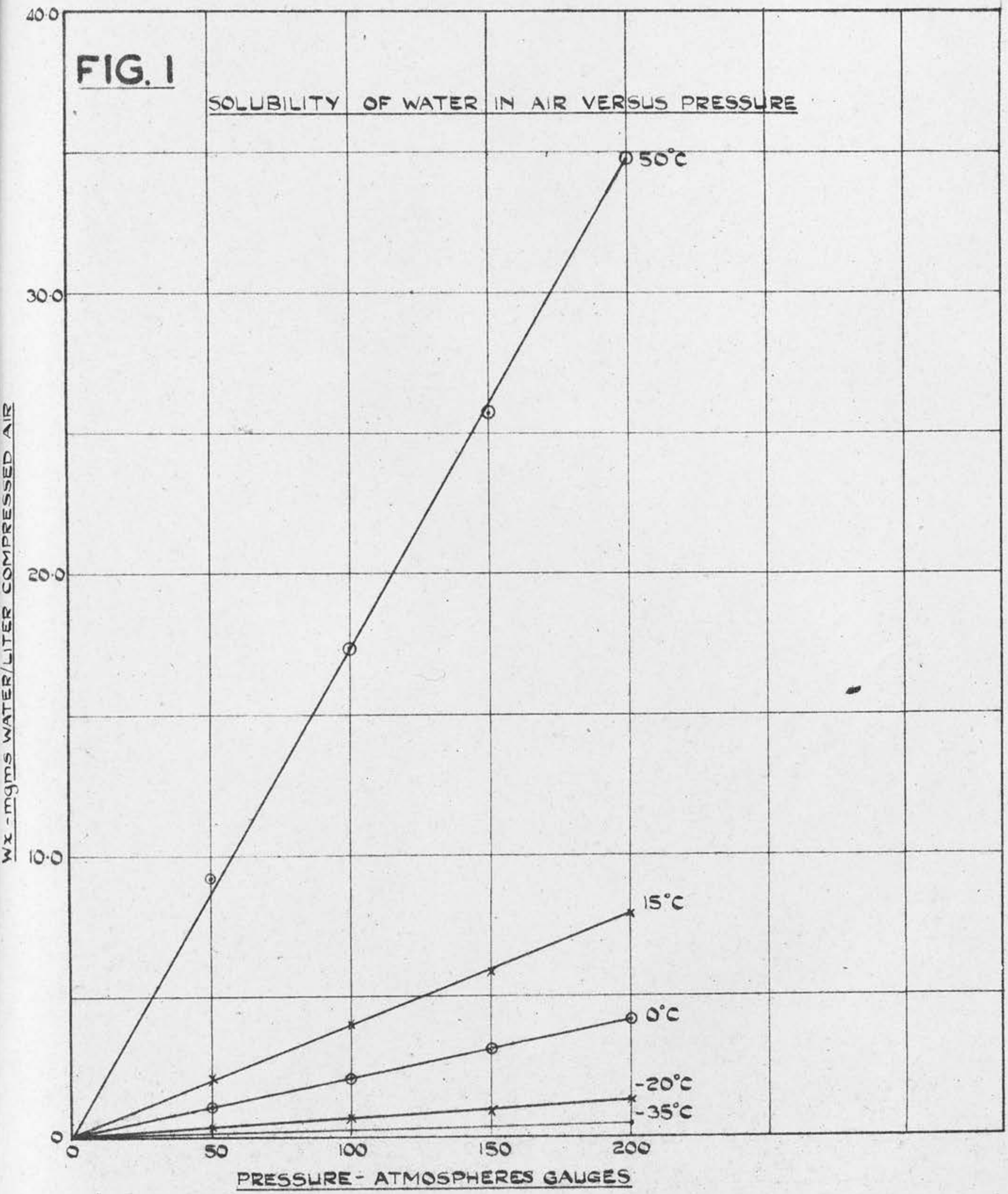
Calculated values Wx for system air-water/ice

Temperature °C	-35	-20	0	15	50
*Ws mgms/litre	.2052	. 866	4.849	12.80	82.77
Pressure atmospheres gauge	Wx = (Fx.Ws)				
50	.111	.302	1.02	2.04	9.11
100	.218	.585	2.04	3.96	17.4
150	.331	.895	3.00	5.89	25.7
200	.436	1 .190	4.02	7.80	34.8

* The values for Ws were taken from reference 14

In Fig.1 the values for Wx at different temperatures are plotted against pressure and it can be seen that straight lines are obtained in each case. The amount of water vapour dissolved by the air expressed as mgms water per litre of compressed air increases linearly with the air pressure. Now the weight of air per unit volume increases linearly with pressure therefore it follows that the weight of water dissolved by a given weight of air remains constant with increasing pressure. This explains why the vapour pressure factors F_A increase with increasing pressure at a given

FIG. 1



SOLUBILITY OF WATER IN AIR VERSUS PRESSURE temperature, for whereas normal vapour pressure considerations lead us to expect a decrease in the amount of water per unit weight of air with increasing pressure, we must include a quantity of water which remains constant with increasing pressure in estimating the actual vapour pressure at some higher pressure. It follows that the relative significance of the solubility effect will increase as the pressure is raised and above a certain pressure it should become the sole factor in determining the water content of the air. With a system in this condition any further increase in pressure should produce no increase or decrease in the amount of water contained in unit weight of air. That this does in fact happen can be seen from the graphs in Fig.2 which show the moisture content of air saturated at different pressures and temperatures, for at the lower temperatures the graphs run parallel to the pressure axis above about 100 atmospheres.

The consistency of the results obtained in studying the solubility of water vapour in air under pressure can probably be attributed to the fact that the air behaves almost as if it were an ideal gas over the range of pressure and temperature investigated. In a system deviating from ideal behaviour the density of the gas may be considerably higher at a given pressure than it would be if the gas were ideal and it is conceivable that the abnormal density of the gas would affect its solvent power. If this were so it would

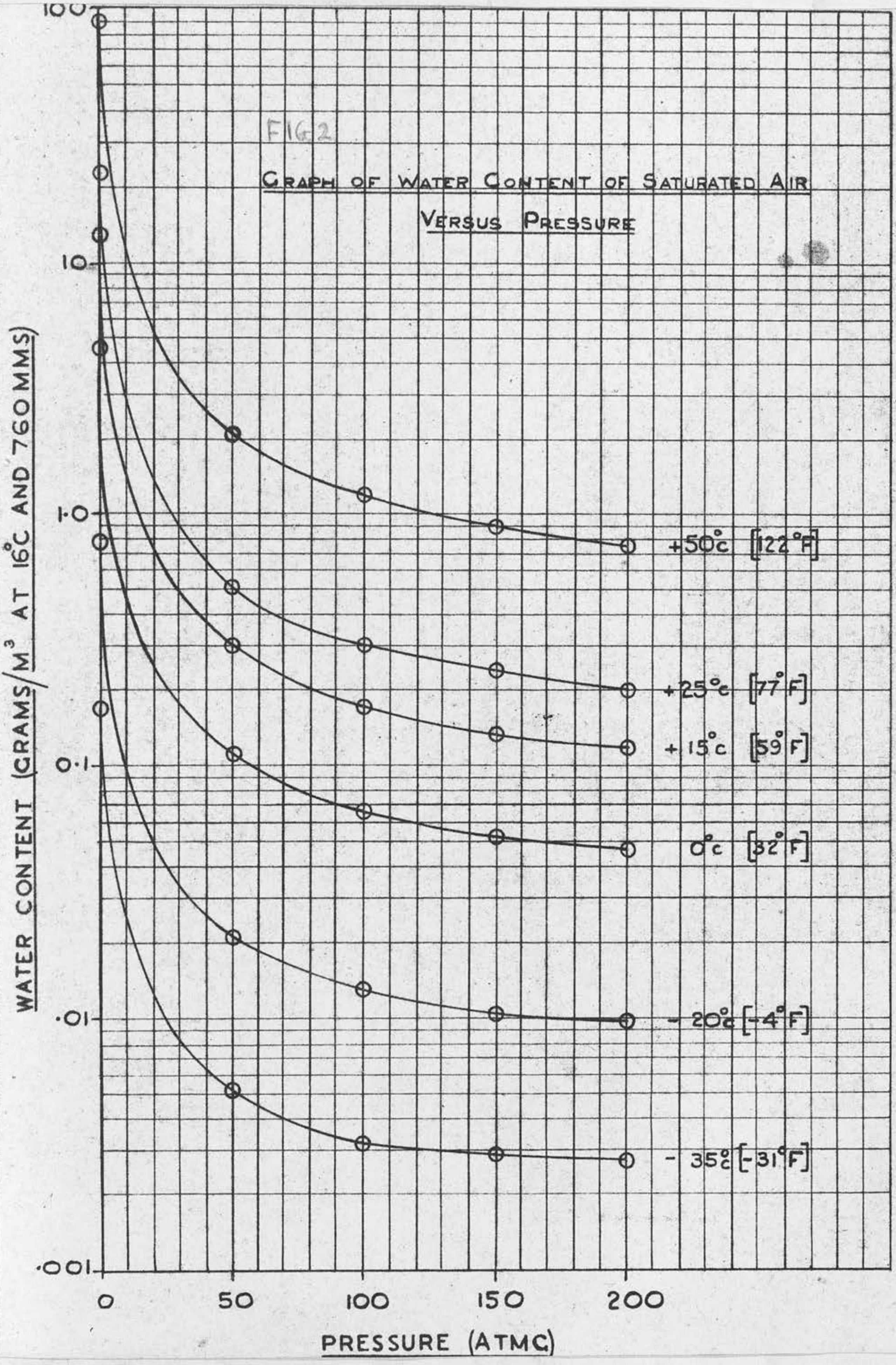


FIG 2

GRAPH OF WATER CONTENT OF SATURATED AIR VERSUS PRESSURE not be unreasonable to anticipate the possibility of having a system in which the solubility of the condensed phase on a gravimetric basis, increased with increasing pressure. It is interesting to note that this behaviour is displayed by the system carbon-dioxide-air which was studied under conditions at which air is known to deviate markedly from the ideal gas laws.

The effect of temperature on the solubility of water vapour in air under pressure can be seen from Tables 12 and 13. The actual weight of dissolved water vapour per litre of compressed air falls with reduction in temperature (Table 13) but in relation to the amount of water present in the air due to vapour pressure, the solubility increases with increasing temperature.

In Fig.3 values of the logarithm of Wx are plotted against corresponding values of $\frac{1}{T^oK}$ and it can be seen that straight lines having the same slope are obtained at different pressures. Each graph in Fig 3 will have the equation

$$\mathrm{Log}_e\ Wx = -\frac{2.3S}{T} + K \qquad \cancel{(4)}\ ⑥$$

where S = the slope which is constant at all pressures

K = a constant which varies with pressure

At a particular pressure P we can evaluate S and K from the results of two experiments carried out at different temperatures.

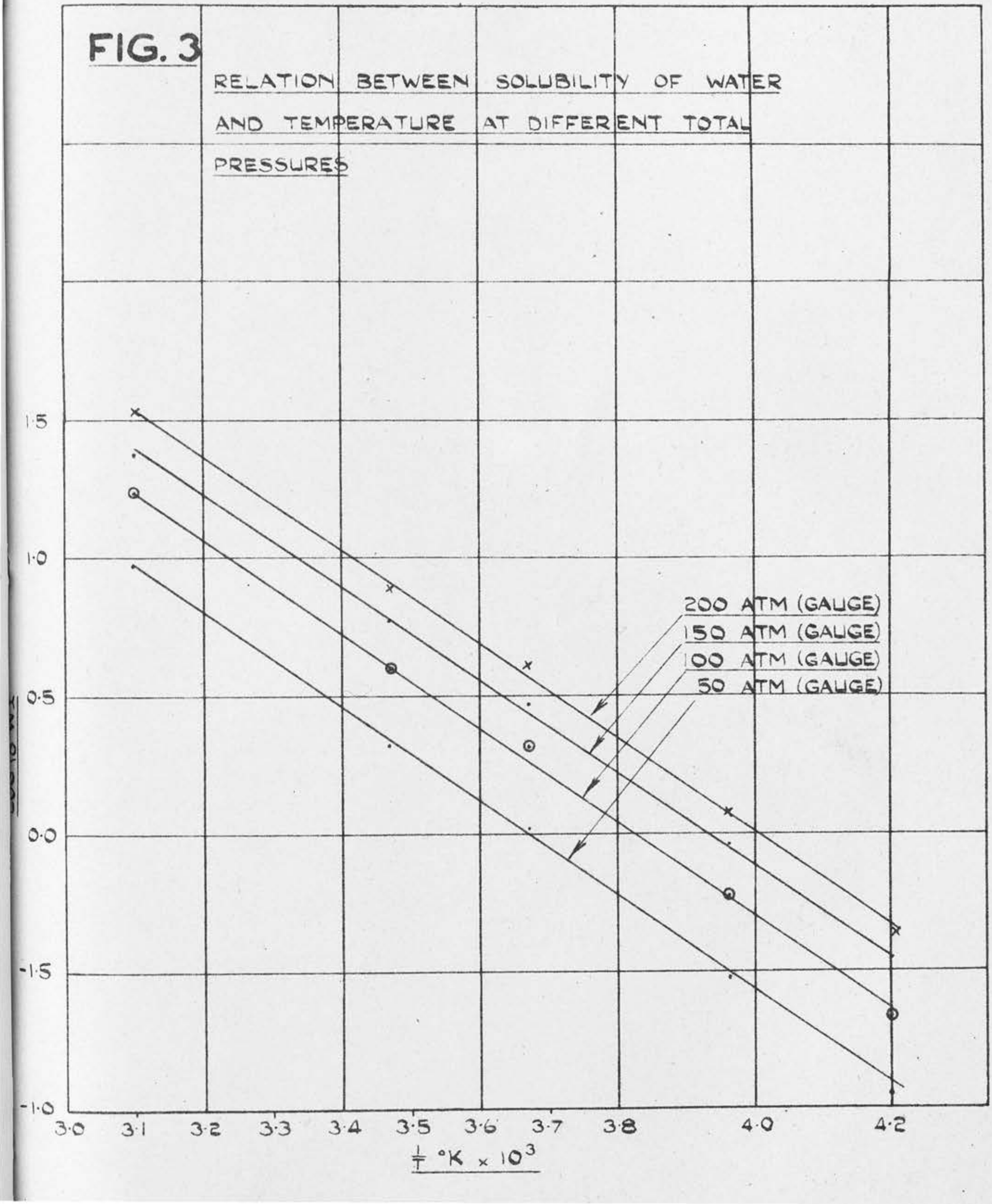


FIG. 3

RELATION BETWEEN SOLUBILITY OF WATER AND TEMPERATURE AT DIFFERENT TOTAL PRESSURES

?

Now from (4) $Wx_{PT} = e^{\left(\frac{-2.3S}{T} + K\right)}$ .. ~~(5)~~ ~~(5)~~ ⑦

in which Wx_{PT} = the value of Wx at pressure P and temperature T°K

Knowing S & K at pressure P we can use ~~(5)~~ ⑦ to calculate Wx at different temperatures and at pressure P

But we also know that

$$\frac{Wx_{P_1T}}{Wx_{PT}} = \frac{P_1}{P}$$ ~~(6)~~ ⑧

From equations ~~(5)~~ ⑦ and ~~(6)~~ ⑧ we obtain the expression

$$Wx_{P_1T} = \frac{P_1}{P} \cdot e^{\left(\frac{-2.3S}{T} + K\right)}$$ ~~(7)~~ ⑨

At 50 atmospheres $S = 1695$, $K = 14.3$ } From Fig 3.

∴ at 200 atmospheres and 50°C (323°K)

$$Wx = \frac{200}{50} \times 2.72^{(-3900 \times .0031 + 14.3)}$$
$$= 4.0 \times 2.72^{(-12.1 + 14.3)}$$
$$= 4.0 \times 2.72^{2.1}$$
$$= 4.0 \times 8.17$$
$$= 32.68$$

In Table (13) the value given for Wx at 200 atmospheres and 50°C is 34.8.

The expression Wx = Fx.Ws enables Fx to be calculated if Wx is known, Ws being calculated from normal vapour pressure data and the total vapour pressure can then be calculated from equation (2) once the Poynting factor has been evaluated.

Thus from the results of only two experiments carried out at a particular pressure in order to fix the constants in equation ~~(7)~~ ⑨ we can estimate with considerable accuracy using the above expressions, vapour pressure factors for the system air-water/ice over the range which has been investigated experimentally. In applying the methods described above to calculate vapour pressure factors outside the field at present investigated experimentally it is probable that reasonable accuracy would be obtained provided deviations from the ideal gas laws were not excessive under the chosen conditions.

On the basis of the results of present study it seems reasonable to conclude that the abnormally high vapour pressure of water or ice observed when the liquid or solid is subjected to pressure by an inert gas is caused by condensed phase molecules dissolving in the compressed gas. The results suggest that the factor of primary importance in determining the concentration of solute molecules in the solvent gas at a given temperature and pressure is the density of the gas at that temperature and pressure, in relation to its density at the same temperature and at atmsopheric pressure. According to this theory increasing pressure will produce no increase in the concentration of water molecules in the air if there is no accompanying change in the density of the air. Now the density of liquid air remains practically unchanged as the pressure is increased, thus at a temperature sufficiently low to maintain the air in liquid form we should expect the solubility of ice in the liquid air to remain constant with increasing pressure. This prediction is consistent with known behaviour, for in general the solid-liquid equilibria of inorganic substances are little affected by pressure.

System Air/Carbon-dioxide

The study of the system air/carbon-dioxide is simplified by the fact that the solubility effect is so much more pronounced than the Poynting effect in increasing the vapour pressure of the carbon-dioxide that the latter effect can be neglected. The factors governing solubility should be similar to those observed in examining the system air-water/ice. Special attention will, however, have to be paid to exceptional conditions arising as a result of deviations of the air from ideal behaviour for the study covers a range of temperature and pressure over which the air can no longer be considered a nearly perfect gas.

The values in Table I reference (17) show the equilibrium molar concentration of CO_2 in air at different temperatures. The molar concentration Mc of CO_2 in the compressed gas will be numerically equal to that in the expanded gas i.e. to the values for x given in the Table1 (17) If Vs and Vo are the specific volumes of air at pressure Ps and at 1 atmosphere respectively then

$$Wc = \frac{Mc}{Vo}$$

where Wc = moles of CO_2 per litre of compressed air.

In the case of the system air-water/ice the weight of water dissolved in unit volume of compressed air at a particular temperature was found to vary directly as the density of the compressed air. If solubility is responsible for Ws moles CO_2 per litre of compressed air, we should expect Ws for the system air-carbon-dioxide to vary directly with density and this would be satisfied if

$$\frac{Ws}{d} = \text{a constant at a given temperature}$$

where d = density of the compressed air.

In order to facilitate the examination of the results for the system air-carbon-dioxide it is first of all necessary to know the specific volume of air at the different temperatures and pressures covered by the experimental investigation. This data was obtained from a paper by Din entitled "A New Thermodynamic Diagram for Air" which is in the course of publication.

TABLE 14

Specific Volume of Air at Different Temperatures and Pressures

Temperature °K	163	152	143	133	128	123	90	79
°C	-110	-121	-130	-140	-145	-150	-183	-196
Pressure atm absolute	V_s litres/mol							
1	13.4	12.5	11.7	10.9	10.5	10.1	.028	.026
11	1.15	1.06	.97	.96	.92	.86	.028	.026
21	.57	.52	.46	.40	.39	.35		
31	.36	.32	.28	.22	.057	.050		
41	.26	.22	.18	.083	.055	.046		
51	.19	.16	.107	.057	.050	.045	.028	
61	.145	.11	.077	.052	.048			
71	.119	.087	.064	.051	.047			
81	.100	.074	.057	.049	.045			
91	.084	.067	–	–	–			
101	.076	.061	.051	.046	.042	.040	.028	.026
151	.057	.050	.047	.042	.040	.038	.028	
201	.052	.047	.045	.040	.038	.035	.028	.026

W_c represents the sum of the carbon-dioxide molecules present in the air due to

(a) the normal vapour pressure of carbon dioxide at the temperature under consideration.

(b) the Poynting effect

and (c) the solubility effect

With increasing pressure (a) will remain constant; the magnitude of the contribution of carbon dioxide molecules at different pressures due to (a) can therefore be estimated from normal vapour pressure data. The Poynting effect can be neglected at all pressures as the increase in vapour pressure which it produces is very small compared with the known solubility at different pressures. With increasing pressure (a) will also become negligible compared with (c) and at pressures in excess of about 60 atmospheres it can be assumed that the solubility effect is responsible for all the carbon dioxide in the gas phase. By sub~~s~~tracting the calculated values for (a) from the total concentration of carbon dioxide present in the air at different pressures we obtain true values for the solubility of carbon dioxide in air at those pressures. Values for Wc at different temperatures and pressures were obtained from the information given in Table 1 (ref.17) and Table 14 using the expression $Wc = \frac{Mc}{Vs}$ (where $Mc = x$ in Table 1 Ref.17)

Ws was then calculated using the equation

$Ws = Wc - Wp$ where

Ws = moles CO_2/litre of air due to solubility

Wp = -do- due to the normal vapour pressure.

To make the method of calculating Ws quite clear the following example is given:

Calculation of Ws at 11 atmospheres absolute and $-110^{\circ}C$.

Mc at 1 atmosphere $= 456 \times 10^{-4}$ mols CO_2/mol air

Mc at 11 atmsopheres $= 49.2 \times 10^{-4}$ mols CO_2/mol air

Vo $= 13.4$ litres/mol air

Vs $= 1.15$ litres/mol air

$$\therefore \quad Wp = \frac{456 \times 10^{-4}}{13.4} = 34.0 \times 10^{-4} \text{ mols } CO_2\text{/litre air at 11 atma}$$

$$Wc = \frac{49.2}{1.15} \times 10^{-4} = 42.8 \times 10^{-4} \text{ mols } CO_2\text{/litre air at 11 atma}$$

$$\therefore \quad Ws = 42.8 \times 10^{-4} = 34.0 \times 10^{-4}$$

$$= 8.8 \times 10^{-4} \text{ mols } CO_2\text{/litre air at 11 atma}$$

The calculated values for Ws over the range of temperatures and pressures covered by the experimental study are given in Table 15.

TABLE 15

Concentration of carbon dioxide in compressed air due to solvent effect.

Temperature °K °C	163 -110	152 -121	143 -130	133 -140	128 -145	123 -150	90 -183	79 -196
Pressure ats. absolute	$W_s \times 10^4$ moles CO_2/litre of compressed air							
1. (Wp)	34.0	9.1	2.6	.52	.21	.08	4.3	.077
11	8.7	3.1	1.7	.30	.11	.04	0.0	0.0
21	25.0	7.6	3.7	1.0	.60	.29		
31	43.2	16.8	9.9	3.4	11.6	10.9		
41	76.0	33.0	25.8	65.5	75.3	82.0		
51	125.0	68.4	66.4	125	116	95.5		
61	218.0	126.9	167.0	149	127		0.0	
71	330	246	264	169	146	-		
81	495	370	327	199	-	-		
91	692	509	-	-	-	-		
101	881	631	446	260	170	121	0.0	
151	1626	1031	578	330	192	145	0.35	
201	2356	1221	667	381	223	169	0.70	.038

If we assume that at each temperature the density of the gas at atmospheric pressure is equal to(d_o)then we get $\frac{W_s . d_o}{d_s} = W_s . \frac{V_s}{V_o}$

in which d_s = density of compressed gas at temperature T_s

V_s = specific volume of compressed at temperature T_s

V_o = specific volume of air at atmospheric pressure and at temperature T_s

If the carbon dioxide content of the compressed air at a particular temperature is proportional to the density of the air and independent of pressure then $Ws.\frac{Vs}{Vo}$ will be constant.

Values for $Ws.\frac{Vs}{Vo}$ have been worked out from the data given in Tables 14 and 15 and the results are shown in Table 16.

TABLE 16

Values $Ws.\frac{Vs}{Vo}$ for the system air-carbon dioxide at different temperatures and pressures

Temperature °K	163	152	143	133	128	123	90	79
°C	−110	−121	−130	−140	−145	−150	−183	−196
Pressure ats.absolute	$\frac{Ws.do}{ds} \times 10^4$ ($= Ws.\frac{Vs}{Vo} \times 10^4$)							
1	–	–	–	–	–	–	–	–
11	0.8	.26	.14	.026	.009	.007	.00	.00
21	1.1	.31	.15	.037	.022	.010		
31	1.2	.43	.24	.068	.063	.054		
41	1.5	.58	.40	.50	.39	.374		
51	1.8	.87	.61	.65	.55	.42		.00
61	2.4	1.12	1.1	.71	.58			
71	2.9	1.7	1.4	.79	.65			
81	3.7	2.2	1.6	.89	–		.00	
91	4.3	2.7	–	–	–			
101	5.0	3.1	1.9	1.1	.68	.48	.00	
151	6.9	4.1	2.3	1.3	.73	.54	.35	
201	9.1	4.6	2.6	1.4	.81	.58	(.70)^{x}	.038

x This value is doubtful

In Figures 4 and 5 values for $(Ws.\frac{do}{ds})$ are plotted against pressure at different temperatures. These graphs show the relation between the gravimetric concentration of carbon dioxide

FIG. 4

CONCENTRATION OF CO_2 IN AIR BY WEIGHT AGAINST PRESSURE AT DIFFERENT TEMPERATURES.

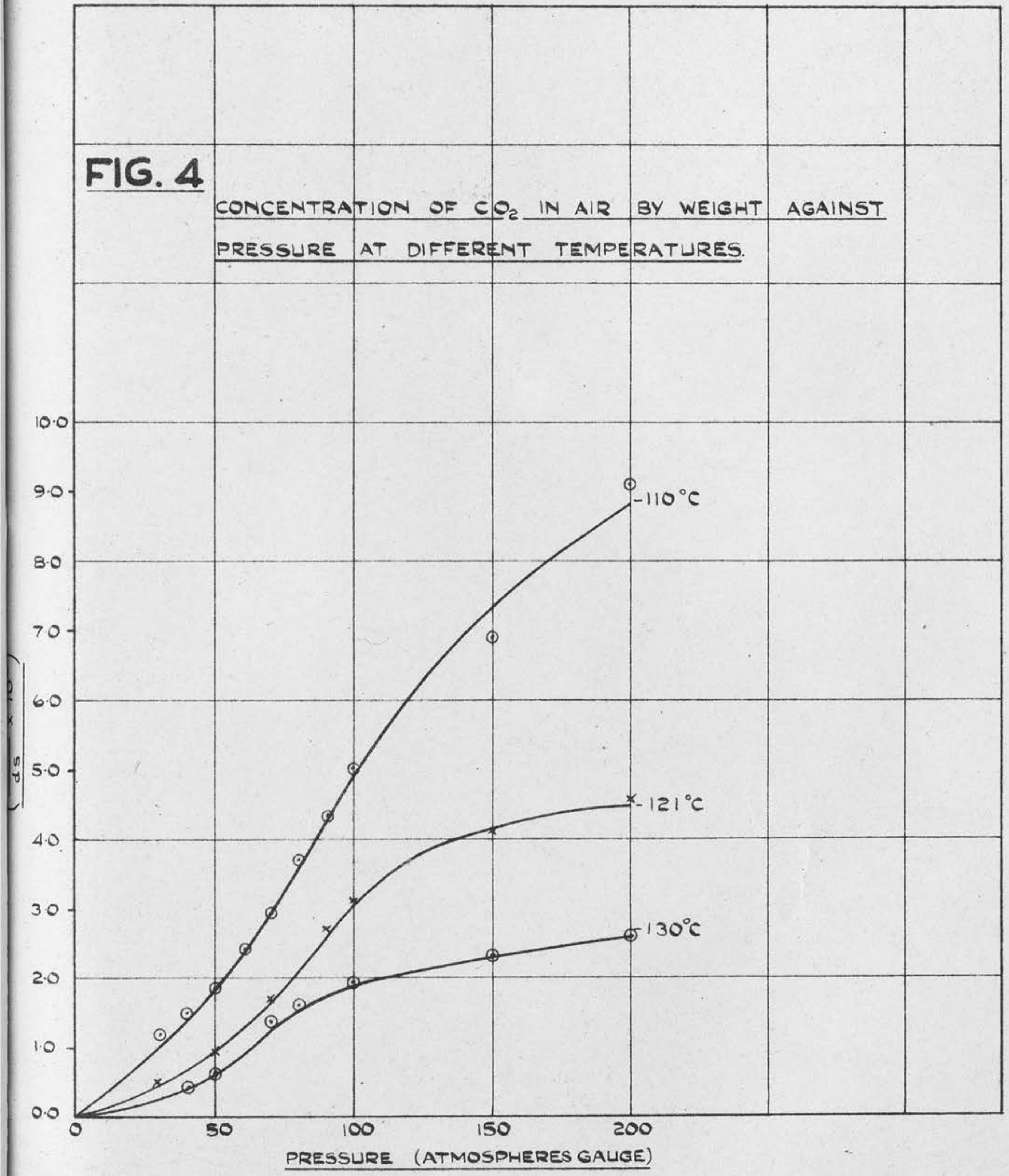
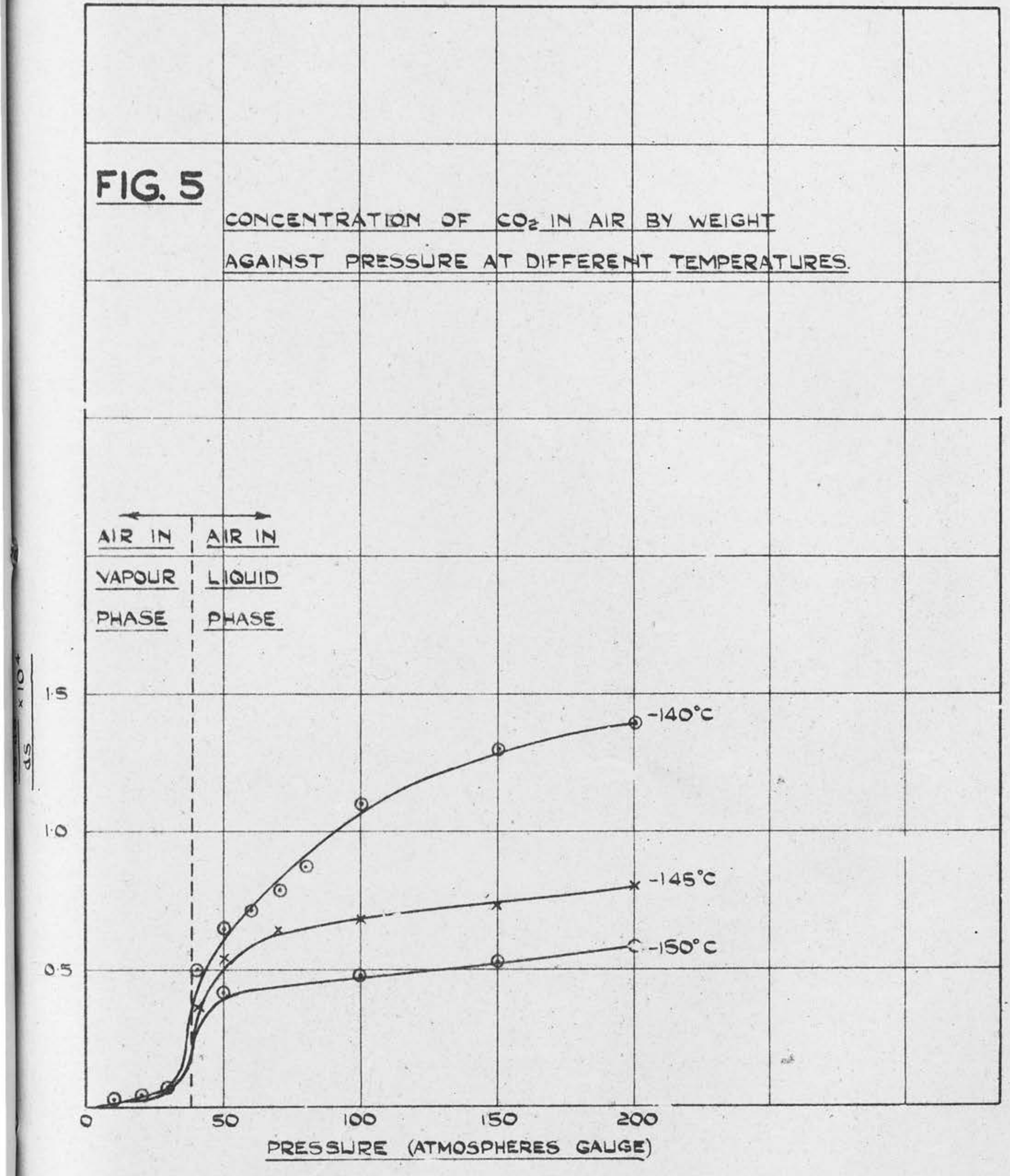


FIG. 5

CONCENTRATION OF CO_2 IN AIR BY WEIGHT AGAINST PRESSURE AT DIFFERENT TEMPERATURES.



in the air and pressure. It is interesting to note that at the highest temperature studied ($-110^{\circ}C$) the relation is almost linear. The curves show an increasing tendency to inflect as the critical temperature for air is approached and below the critical temperature (see Fig.5) they become discontinuous at the condensation pressure for air, the solubility of carbon dioxide in liquid air being much greater than in gaseous air. The curves at $-145^{\circ}C$ and $-150^{\circ}C$ show clearly that the solubility of CO_2 in liquid air increases slightly with increasing pressure.

It can be seen from the results in Table 16 that a particular temperature the factor $\frac{Ws}{1} \frac{dc}{ds}$ for the system air-carbon dioxide does not remain constant with increasing pressure. For this system gas density is not the sole factor determining the solubility of condensed phase molecules; superimposed on the density effect there appears to be a specific effect of pressure in increasing the solubility of the carbon dioxide in the air. Unfortunately however the relationship between pressure and solubility under the conditions studied is too complex to yield an expression which would enable the solubilities at different pressures to be calculated from the known solubility at a particular pressure. At the highest temperature covered by the experimental investigation ($-110^{\circ}C$) the relation between pressure and solubility is almost linear and may become definitely linear at higher temperatures. The graphs in Fig.5 show that at temperatures sufficiently low to enable the air to be liquefied pressure has an increased effect on solubility when it is accompanied by the liquefaction of the air.

It is interesting to note (Fig.5) that the solubility of carbon dioxide in liquid air increases slightly as the pressure is increased. This could explain the difference in behaviour of the systems air-water/ice and air carbon-dioxide when they are subjected to increasing pressure at a particular temperature, if it is assumed that increasing pressure has no effect on the solubility of ice in liquid air. We should not expect a specific effect occuring when the air is in the liquid state to disappear under conditions in which the air exists as gas. As the solubility of carbon dioxide in liquid air increases with increasing pressure we should expect pressure to influence the solubility of carbon dioxide in gaseous air; we should not however expect pressure to influence the solubility of ice in gaseous air.

It has not been found possible to obtain an expression for the system air-carbon dioxide relating temperature and solubility in the gas phase, consequently no attempt can be made to calculate values for the vapour pressure of carbon dioxide at different temperatures and pressure.

It must be concluded that the extent of the vapour pressure increase obtained when a particular 2-component system is subjected to pressure depends to a large extent on the specific influence of the nature of the components comprising the system and is therefore almost impossible to estimate from physical data. The important factor in determining the vapour pressure of the condensed phase appears to be its solubility in the gas phase when the system is subjected to pressure. We cannot predict the extent of this solubility in the complete absence of experimental data but in the case of certain ideal systems expressions can be derived which enable the prediction of vapour pressure over a wide range of temperature and pressure from the results of a few experiments carried out under known conditions of temperature and pressure.

TJW/RKM

25.2.53.

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PAPER 6

A New Type of Electrical Hygrometer

by T.J.Webster.

Date : 18.9.52.

British Patent Application No. 8180/51.

Patent applications for the Contact Hygrometer have been made in this country, America and in several foreign countries, the author of this paper being named as the sole inventor.

A Contact Hygrometer embodying many of the refinements suggested in this paper was displayed by the British Oxygen Company at the Exhibition of Physics in London in 1952.

SUMMARY

A new type of electrical ice-point hygrometer known as the contact hygrometer, which was designed by the author is described in this paper . In this instrument the ice point of the gas being tested for humidity is indicated by the break in an electric circuit caused by the deposition of ice on an electrical conductor which is cooled to the saturation temperature of the gas. The instrument can be used to detect the deposition of any electrically non-conducting solid from a gas.

Ice points between 0° and $-80^{\circ}C$ have been determined with an accuracy of one or two degrees by the contact hygrometer and it has been shown that the instrument is capable of determining ice points as low as $-100^{\circ}C$. These results were obtained on a preliminary design of contact hygrometer and higher accuracy has been obtained from a fully automatic instrument which is being developed. The method is not suitable for the measurement of dew points above $0^{\circ}C$.

Introduction

In oxygen manufacture the importance of having a simple and reasonably accurate method for determining the moisture content of gases is well known. Information concerning the degree of dryness of the air leaving liquid oxygen plant drying units is necessary in evaluating their efficiency and in deciding how best they can be operated. In the purification of rare gases it is frequently necessary to know accurately the moisture content of the gas at some stage in the purification process. Certain cylinder gases are required to contain less than a certain maximum concentration of water. It is therefore desirable to have a method of testing the moisture content of these gases and as it would be undesirable to withdraw a large volume of gas from a cylinder for test the method chosen must be capable of giving an accurate result on a very small gas sample .

The moisture content of a compressed or uncompressed gas can be measured accurately using a gravimetric method (1) but the procedure is invariably tedious, it demands the attention of a skilled tester and it necessitates the withdrawal of large gas samples for each test. Knowing the dew point or ice point of a gas, it is possible to evaluate its moisture content from data on the vapour pressure of water. Several types of hygrometer are available for

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determining the dew and ice points of gases, but none of these is entirely suitable for the measurements required in the oxygen industry. For instance the optical hygrometer cannot be employed above a moderate pressure and there is reason to doubt its accuracy in very dry gas; the electrical conductivity hygrometer can be designed to operate under pressure, but it is inaccurate in relatively dry gases also it is inconvenient to operate as it has to be recalibrated before practically every dew point determination.

The preliminary design of contact hygrometer described in this paper has been subjected to tests which have shown that it is capable of measuring ice points from 0° to -100°C and even lower. The hygrometer requires very little gas for an ice point determination and it could readily be modified to operate at high pressure. An important feature of the hygrometer is that it could be arranged for fully automatic and recording operation; these refinements have in fact been successfully included by other workers who are engaged in the development of the instrument. It is believed that the hygrometer will eliminate many of the present difficulties of moisture determination in the liquid oxygen industry and that the instrument will find application in other fields.

Difficulties in Assessing Moisture Traces

Most of the hygrometers at present available are not entirely suitable when used to estimate low concentrations of water vapour in gases. The hair hygrometer and goldbeater's skin hygrometer have a considerable lag and are insufficiently sensitive at low temperatures to permit their use in determining the dew point of relatively dry gas. Although considerable success has been achieved by Dunmore (2)(3) in developing the electrical conductivity hygrometer for meteorological work the instrument has many disadvantages which militate against its general use in industry. Briefly, the method depends on the variation in electrical resistance of surfaces coated with films of certain acids and salts, with the humidity of the air in contact with the surfaces. The complete unit comprises a moisture sensitive element included in an electrical circuit capable of measuring or balancing the resistance of the element. Unfortunately many factors influence the satisfactory operation of the instrument. On over-exposure to moisture the film is displaced. Chemical action may take place between the film and its support, adsorption effects may occur due to the crazing of the film support, also polarisation may be encountered. The resistance of the element varies with temperature necessitating the use of corrective devices which add to the complexity of the instrument. The next serious disadvantage of the conductivity method is the failure of the elements to retain their original characteristics and although considerable success has been achieved in producing elements of increased stability the necessity for recalibration at frequent intervals has as yet by no means been obviated where high accuracy in moisture determination is essential.

An extremely sensitive optical hygrometer has been developed by the Air Ministry (4) for the determination of frost points as low as -90°C. Although this instrument is sensitive over the range of humidity normally encountered in the oxygen industry there are several reasons why it cannot readily be adopted in that particular branch. The method involves the observation either visually or by some photoelectric means of the formation of ice crystals on a cooled polished element over which is passed the air or gas whose moisture content it is required to determine. The temperature of the cooled element at that instant when the first appearance of a deposit is noted measures the frost point of the gas being tested. In using such an instrument difficulty is frequently occasioned by the fact that the deposit does not always appear in the form of hoar frost but may be in the form of liquid even at temperatures as low as -90°C. As there is an appreciable difference between the vapour pressure of ice and that of water at a given low temperature a considerable error may be introduced in calculating the moisture content of the air if the nature of the deposit is not recognised by the tester. The range of the instrument is limited by the fact that at temperatures below -90°C the deposit is in the form of a glass which cannot readily be detected by the person using the instrument. Another source of error in determination lies in the fact that certain gases, for example air, tend to become supersaturated with water on being cooled below the condensation point so that the observed ice formation takes place at a temperature below the true ice point. The instrument cannot be employed directly to determine the dew point of high pressure gas owing to the difficulties in construction imposed by the necessity for using transparent materials nor can it readily be adapted for fully automatic and recording operation.

Operating Principle of Contact Hygrometer

If a gas containing water vapour is passed over a cooled element water will condense on the element as soon as its temperature is reduced to the point at which the gas is saturated with water vapour. If the saturation point is below 0°C the condensate will be in the form of ice. In **the contact hygrometer a copper element which can be cooled** at a controlled rate is made to form part of an electric circuit which is closed at frequent intervals by causing a platinum wire to touch the surface of the cooled element. A slow stream of the gas being tested is passed over the cooled surface, the temperature of which is gradually reduced to the ice point of the gas. As soon as the ice point is reached ice begins to condense on the copper element on which it forms an insulating layer and subsequent contact with the platinum wire fails to complete the electrical circuit. A~~n~~ micro-ammeter placed in the circuit shows clearly when this stage is reached. The temperature of the cooled surface when the micro-ammeter first indicates the failure of the platinum to make electrical contact with the copper is the saturation temperature or ice point of the gas being tested. A thermocouple positioned immediately under the surface of the copper enables this temperature to be determined.

There is nothing in the princip~~al~~le employed in the contact hygrometer which precludes the construction and operation of a high pressure instrument. The marked sensitivity of the device in the presence of very dry gas suggests, however, that for most industrial purposes sufficiently accurate results could be obtained by testing the gas after expanding it to atmospheric pressure. The method is not suitable for the determination of dew points above 0°C as the water film then obtained does not form an efficient insulating layer.

Nature of Ice Deposits

In using the contact hygrometer it has been found that below about -20°C the ice film is not deposited uniformly over the whole of the polished copper surface but occurs preferentially at the point of contact between the cooled surface and the platinum wire. This increases considerably the sensitivity of the instrument as it concentrates the formation of the ice film within a very small area. It is clear that the moving contact tends to "seed" the formation of ice crystals from the air and it is probable that this prevents the air from becoming supersaturated with water as it is cooled down below the condensation point. Careful visual observation has never revealed the formation of liquid water on the cooled element of the contact hygrometer although the tendency for water vapour to condense as liquid on a polished surface even at very low temperatures is well known. The occurrence of the deposit at that point of disturbance where the moving contact strikes the polished surface probably accounts for the fact that the water vapour always condenses in the form of ice in the hygrometer. At temperatures below -90°C when it has not been possible to observe any ice formation the instrument has given a clear ice point indication. Under these circumstances it is probable that the ice is present in the form of a glass which is extremely difficult to observe visually.

Description of Contact Hygrometer

The constructional details of the hygrometer are described with reference to Figure 1a. The polished end of a $\frac{1}{4}$" dia copper rod A is inserted into a rubber bung B which is fitted in the end of a glass vessel through which the air being tested is passed at atmospheric pressure. The end of the copper rod remote from the polished surface is cooled by immersion in a Dewar flask containing liquid nitrogen or liquid oxygen. In this way heat is removed from the polished surface, the temperature of which can be reduced at any desired rate and to any desired value by adjusting the depth of immersion of the copper bar in the liquid coolant. A calibrated copper constantan thermocouple inserted in the copper bar just below the polished surface enables the temperature of the surface to be determined accurately. The copper bar forms part of an electrical circuit in which is included an Avo-meter and a fine platinum wire suspended from a torsion bar in such a way that the lower end of the platinum wire, which is curved, can be brought into mechanical contact with the polished copper surface, by depressing the lever attached to the free end of the torsion bar. Each time mechanical contact is established between the platinum and the copper the electrical circuit is completed and the Avo-meter is caused to deflect. Figures 1b and 1c shown an end-elevation and plan of the hygrometer respectively.

Method of Operation

The gas undergoing the humidity test is passed through the hygrometer at a rate of about 10 litres/hour. The Dewar flash is charged with sufficient liquid nitrogen to cause the temperature of the polished end of the copper rod to decrease gradually and the lever attached to the torsion bar is operated at intervals of a few seconds. Provided there is no ice on the cold copper surface a full scale deflection of the Avo-meter will occur each time the torsion bar lever is depressed. As soon as ice begins to condense, however, the deflections of the Avo-meter will become erratic and a few seconds later it will cease to give any response. The temperature indicated by the Avo-meter when the erratic behaviour of the Avo-meter is first observed is the saturation temperature or ice point of the air passing through the hygrometer.

The ice film usually becomes visible a few seconds after the electrical indication. At temperatures between 0°C and about -20°C. a uniform coating of ice usually forms over all the polished surface. At temperatures below -20°C the ice is precipitated initially only at the point of contact between the platinum and the copper and a patch of ice grows radially from this nucleus as deposition proceeds. When the ice point is below -90°C the film cannot usually be seen even after the instrument has given a clear indication that the ice point has been reached.

The results of a series of experiments in which the contact hygrometer was employed to determine the ice points of air saturated with water at different temperatures are given in Table 1

TABLE I

Ice point determinations by Contact Hygrometer

Saturation Temperature of air °C	Ice point indicated by Hygrometer °C	Moisture content of saturated air mgms/1 at 16°C and 760 mms *
-13.0	-15.0	1.44
-24.0	-22.0	0.64
-35.0	-34.0	0.21
-38.5	-38.5	0.12
-43.0	-43.0	0.07
-54.0	-51.0	0.025
-55.0	-55.0	0.016
-56.0	-52.0	0.023
-56.0	-56.0	0.014
-60.0	-58.0	0.011
-69.0	-70.0	0.0019
-74.0	-75.0	0.0009
-76.0	-76.0	0.0008
-85.0	-81.0	0.00035
-87.0	-84.0	0.00020
-183.0	-95.0	0.000027
-183.0	-95.0	0.000027
Air ex P_2O_5 tube	-100.0	
-do-	-103.0	< 0.000005

* As indicated by Hygrometer

The above results show clearly that the Contact Hygrometer is capable of determining ice points as low as -80°C with an accuracy of about one or two degrees. The discrepancy between the ice point determination and the saturation temperature at $-183^{\circ}C$ can probably be accounted for by the evaporation of occluded moisture from the glass lines and the rubber bungs used to seal the hygrometer from the atmosphere, also fine particles of ice may have been carried forward from the saturator despite the precautions taken to prevent entrainment. The results at -100° and $-103^{\circ}C$ obtained on the air leaving a phosphorous pentoxide tube would probably have been lower had rubber been eliminated from the apparatus; they are not however unreasonable and suggest that the instrument is capable of determining ice points as low as $-100^{\circ}C$ with considerable accuracy. Bearing in mind the somewhat crude design of instrument on which the above results were obtained a higher accuracy can be anticipated from a well designed automatic instrument.

Development of Contact Hygrometer

The instrument described in this paper represents a preliminary design of which the chief merit is that it has amply demonstrated the possibilities of the method which promises to be more sensitive and in several respects more convenient than any other at present available. There is still much scope for improvement in design and much development is required to produce a satisfactory instrument

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for routine operation but some suggestions may be offered concerning the lines on which a fully automatic instrument might be designed.

The moving contact could be operated mechanically or electromagnetically at regular intervals and an electric heater placed near the warm end of the copper conductor could be arranged to increase the temperature of the polished end of the conductor as soon as the formation of ice on the polished surface was detected by the electrical indicating circuit. The indicating circuit could be arranged to switch off the electric heater as soon as the ice on the polished surface had evaporated so that the surface would be cooled until the formation of ice was again detected. Recorders showing the temperature of the cooled copper surface and the resistance of the indicating circuit could be fitted to plant instruments to give a permanent record of each ice point determined by an automatic instrument.

The instrument described in this paper could probably be improved considerably by covering the surface of the copper with a non-oxidisable metal such as platinum, palladium or gold. Little information has as yet been obtained concerning the optimum dimensions of the moving platinum contact or the optimum bearing pressure of the platinum on the polished surface.

Since the method does not depend upon visual observation for the detection of the ice film, the detecting device could be totally enclosed within a vessel containing gas at high pressure. As it would then be unnecessary to expand the gas to a low pressure before testing,the sensitivity of the determination would be greatly increased. In assessing the moisture content of high pressure gas it would of course be necessary to have information concerning the effect of pressure on the vapour pressure of ice at the particular ice point temperature indicated and in this connection the experimental data which has been obtained by the author (1) would prove of considerable value. As the contact hygrometer can determine ice points directly in high pressure gas it could prove a valuable tool in assessing the effect of different high pressure inert gases on the vapour pressure of ice. Unfortunately the instrument was not available when the effect of pressure on the equilibrium between ice and air was being investigated for by speeding up the work it would have enabled studies to be carried out over a wider range of temperature and pressure than was possible in the time available.

? The principle could be employed to detect the pressure of any electrically non-conducting solid on an electrical conductor and it is not unreasonable to suppose that many applications will be found for the instrument in addition to the specific application referred to in this paper.

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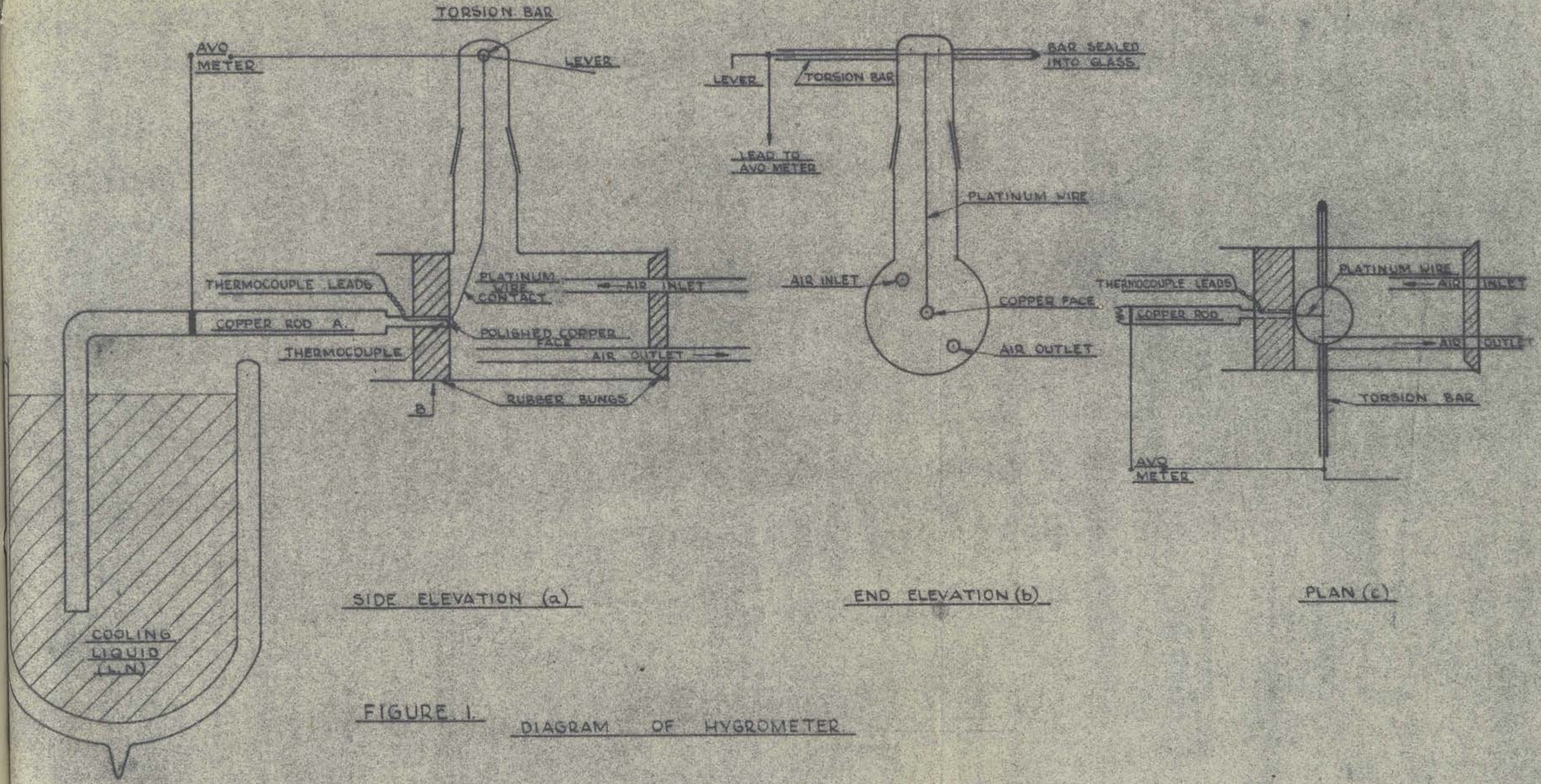

SIDE ELEVATION (a)

END ELEVATION (b)

PLAN (c)

FIGURE 1. DIAGRAM OF HYGROMETER

See Proceedings P. 101

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Advance Proof

The Eighth International Congress of Refrigeration

COMMISSION I

The Effect of Indifferent Gases on the Vapour Pressure of Carbon-Dioxide

By T. J. Webster

Introduction

In the low temperature separation of air the carbon-dioxide must be removed to prevent the occurrence of plant blockages. It is frequently inconvenient to employ the standard method of carbon-dioxide removal by sodium hydroxide and an alternative method is to condense the carbon-dioxide as solid in liquid air from which it is separated by filtration. Calculations based on Dalton's Law suggest that the carbon-dioxide would be precipitated from the cooled compressed air before reaching the point at which the air is liquefied. It is known, however, that the carbon-dioxide only begins to condense at temperatures lower than would be expected, but there is no certain theoretical method of predetermining the actual saturation temperature and it is therefore very important to determine it experimentally. The work described in this report was carried out in order to obtain the desired information.

The means employed was to measure by a dynamic method the carbon-dioxide content of gaseous and liquid air in equilibrium with solid carbon-dioxide under known conditions of temperature and pressure. Experimental studies were carried out at pressures up to 200 ats over the temperature range –110° to –196°C. At the higher pressures and lower temperatures the air in the apparatus was condensed to the liquid phase, and the measured concentration of carbon-dioxide therefore represented its solubility.

Apparatus

The apparatus which was designed to operate at a maximum pressure of 200 ats and a minimum temperature of –200°C. consisted of a stainless steel saturator by means of which air at a fixed temperature and pressure was saturated with carbon-dioxide. This was followed by an expansion valve, a metal heating coil and a carbon-dioxide filter maintained at the temperature of liquid oxygen in which all the carbon-dioxide present in the air was precipitated. The volume of the air leaving the filter was measured on a wet gas meter. A line diagram of the apparatus is shown in fig. 1.

After each experiment the carbon-dioxide retained by the filter was evaporated by warming the filter, the gas being displaced by a stream of purified air to a train of weighed U-tubes containing soda asbestos and magnesium perchlorate. The weight of the CO_2 which had been precipitated in the filter was thus determined. In those experiments in which the carbon-dioxide content of the air was relatively high the carbon-dioxide filter was dispensed with and the expanded air was passed directly through the soda asbestos tubes before entering the wet gas meter.

The saturator (see fig. 2) which was preceded by a high pressure activated alumina drier consisted of a stainless steel coil ($\frac{3}{8}$ inches I.D. and 6.0 feet long) followed by a stainless steel tube fitted internally with a 1 inch plug of tightly wound glass tape to act as a carbon-dioxide filter. The coil and filter tube were immersed in the bath of a cryostat, the temperature of which was controlled by an ethylene vapour pressure thermometer and a gas thermometer at the higher and lower temperatures respectively. A small electric heater placed in the cryostat was operated by the appropriate controlling thermometer on a make and break electrical circuit. The heater was designed to compensate the fall in temperature of the cryostat fluid produced by the passage of liquid nitrogen at a roughly controlled rate through a copper coil immersed in the fluid.

The temperature of the cryostat was measured to an accuracy of ±0.1°C. using a calibrated copper-constantan thermocouple. The air pressure was measured by means of a Bourdon gauge reading to 400 ats and accurate to 0.8 at.

The filter employed to remove the carbon-dioxide from the saturated air consisted of a metal cooling coil followed by a 3 inch length of copper tube containing six closely fitting fibre plugs.

The same equipment was used both for the vapour pressure and solubility measurements, the nature of the determination being fixed by the experimental conditions. Experiments carried out at different air velocities gave consistent results and thereby established that the saturator prevented entrainment. That equilibrium was established in the saturator was proved by employing the apparatus to determine the vapour pressure of carbon-dioxide at atmospheric pressure and at different temperatures.

Experimental Results

The results are given in Table 1 expressed as a factor F equal to the ratio $\frac{p}{p_s}$ in which p is the nominal partial vapour pressure of carbon-dioxide in the compressed gas saturated at the experimental temperature T. and p_s is the normal vapour pressure of carbon-dioxide at the same temperature. The partial vapour pressure p is the product of the total saturation pressure P and the molar concentration of carbon-dioxide (x) in the saturated air. Each value of F is calculated from the average of six experimental determinations of (x) among which the standard deviation did not exceed 2.0% at the higher temperatures and 10% at the lower temperatures. Values for p_s were obtained from published data on the vapour pressure of carbon-dioxide.[1]

TABLE 1

Factors F ($= \frac{P.x}{p_s}$) found by experiment

Temperature	−110°C.	−121°C.	−130°C.	−140°C.	−145°C.	−150°C.
p_s (mms of Hg)	34.63	8.57	2.31	0.431	0.168	0.060
Pressure P (atmg)	Factor F ($= \frac{P.x}{p_s}$)					
10	1.19	1.25	1.50	1.5	1.5	1.4
20	1.55	1.61	2.02	2.3	3.0	3.4
30	1.92	2.28	3.61	4.8	9.4	21.3
40	2.6	3.4	7.0	39.5	78	195
50	3.4	5.5	12.4	65.0	134	275
60	4.9	8.2	26.3	84.0	169	—
70	6.7	14.0	40.0	108	220	—
80	9.4	20.1	50.1	140	245	485
100	15.4	34.9	76.1	215	327	611
150	31.2	69.2	136	370	527	1040
200	54.0	103.0	200	542	775	1481

Discussion of Results

Graphs showing the relation between the experimentally determined factors and the superimposed pressure at different temperatures are shown in fig. 3. The factor F shows the ratio of the actual concentration of carbon-dioxide to the concentration that would be found if Dalton's Law and the perfect gas laws were obeyed. It can be seen that the relative increase in vapour pressure becomes greater as the temperature falls and as the superimposed air pressure is increased and that the actual vapour pressure may be a thousand times as high as would otherwise be expected. The practical significance of this is that it becomes possible to cool the air to a much lower temperature than would be expected before the carbon-dioxide is precipitated. This behaviour may be used to advantage in the removal of carbon-dioxide in the process of air separation. If the air is compressed above 40 ats. it can be cooled to a temperature of −150°C. without depositing carbon-dioxide. If it be then expanded to atmospheric pressure the air will be partially liquefied, and the carbon-dioxide will appear as a solid suspension in the liquid fraction, from which it can be removed by filtration. Graphs showing the relation between the experimentally determined equilibrium carbon-dioxide concentration (x) and the superimposed air pressure at different temperatures are given in fig. 4. It can be seen that at pressures in excess of about 25 atmospheres the molar concentration of carbon-dioxide in the saturated air increases as the pressure of the system is increased. This means that in contrast with normal behaviour increasing compression would cause evaporation of carbon-dioxide instead of condensation. At −130°C. the carbon-dioxide content of the air compressed to 200 ats.

is approximately equal, as a result of the pressure effect, to the saturation value at atmospheric pressure; at lower temperatures the equilibrium carbon-dioxide concentration actually exceeds the normal value.

The apparent anomaly shown by the crossing of the low temperature isotherms in the region of the critical pressure for air is explained by the fact that the air liquefies at progressively lower pressures as the temperature is reduced below the critical value.

The experimentally determined solubilities at –183°C. and –196°C. expressed as molar concentrations (x) were 0.12×10^{-4} and $.003 \times 10^{-4}$ respectively and with increasing pressure no increase in these values was obtained. The isotherms at these temperatures have been omitted from fig. 4 as the molar concentrations would appear insignificant on the scale used.

Phase Rule Consideration

The remarkable behaviour of carbon-dioxide in the presence of compressed air can be explained if one considers in general terms the behaviour of a two-component system in which one component condenses to a solid and the other to a liquid phase. A full discussion would be beyond the scope of this paper, but it is hoped to give elsewhere a more detailed account of the theoretical aspects of the experimental results.

Acknowledgment

The author is indebted to the Directors of the British Oxygen Company Limited for permission to publish this work.

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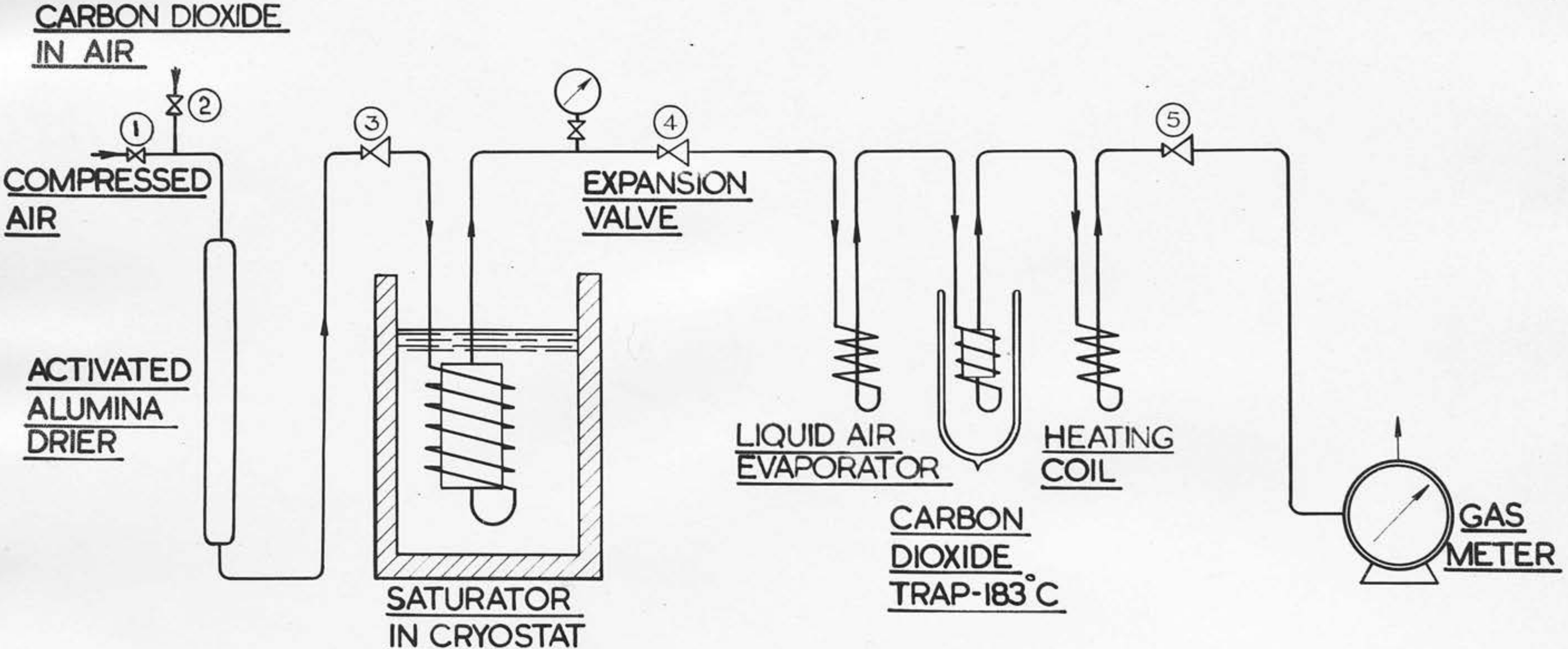
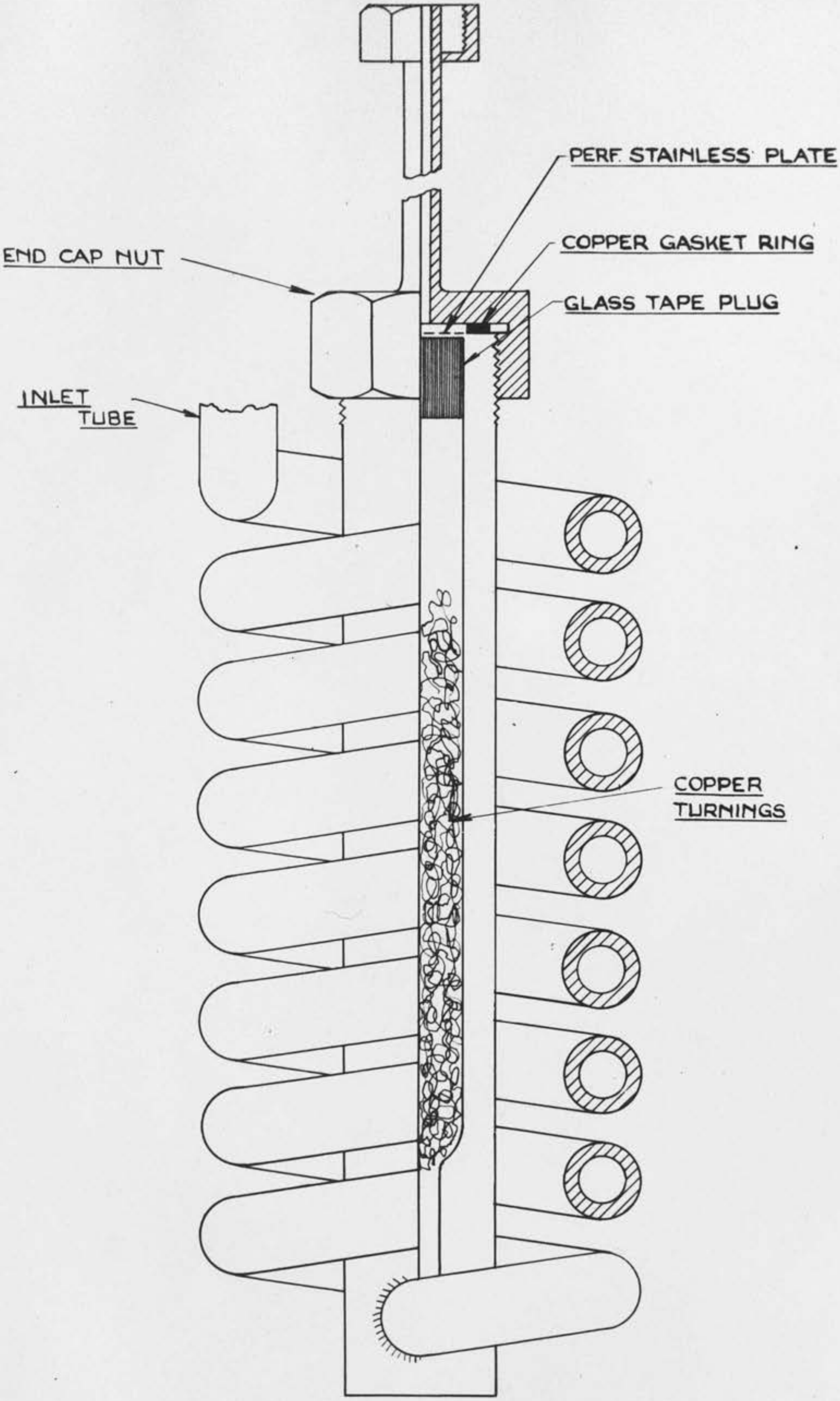


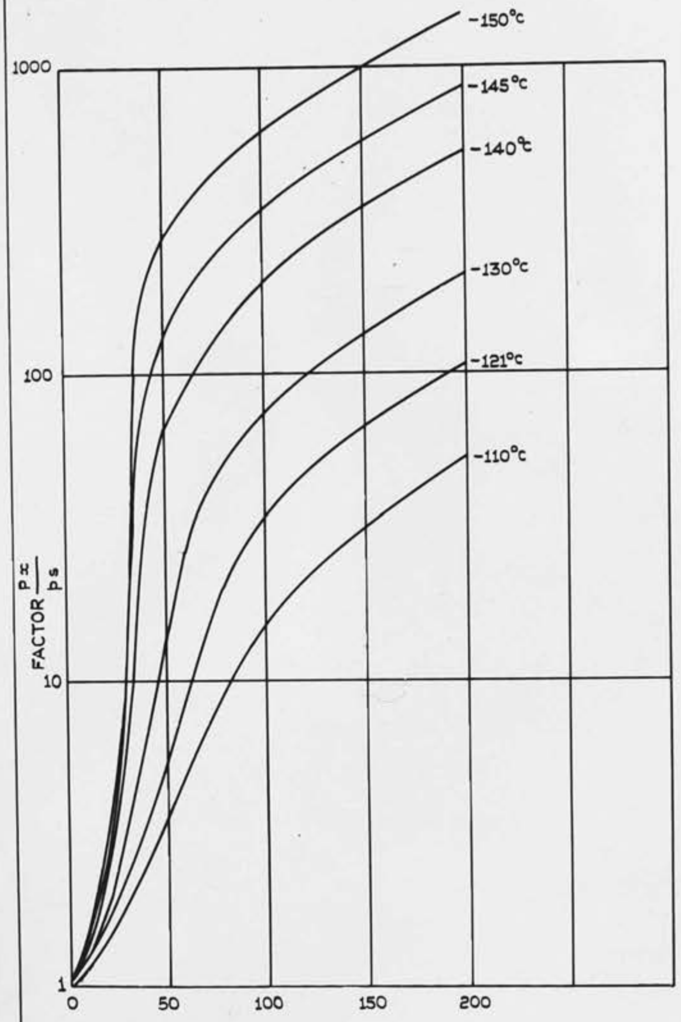
FIG I

LINE DIAGRAM OF APPARATUS



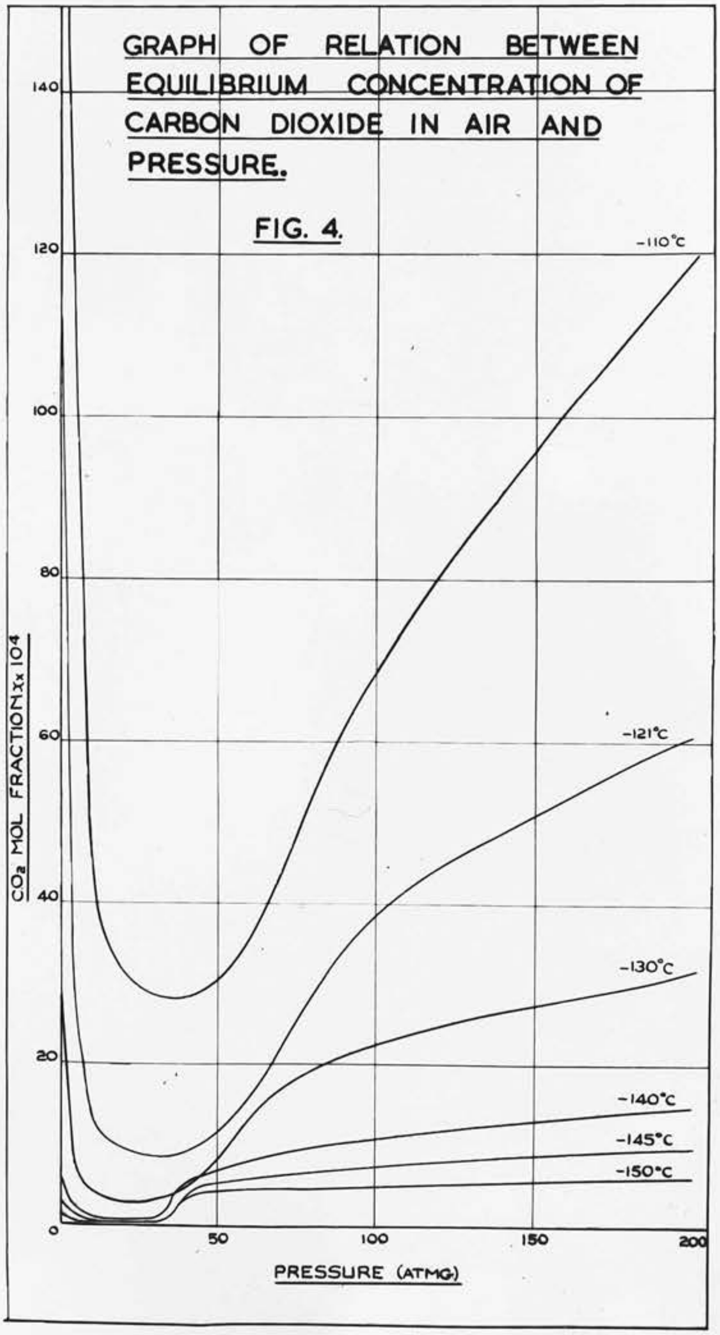
SCALE DRAWING OF SATURATOR

FIG.2



GRAPH OF RELATIVE CARBON DIOXIDE VAPOUR PRESSURE VS SUPERIMPOSED PRESSURE.

FIG. 3



GRAPH OF RELATION BETWEEN EQUILIBRIUM CONCENTRATION OF CARBON DIOXIDE IN AIR AND PRESSURE.

FIG. 4.

British Patent Application No.24989/51 - Improvements in or Relating to the Separation of Air.

by T.J.Webster

On the basis of the experimental results given in the preceding paper a patent application relating to a method for the removal of carbon-dioxide in air separation units has been made, the author being named as the sole inventor. The manner in which the results have been applied in developing this method is discussed below and the method is described.

Significance of Experimental Results in Oxygen Manufacture

Carbon- dioxide occurs to the extent of about .03% by volume in atmospheric air and an oxygen plant must be provided with some means of removing this impurity which would otherwise condense in the cold sections of the plant and cause stoppages. On most liquid oxygen plants the carbon dioxide is removed completely by scrubbing the air with caustic soda before it enters the low temperature sections of the plant. The complete removal of the carbon-dioxide by this method entails the use of purification equipment of considerable size and on very large air separation units the provision of caustic soda scrubbers of the requisite size is frequently impracticable.

A non-chemical carbon dioxide purification process has recently been developed and successfully operated in America. In this process the carbon-dioxide is removed as solid by filtration from the liquid air passing into the rectification column. The success of this method depends on the passage of the carbon-dioxide in the presence of high pressure air through the plant heat exchangers without precipitation. After expansion of the air leaving the main heat exchanger the carbon-dioxide is collected as solid in the liquid air formed, the precipitated carbon-dioxide being removed by filtration together with other impurities. Technical aspects of this method are discussed below on the basis of the results obtained in the experimental study.

Carbon-dioxide will not be precipitated from the air passing through an oxygen plant unless its molar concentration in the air exceeds the saturation value at the temperature and pressure existing at some point in the plant circuit. Atmospheric air contains .03% by volume of carbon-dioxide which is equivalent to a molar concentration of 3.0×10^{-4}. At atmospheric pressure the carbon-dioxide would condense from this mixture at a temperature of -143.5°C at which the vapour pressure of solid carbon-dioxide is 0.228 mms. If the air were compressed say to 165 atmospheres it would begin to deposit solid carbon-dioxide at a temperature of -109°C if the gas obeyed Dalton's Law. It can be seen, however, from Fig 4 in the preceding paper that the molar concentration of carbon-dioxide in air saturated at -109°C and 165 atmospheres is about 100×10^{-4}, due to the effect of the inert gas. At this pressure precipitation of the carbon-dioxide from the air would not in fact begin until the temperature of the system was reduced to about -155°C. The experimental results have thus shown that the condensation temperature of carbon-dioxide in air compressed to 165 atmospheres is much lower than it would be in air at atmospheric pressure. The temperatures to which it is necessary to cool atmospheric air at different pressures before solid carbon-dioxide will be precipitated are given in Table 1 below. The saturation temperatures at different pressures have been obtained from the T - x diagrams Fig 4 (Proc. Roy. Soc. paper) assuming that the mol fraction of carbon-dioxide in atmospheric air is 3.0×10^{-4}.

TABLE 1

Saturation Temperatures of Carbon-dioxide in Atmospheric Air at different Pressures.

Air Pressure (Atmospheres gauge)	0	10	20	30	40	50 to 200
Saturation Temperature °C (below which CO_2 is precipitated)	-143.5	-130	-129	-128.5	-150	-155(approx)

These values show that carbon-dioxide will not be precipated from atmospheric air at temperatures above -155°C if the air pressure exceeds 50 atmospheres; precipitation will however occur at about -130°C if the air pressure is between 10 and 30 atmospheres. A liquid oxygen plant usually operates at a pressure in excess of 50 atmospheres and it is clear from the above results that if such a plant is equipped with a filtration system for the removal of carbon-dioxide, the temperature of the high pressure air passing through the exchangers must not be allowed to fall below about -155°C if blockage is to be avoided. This places a serious limitation on the process of carbon-dioxide removal by filtration for in order to obtain the maximum thermodynamic efficiency from the liquefaction cycles generally employed in liquid oxygen manufacture it is necessary to cool the air to -170°C in the main heat exchanger of the plant before expanding it into the rectification section. The filtration process can however be retained without loss of cycle efficiency if the concentration of carbon-dioxide in the air entering the plant is reduced below the equilibrium value in the presence of the high pressure air at -170°C. The experimental results enable us to assess how much of the naturally occurring carbon-dioxide must be removed from the air in order to satisfy this condition. The experimental equilibrium molar concentrations of carbon-dioxide in air at 50 and 150 atmospheres pressure at different temperatures between -140°C and -183°C are shown in Table 2.

TABLE 2

Equilibrium molar concentrations of carbon-dioxide in air at 50 and 150 atmospheres

Temperature $^{\circ}$C	-140	-145	-150	-183
Pressure (atmospheres gauge)	Molar Concentration $x \times 10^4$			
50	7.0	5.5	4.3	0.1
150	13.0	8.6	5.5	0.1

The above values have been plotted in Figure 1 to enable the equilibrium values at -170°C to be interpolated. It can be seen from the graphs in Figure 1 that at -170°C the equilibrium molar concentration of carbon-dioxide in air compressed to above 50 atmospheres exceeds the value 1.0×10^{-4} which is equivalent to 100 parts per million by volume. This means that no deposition of carbon-dioxide will occur in a heat exchanger in which air compressed to above 50 atmospheres is cooled to -170°C provided the carbon-dioxide content of the air does not exceed 100 p.p.m. by volume. Atmospheric air normally contains about 300 p.p.m. of carbon-dioxide, therefore in order to avoid blockage it is necessary to remove only two thirds of the CO_2 present in the air before the air is passed through the low temperature heat exchanger. The size of the caustic soda scrubber required to effect this partial purification is of course much smaller than that of a scrubber designed to eliminate completely the carbon-dioxide present in atmospheric air. The carbon-dioxide remaining in the purified air can readily be removed by filtration from the liquid air as explained earlier. The removal of carbon-dioxide from air by partial purification followed by filtration is the process to which the British Patent Application 24989/51 relates.

The invention provides a method for the low temperature separation of air which, while fully protecting the separation plant heat exchangers and rectification section against carbon-dioxide blockage, enables the size of the purification equipment and the consumption of chemicals therein to be decreased, whilst permitting the plant to be operated at its maximum thermodynamic efficiency. According to the invention a process for the separation of air by liquefaction and subsequently rectification comprises reducing the carbon-dioxide content of the air to not more than 100 p.p.m., compressing the air to at least 50 atmospheres pressure, cooling the compressed air in heat exchangers, liquefying at least part of the cooled compressed air whereby the residual carbon-dioxide is precipitated as solid therein, removing the precipitated carbon-dioxide from the liquid air and thereafter feeding the air to a rectification zone.

Since the initial reduction of the carbon-dioxide content of the air is only to 100 p.p.m., the purification apparatus necessary is considerably smaller than would be required to eliminate the carbon-dioxide completely and the quantity of chemical absorbent required is also proportionately smaller.

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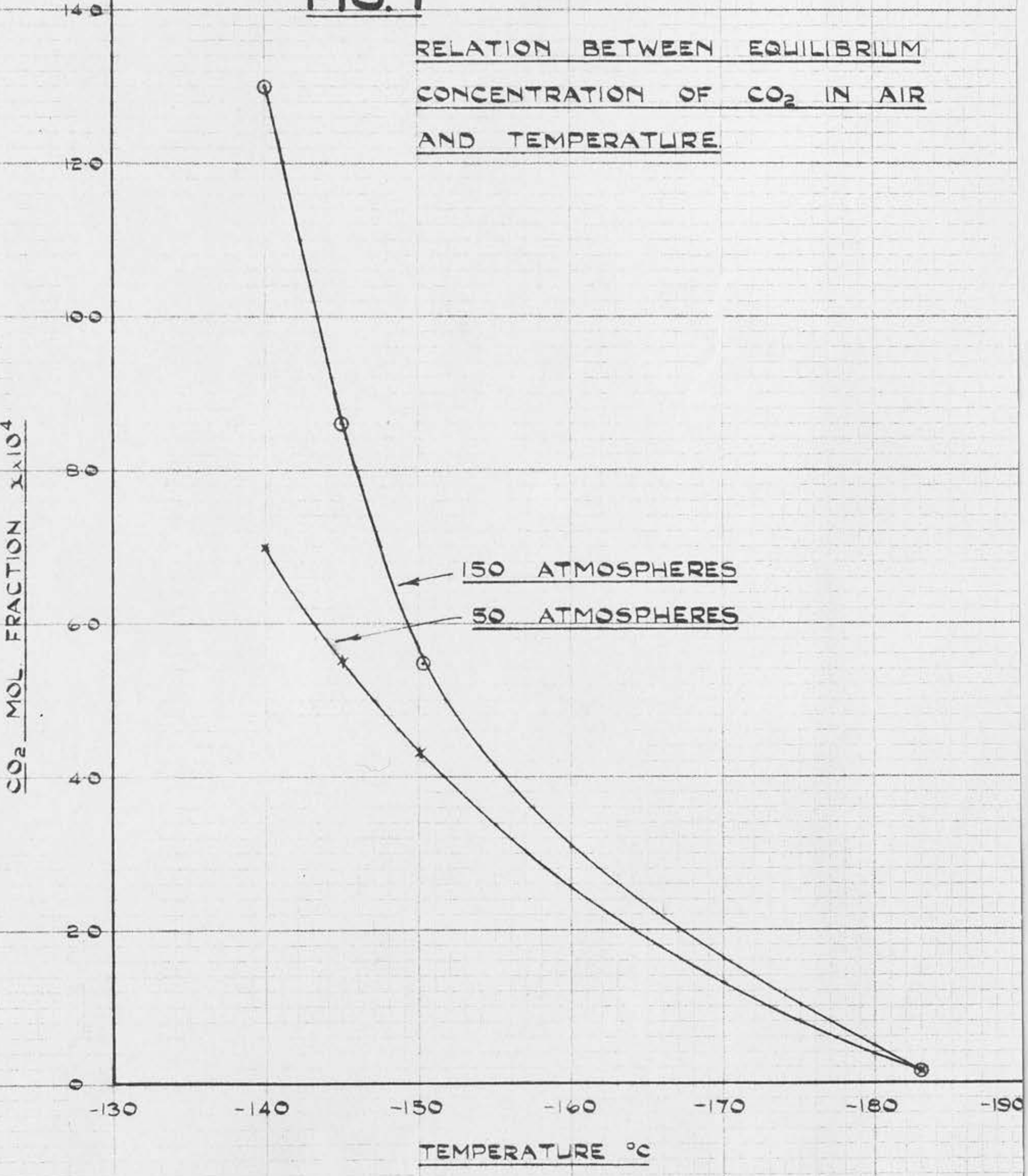
FIG. I



RELATION BETWEEN EQUILIBRIUM CONCENTRATION OF CO_2 IN AIR AND TEMPERATURE.

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The influence of pressure on the equilibrium between carbon dioxide and air

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The equilibrium between solid carbon dioxide and air has been examined at pressures from atmospheric to 200 atm and at temperatures from −110 to −196° C. At the lower temperatures and higher pressures within this range the air was condensed to the liquid state.

The concentration of carbon dioxide in the mixed phase, particularly at high pressures and the lowest temperatures, was found to be many times greater than would be expected from Dalton's law, even when modified by Poynting's relation for the effect of the compressed gas phase. Under extreme conditions the deviation was more than a thousandfold.

The behaviour of this system is shown, by general phase-rule considerations, to be consistent with that of a binary system in the neighbourhood of the critical point of the more volatile component when the second component separates as the solid phase.

INTRODUCTION

Dalton's law of partial pressures is found to be inaccurate when it is applied to calculate the condensation temperature of a condensable component from a gas phase which contains indifferent gas at high pressure. The deviation from Dalton's law is usually much greater than that predicted by Poynting's equation (Poynting 1881; Porter 1907, 1908). This behaviour was recognized in the early studies of the critical phenomena of gases (Hannay & Hogarth 1880), but few quantitative measurements of the effect have been made.

Recent developments in the methods employed to eliminate carbon dioxide in the separation of air at low temperatures have prompted a comprehensive study of the influence of an indifferent gas (air) at pressures up to 200 atm on the apparent vapour pressure of solid carbon dioxide. The experimental technique employed in this work is described, and the results, which were obtained over the temperature range −110 to −196° C, are presented in detail. It has been found that the apparent vapour pressure of carbon dioxide under these conditions may be several hundred times its normal value. At the higher pressures and lower temperatures covered by the experiments the air was condensed within the apparatus. Under these circumstances the concentration of carbon dioxide in the condensed phase represented its solubility.

APPARATUS

The arrangement of the apparatus, which was designed to operate at a maximum pressure of 200 atm and a minimum temperature of −200° C, is shown in figure 1. The compressed air was first dried by passage through activated alumina and brought to equilibrium with solid carbon dioxide at the experimental temperature. It was then expanded to a pressure low enough to avoid condensing the air and cooled to the temperature of liquid oxygen. The carbon dioxide was precipitated and retained by a filter immersed in the liquid-oxygen bath. The air was finally expanded, heated to atmospheric pressure and temperature, and measured by passage through a rotary gas meter which had been previously calibrated. The carbon dioxide was subsequently displaced by warming the filter and passing through it a slow stream of purified air. From this the carbon dioxide was collected and weighed in a train of U-tubes containing soda asbestos and magnesium perchlorate. When the carbon dioxide concentration in the compressed air was reasonably high it became unnecessary to collect it in the liquid-oxygen trap, and it was absorbed directly in the soda-asbestos tubes.

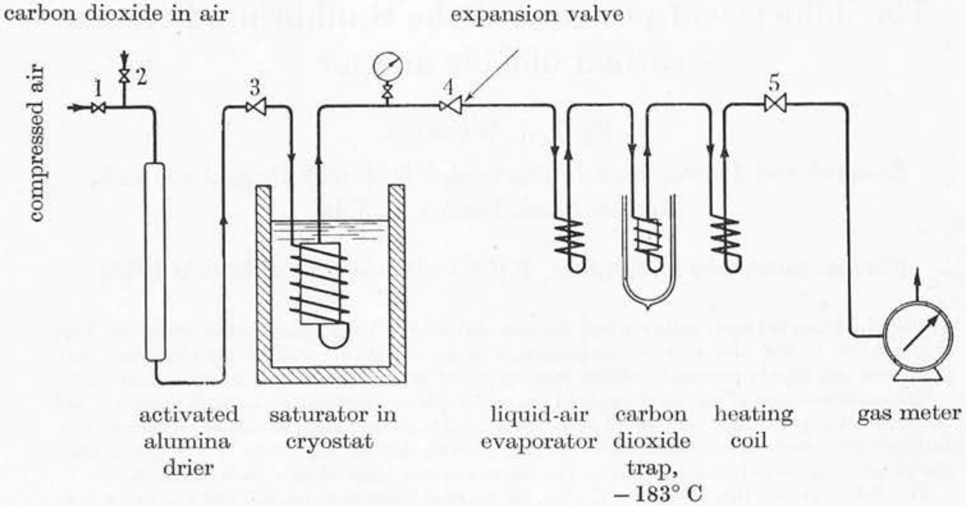


FIGURE 1. Line diagram of apparatus.

The saturator, or equilibrium vessel, consisted of a stainless steel coil, of 6 ft. total length, and 0·375 in. bore, followed by a vertical stainless steel tube of $\frac{1}{2}$ in. internal diameter filled with copper turnings and fitted at the outlet end with a filter consisting of a plug of tightly wound glass tape 1 in. wide. The complete assembly was immersed in a cryostat.

The cryostat consisted of a bath of liquid which was cooled by a stream of liquid nitrogen passing through a submerged coil at a controlled rate. The rate was adjusted to cool the bath slightly below the required operating temperature, and the cooling effect was compensated for by means of an electrical heater within the bath. The heater was controlled to maintain the required temperature by a relay system operated in the temperature range between −110 and −130° C by an ethylene vapour-pressure thermometer, and at lower temperatures by a gas thermometer. Different cryostat fluids were used according to the temperature to be maintained, and are listed in table 1. The temperature of the cryostat bath was measured with an accuracy within 0·1° by means of a calibrated copper-constantan thermocouple in conjunction with a Cambridge potentiometer reading to 0·003 mV.

TABLE 1

temperature (° C)	cryostat fluid
−110 to −130	5-component mixture of organic liquids (Scott 1941)
−140 to −145	petroleum ether (b.p. 40 to 60° C)
−150	liquid propane
−183	liquid oxygen boiling at 1 atm
−196	liquid nitrogen boiling at 1 atm

The supply of compressed air was obtained from a battery of three cylinders each of 2·0 cu.ft. actual capacity, and charged to a maximum pressure of 250 atm. The pressure within the saturator was measured by means of a Bourdon-type gauge reading to 400 atm and accurate within 0·8 atm.

The trap and filter used to collect the carbon dioxide from the air leaving the saturator consisted of a copper cooling coil followed by a brass tube 3 in. long containing six closely fitting felt plugs.

METHOD OF OPERATION

The method of operating the apparatus is described with reference to figure 1. Before starting an experiment the cryostat temperature was adjusted, and a quantity of carbon dioxide was condensed within the saturator by passing through it a stream of air laden with carbon dioxide. The carbon dioxide, diluted with air, was admitted through valve 2, and a quantity of several grams was introduced for each experiment. The air was allowed to escape to atmosphere through the carbon dioxide trap, which at this stage in the experiment was not cooled. Dry air was then slowly admitted to the saturator by opening valves 1 and 3, and as soon as the desired pressure had been reached the flow through the apparatus was set at the required rate by adjustment of valves 3, 4 and 5. The pressure in the saturator was maintained by adjusting valve 3, and the flow-rate was controlled by valve 4. After steady conditions had been maintained for about 15 min the experiment was started by simultaneously immersing the carbon dioxide trap in liquid oxygen and noting the reading of the gas meter. After each experiment the gas meter was replaced by the train of U-tubes used for collecting the carbon dioxide, and the carbon dioxide trap was gently warmed in a bath of water. Any carbon dioxide remaining as gas in the filter was displaced by a slow stream of purified air. The amount of carbon dioxide collected during the experiment was measured by weighing the U-tubes. To ensure that no trace of water or carbon dioxide entered the soda-asbestos tubes from the atmosphere they were followed in each experiment by protective tubes.

In those experiments in which the expanded air was passed directly into the absorbent tubes, a by-pass was fitted to ensure that no air passed through the tubes before starting the actual experiment.

DISCUSSION OF EXPERIMENTAL TECHNIQUE

The experiments described in this paper presented three major difficulties. First, it was necessary to ensure that the air in the saturator, which was in the form of compressed gas or liquid according to circumstance, achieved complete equilibrium with carbon dioxide at the fixed temperature and pressure, but emerged free from suspended particles of solid carbon dioxide. The second difficulty was to collect and measure accurately the carbon dioxide, which in many cases was in volumetric proportions of only a few parts per million in the expanded air. Thirdly, it was necessary to maintain accurate control of the cryostat temperature over a wide range.

The apparatus and methods which have been described were devised to overcome these difficulties, and proved very successful in practice. The activated alumina effectively dried the air and also removed from it all traces of oil and suspended impurities. Experiments in which air was passed through the saturator at different velocities gave consistent results. This established that equilibrium was attained within the saturator, and that carbon dioxide was not carried forward by entrainment. The capacity of the saturator coil was adequate to ensure that the air passing through it reached the temperature of the cryostat. This was proved by using the apparatus to measure the vapour pressure of carbon dioxide at atmospheric pressure. The results obtained were in close agreement with published values (*Handbook of chemistry and physics*).

The solubility of carbon dioxide in liquid air under pressure at -183 and $-196°$ C is very low. When the solution is evaporated and the gas is brought to room temperature the volume of gas necessary to give a weighable amount of carbon dioxide is large, and the carbon dioxide cannot conveniently be collected by passing the whole of the air through glass U-tubes packed with an absorbent mass. This difficulty was overcome by the use of the carbon dioxide trap and filter. Calculations based on published values of the vapour pressure of carbon dioxide indicated that the amount of carbon dioxide vapour in the air leaving the trap under low pressure at $-183°$ C would be negligible. No trace of carbon dioxide could be detected experimentally in the air leaving the filter.

The ethylene vapour-pressure thermometer and the gas thermometer employed to control the temperature of the cryostat were effective in maintaining the temperature of the cryostat within the accuracy of measurement, which was $\pm 0{\cdot}1°$ C. Liquid oxygen and liquid nitrogen boiling at atmospheric pressure were used in the cryostat to maintain the temperatures of −183 and −196° C respectively.

In the experiments carried out at −183 and −196° C sufficient air was passed through the apparatus to deposit between 25 and 50 mg of carbon dioxide in the carbon dioxide filter; at higher temperatures amounts up to 100 mg were collected.

RESULTS

The experimental results are given in table 2 and are depicted graphically in figure 2, which shows the relation between the molar fraction of carbon dioxide (x) in the equilibrium mixture, and the superimposed air pressure at different temperatures.

TABLE 2. EQUILIBRIUM MOLAR CONCENTRATION OF CARBON DIOXIDE IN AIR AT DIFFERENT TEMPERATURES AND PRESSURES

temperature (°C) ...	−110	−121	−130	−140	−145	−150	−183	−196
pressure (atm gauge)	equilibrium molar concentration of carbon dioxide in air (x) × 10^4							
				air in vapour phase				
0	456·0	113·0	30·4	5·67	2·21	0·80	—	—
10	49·2	12·8	4·19	0·77	0·30	0·10	0·12	0·002
20	33·6	8·65	2·92	0·62	0·32	0·13	0·11	0·002
30	28·1	8·33	3·54	0·87	0·67	0·55	—	0·002
40	28·5	9·33	5·19	5·46	4·15	3·8	—	—
50	30·6	12·2	7·39	7·21	5·81	4·3	—	—
60	36·5	15·1	13·1	7·82	6·16	—	0·12	0·003
70	43·3	22·2	17·1	8·65	6·88	—	—	0·004
80	52·9	28·0	18·8	9·79	6·70	4·78	0·11	—
90	61·0	34·7	—	—	—	—	—	—
100	69·5	39·0	22·9	12·0	7·14	4·86	0·12	0·002
150	94·9	52·0	27·3	13·9	7·69	5·50	0·13	—
200	123·0	58·1	30·2	15·3	8·49	5·90	0·14	0·003
						air in liquid phase		

For temperatures from −110 to −130° C each value of x is the average of six experimental determinations among which the standard deviation was less than 2·0%; at the saturation temperatures −140, −145 and −150° C the results showed a standard deviation between 5 and 10 %. The values given for the temperatures −183 and −196° C were obtained from single experiments. The values of x at atmospheric pressure were computed from published data concerning the vapour pressure of carbon dioxide (*Handbook of chemistry and physics*). A line is drawn in table 2 to indicate the division between cases in which the air was in the liquid and vapour phases respectively under the conditions of experiment.

According to Dalton's law of partial pressures the molar fraction of carbon dioxide in the vapour phase should be expressed by

$$x = \frac{p_s}{P},$$

in which p_s is the saturated vapour pressure of carbon dioxide at the temperature of experiment, and P is the total pressure. If this rule were obeyed the curves of figure 2 should be rectangular hyperbolae asymptotic to the pressure axis. Considerable deviations are evident, and it is convenient to express the deviation by means of a factor (F) defined by $F = Px/p_s$, which is the ratio of the real and ideal molar concentrations.

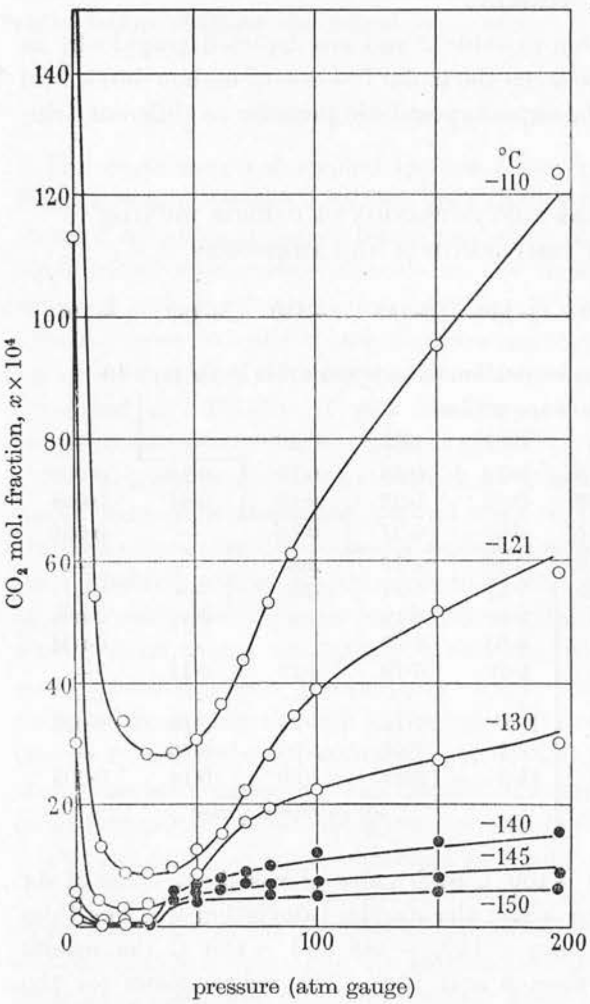


FIGURE 2

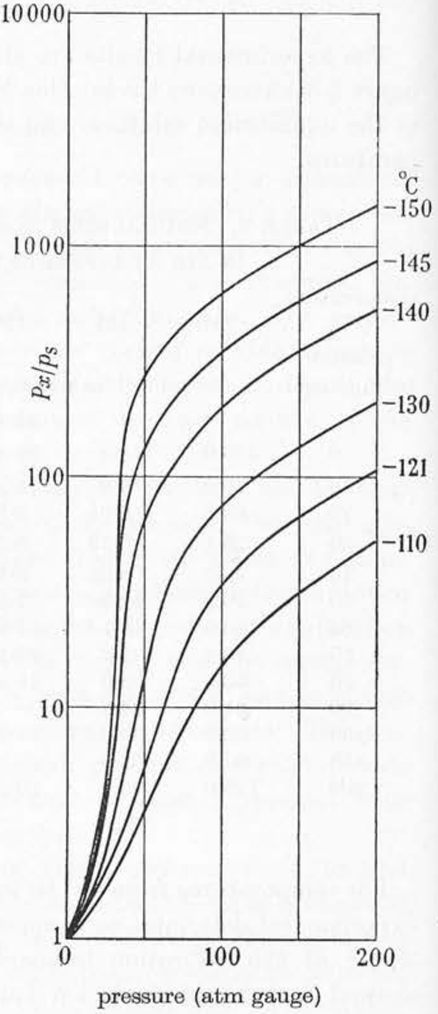


FIGURE 3

FIGURE 2. Equilibrium concentration of carbon dioxide in air in relation to pressure. ○, air in gaseous phase; ●, air in liquid phase.

FIGURE 3. Relative carbon dioxide vapour pressure against superimposed pressure.

The calculated vapour-pressure factors are given in table 3 in comparison with those obtained by Gratch (1946) which are shown in brackets. The normal vapour pressure of carbon dioxide (p_s) is expressed in millimetres of mercury, and the values were derived from published data (*Handbook of chemistry and physics*).

The relation between the logarithms of the vapour-pressure factors given in table 3 and the superimposed air pressure at different experimental temperatures is shown in figure 3.

TABLE 3. DEVIATION OF CARBON DIOXIDE IN AIR FROM DALTON'S LAW

temperature (°C)...	−110	−121	−130	−140	−145	−150
saturated vapour pressure of carbon dioxide (mm of Hg) ...	34·63	8·57	2·31	0·431	0·168	0·060
total pressure (atm)			factor $F = Px/p_s$			
10	1·19	1·25	1·50	1·50	1·5	1·4
20	1·55	1·61	2·02	2·3	3·0	3·4
30	1·92	2·28 (2·6)	3·61 (3·3)	4·8 (4·6)	9·4 (6·6)	21·3
40	2·6	3·4 (3·9)	7·0 (6·0)	39·5	78·0	195
50	3·4	5·5 (5·5)	12·4 (10·0)	65·0	134	275
60	4·9	8·2	26·3	84·0	169	—
70	6·7	14·0	40·0	108	220	—
80	9·4	20·1	50·1	140	245	485
100	15·4	34·9	76·1	215	327	611
150	31·2	69·2	136	370	527	1040
200	54·0	103·0	200	542	775	1481

Graphs showing the relation between the measured concentration of carbon dioxide in the fluid phase x and the saturation temperatures at different pressures (in atmospheres) are shown in figure 4.

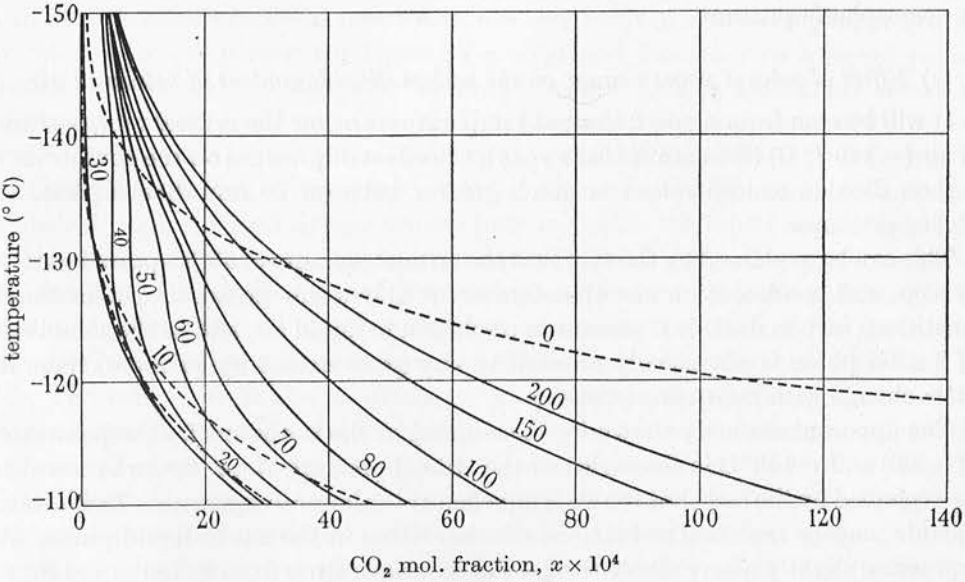


FIGURE 4. Relation between equilibrium concentration of carbon dioxide in air and temperature.

DISCUSSION OF RESULTS

(a) *The effect of pressure on carbon dioxide vapour pressure*

It can be seen from the results plotted in figure 3 that the apparent vapour pressure of carbon dioxide is increased when the solid is in contact with a compressed gas, and that this increase becomes progressively greater as the temperature falls and as the superimposed air pressure is increased. Similar behaviour has been observed by Gratch (1946), who measured the concentration of carbon dioxide in the vapour phase at different temperatures under superimposed air pressures up to 50 atm. Where comparison is possible there is, in general, good agreement between corresponding values (see table 3), the only significant discrepancies occurring at the temperatures −130 and −145° C at pressures of 50 and 30 atm respectively. It is interesting to note that the vapour pressure of solid carbon dioxide at −150° C is increased to more than a thousand times its normal value in presence of air at 200 atm.

(b) *The effect of pressure on carbon dioxide concentration in air*

It can be seen from figure 2 that at total pressures above 20 to 30 atm the molar fraction of carbon dioxide in the saturated air increases as the pressure of the system is increased. This means that in contrast with normal behaviour increasing compression would cause evaporation of the carbon dioxide instead of condensation.

At the saturation temperature −130° C the carbon dioxide content of air compressed to 200 atm is approximately equal, as a result of the pressure effect, to the saturation value in the absence of air pressure. At lower temperatures the carbon dioxide content of air saturated at 200 atm exceeds the normal saturation value at atmospheric pressure.

(c) *Effect of solvent phase change on the carbon dioxide content of saturated air*

It will be seen from figure 2 that, at temperatures below the critical temperature of air (−140·7° C) (Keunan & Clark 1917), the effect of pressure on the equilibrium carbon dioxide concentration is much greater between 30 and 40 atm than at higher pressures.

This can be explained by the fact that the critical pressure of air is approximately 37 atm, and condensation can therefore occur above this pressure. Under these conditions carbon dioxide is present as a solution in liquid air, and as the solubility of a solid phase is not usually affected to any great extent by pressure, there is little change with increasing pressure.

The apparent anomaly shown by the crossing of the isotherms for temperatures of −130 and −140° C in the region of the critical pressure of air (figure 2) can also be explained by the fact that the air is liquefied at the lower temperature. The carbon dioxide may be regarded as being in solution either in the gas or liquid phase. At a pressure slightly above the critical, a fall in temperature from −130 to −140° C is accompanied by condensation. As carbon dioxide is more soluble in the liquid than in the gas phase the effect of decreasing temperature on solubility will be more than compensated for by that due to change of phase. The condensation pressure falls with temperature, and the pressure at which consecutive isotherms intersect therefore becomes lower as the temperature falls. The isotherms for −150 and −183° C intersect at a pressure of about 6 atm.

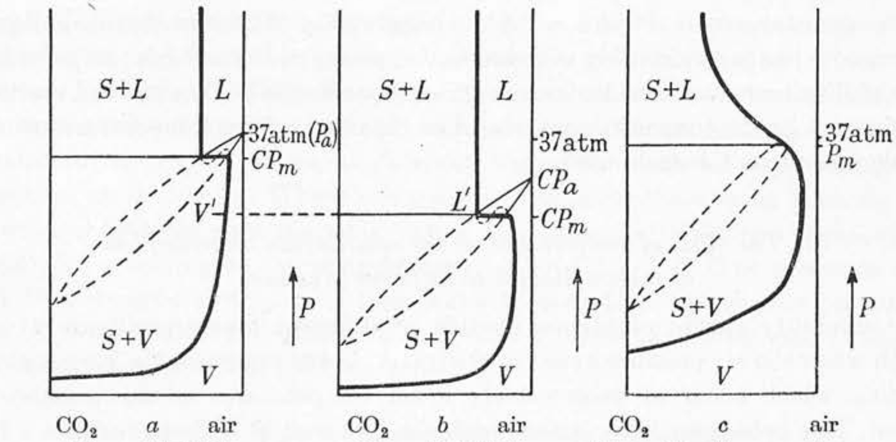
At temperatures of −183 and −196° C the solubility of carbon dioxide in liquid air does not change appreciably with increasing pressure, but at high temperatures the solubility increases. The isotherms at −183 and −196° C have been omitted from figure 2, as the concentrations of carbon dioxide at these temperatures would be insignificant on the scale used.

(*d*) *The effect of temperature on the equilibrium concentration of carbon dioxide at different pressures*

The solubility curves of carbon dioxide at different pressures (figure 4) are smooth when the air pressure exceeds 90 atm. At lower pressures the curves show inflexions which occur at progressively lower temperatures as the pressure is reduced. This behaviour is consistent with the fact that at higher pressures a fall in temperature below −140° C produces no discontinuous phase change of the air, whereas at pressures below the critical (37 atm) there is a discontinuous phase change accompanied by an increase in the carbon dioxide concentration owing to solution in the liquid phase. At pressures below 20 atm the condensation temperature would fall below −150° C, and the inflexion of these isobars, if it occurs, is outside the range of the diagram.

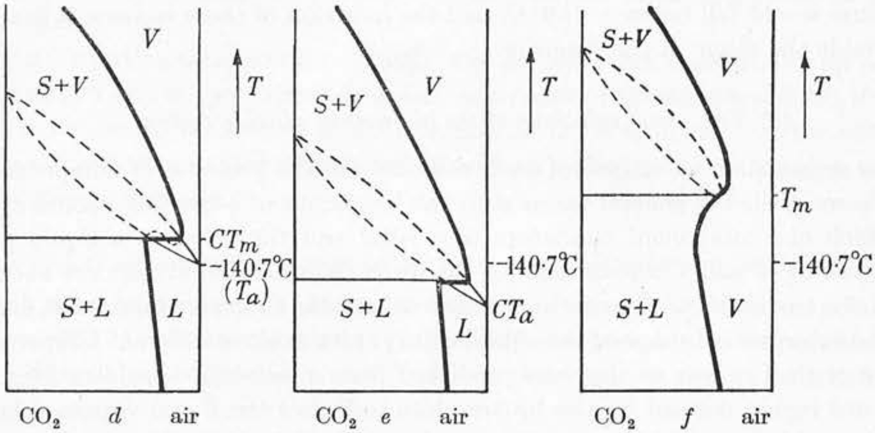
(*e*) *The phase relations of the air/carbon dioxide system*

The remarkable behaviour of carbon dioxide in the presence of compressed air can be reconciled in general terms with the behaviour of a two-component system in which one component condenses to a solid and the other to a liquid phase. Schematic P-x and T-x diagrams for the air/carbon dioxide system are shown in figure 5 *a* to *c* and *d* to *f* respectively. The schematic diagrams (figure 5 *a*, *b* and *c*) indicate the general shape of the equilibrium curves at three different temperatures in the critical region as they are predicted from phase-rule considerations. The elliptical region defined by the broken lines indicates the liquid-vapour relations which would occur if there were no separation of solid phase. Clearly, each curve representing the equilibrium of the solid phase (shown by thickened lines) will have a definite point of inflexion at the condensation pressure of the air/carbon dioxide mixture, the critical pressure of the mixture being slightly below that of air. The behaviour as the temperature of the system is reduced is indicated by figure 5, graphs *c*, *a* and *b* consecutively. The inflexions in the different equilibrium curves will occur at progressively lower pressures as the condensation pressure falls. Above the critical temperature of the mixture no liquid will be formed as the pressure on the system is increased; inflexions will still occur, however, in the equilibrium isotherms, but with increasing temperature they will tend to become less marked and they will occur at progressively higher pressures. Figure 5, graphs *a* and *b*, illustrate the possibility that air saturated at a given temperature may contain more carbon dioxide than air saturated at a higher temperature but at the same pressure, the liquid L' in figure 5b having a higher carbon dioxide content than the vapour V' in figure 5a.



$T = -140{\cdot}7^\circ$ C (critical temperature for air) $T < -140{\cdot}7^\circ$ C T = critical temperature of mixture ($> -140{\cdot}7^\circ$ C)

P_a, P_m, critical pressures of air and mixture;
CP_a, CP_m, condensation pressures of air and mixture.



$P = 37$ atm $P < 37$ atm $P > 37$ atm

T_a, T_m, critical temperatures of air and mixture;
CT_a, CT_m, condensation temperatures of air and mixture.

FIGURE 5

The experimental P-x curves in figure 2 show all the characteristics described above, and these considerations show that their behaviour is consistent with phase-rule theory.

The T-x diagrams (figure 5, graphs d, e and f) show that the equilibrium curves will have an inflexion at the condensation temperature of the mixture, which at 37 atm will be slightly above the critical temperature of air. The temperature at which the inflexion occurs will be inversely related to the pressure. At pressures considerably above the critical pressure for air the equilibrium curves will tend to become continuous. All these characteristics are shown by the experimental T-x curves in figure 4.

General

The remarkable solvent ability of gases under pressure was recognized in the early studies of the critical phenomena of gases. Hannay & Hogarth (1880) showed that a solution of potassium iodide in alcohol could be heated above the critical temperature of the alcohol without the precipitation of the involatile potassium iodide. Recently it has been shown by Diepen & Scheffer (1948) that the concentration of naphthalene in ethylene vapour compressed to 100 atm at 12° C is 25600 times as great as the value based on Dalton's law and the normal vapour pressure for naphthalene. The apparent vapour pressure of ice at -35° C in the presence of air at 200 atm has been shown to be more than three times its normal value at atmospheric pressure (Webster 1950).

Clearly the effect of compressed inert gas in increasing the apparent vapour pressure of a solute of low volatility is common to many systems in addition to that described in this paper. The magnitude of the effect cannot be predicted quantitatively, but it is qualitatively consistent with normal phase relations.

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THE EFFECT ON WATER VAPOUR PRESSURE OF SUPERIMPOSED AIR PRESSURE

By T. J. WEBSTER

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THE EFFECT ON WATER VAPOUR PRESSURE OF SUPERIMPOSED AIR PRESSURE

By T. J. WEBSTER

In a compressed gas saturated with water vapour the vapour pressure of the water exceeds the normal value by an amount which is greater than can be predicted by Poynting's thermodynamic relationship. A quantitative knowledge of this behaviour is important in the design of equipment for drying compressed gases, particularly for drying by refrigeration, which is commonly used in the low-temperature separation of air.

The equilibrium moisture-content of compressed air at pressures from atmospheric to 200 atm. has been experimentally determined at temperatures between 15° C. and − 35° C. It has been found that the vapour pressure of water and ice increases progressively as the total pressure on the system is increased and that the relative increase in vapour pressure at a particular pressure becomes greater as the temperature of the system is lowered. At a total pressure of 200 atm. and a temperature of − 35° C. the water content of saturated air is more than three times the calculated value assuming the normal vapour pressure and 2·6 times that derived from Poynting's relationship.

Many industrial drying processes involve the removal of moisture from air or gas which is highly compressed. It has been demonstrated both theoretically and experimentally that, at high pressures, the concentration of water in the vapour phase at saturation point is greater at any particular temperature in the presence of an inert gas than it would be in its absence.

It is therefore necessary in deciding the performance of high-pressure drying equipment to know the magnitude of the effect of inert-gas pressure on water-vapour pressure.

The theoretical increase in the vapour pressure of water when the liquid is subjected to an increasing pressure can be calculated by Poynting's thermodynamic relation[1, 2]:

$$\left[\frac{\mathrm{d}p}{\mathrm{d}P}\right]_T = \frac{V_L}{V_G}$$

Where p is the vapour pressure of the liquid, P is the total pressure on the liquid, and V_G and V_L are the molal volumes of vapour and liquid under pressures p and P respectively.

It has been shown however that the increase in vapour pressure predicted by this equation is usually much less than that found by experiment. Superimposed on the pressure effect there appears to be a solvent effect of the indifferent gas.[3]

Previous workers[4–6] have measured the increase in vapour pressure at temperatures above atmospheric, but no information has been published concerning the effect at lower temperatures. In the separation of air by low-temperature fractionation it is necessary to dry the air very thoroughly in order to avoid obstruction of the heat exchangers and other parts of the equipment by ice deposits. The pressures used in these processes vary between 15 and 200 atm. and the method most frequently used for removing the last traces of water is to cool the air, after compression, to a temperature at which the residual vapour pressure of water becomes negligible. The work described in this paper was undertaken in order to provide information for the design of refrigeration-drying systems of this type. The means employed was to measure by a dynamic method the water content of air saturated with water vapour at a fixed temperature and total pressure. The range of temperature covered was from 15° C. to − 35° C., and the air pressure was varied between atmospheric pressure and 200 atm. (gauge).

Apparatus

The apparatus consisted of a saturator in which air at a fixed temperature and pressure was saturated with water vapour followed by an analytical train for the purpose of estimating the water content of the saturated air.

A line diagram of the apparatus is shown in Fig. 1; detailed sketches of the saturator and the ice filter used in the moisture analyses are given in Figs. 2 and 3 respectively. The compressed air was first dried and purified by passage through a vessel containing activated alumina. It was then passed through the saturator which consisted of a mild-steel coil ($\frac{3}{16}$ in. I.D. and 8 ft. long) fitted internally with a cotton tape moistened with water. The coil was followed by a mild-steel tube ($\frac{1}{2}$ in. I.D. and 6 in. long) packed with copper rivets to ensure temperature equilibrium, and to separate any entrained water. The coil and filter tube were totally immersed in a bath of methanol, the temperature of which was kept constant by the controlled addition of solid carbon dioxide. A calibrated alcohol thermometer was used to measure the temperature of the methanol. The gas pressure was measured by means of a Bourdon-type gauge reading to 400 atm. and accurate to within 0·8 atm. The water contained in the air leaving the saturator was collected by passing the compressed gas through cold traps fitted with filters and totally immersed in a bath of trichloroethylene cooled with solid carbon dioxide to a temperature of − 80° C. This water was subsequently displaced by a stream of warm dry air at atmospheric pressure and absorbed by phosphorus pentoxide. The quantity of water was estimated by weighing the tubes containing the phosphorus pentoxide before and after absorption.

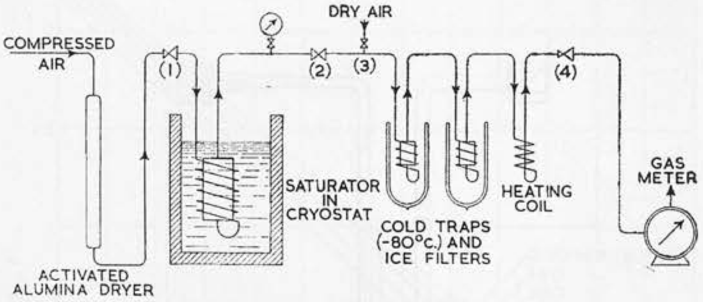

FIG. 1. *Line diagram of apparatus*

The cold traps consisted of metal cooling-coils, and the filters were each packed with six closely-fitting fibre plugs. After

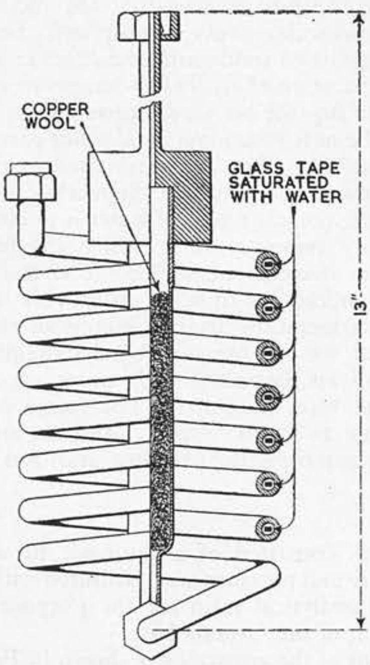

FIG. 2. *Detail of saturator*

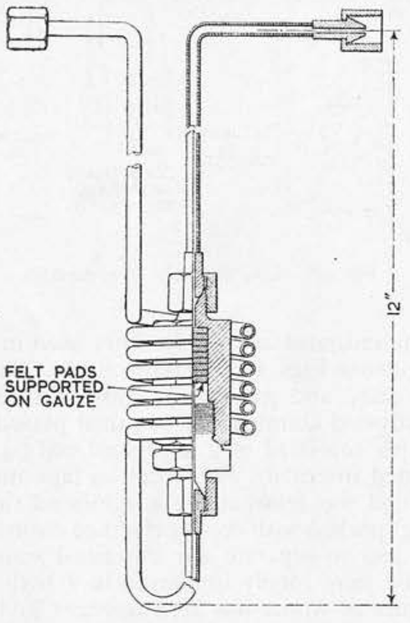

FIG. 3. *Detail of ice filter*

the second filter the compressed air was passed through a heating coil; then it was expanded through a valve to atmospheric pressure, and it was finally measured with a dry gas-meter. The air supply was obtained from a battery of three high-pressure cylinders each of 2-cu.ft. actual capacity.

Method of operation

The method of operation is described with reference to Fig. 1. Before starting an experiment the ice filters were immersed in a bath of hot water and thoroughly dried by a stream of dry air introduced at (3), after valve (4) had been fully opened. All the valves were then shut, the ice filters were immersed in the baths of trichloroethylene cooled with solid carbon dioxide, and the cryostat was adjusted to the temperature of the experiment. Dry air was admitted to the saturator by opening valve (1). As soon as the pressure gauge indicated that the desired pressure had been reached the flow of gas through the apparatus at that pressure was set at the required rate by slowly opening valve (2) and carefully adjusting the needle-valve (4). The pressure required in the saturator was maintained by adjustment of valve (1). The capacity of the saturator was adequate to ensure that the air passing through it reached the temperature of the cryostat. The volume of air passing through the saturator was measured on the dry gas-meter after it had expanded to atmospheric pressure. After each experiment the ice filters were immersed in hot water and the dry gas-meter was replaced by a weighed P_2O_5 tube. The moisture was then removed from the filter elements by evaporating it in a stream of dry air, introduced at (3), from which it was absorbed in the P_2O_5 tube and weighed.

Experiments were carried out at saturation temperatures of + 15·0°, 0°, − 20° and − 35° C. under superimposed air pressures up to 200 atm.

Discussion of experimental technique

The chief difficulties in technique presented by these experiments were first, to ensure that the compressed air was fully saturated with water vapour at the required temperature, but free from suspended particles of water or ice; and secondly, to estimate the water vapour in the saturated gas with a high degree of accuracy. The first difficulty was overcome by the use of cotton tape in the saturator coil, which provided a large surface of contact with the gas, even when the water with which it was impregnated was frozen. It was established, by experiments at different air velocities, which gave consistent results, that this device also prevented entrainment. The accuracy of the experimental method was proved by measurements of the vapour pressure of water at atmospheric pressure which gave results in close agreement with accepted values.

At low temperatures and high pressures the moisture content of saturated air is so low that a large quantity of air is necessary to contain a weighable amount of water. If the air were expanded before attempting to remove this water by absorption, the time required for the treatment of a suitable quantity of air with P_2O_5 would be very long, or the size of the P_2O_5 tubes would be excessive. This difficulty was avoided by freezing out the water before expanding the air, and subsequently displacing the water at low pressure. The loss of water vapour in the compressed air leaving the cold traps at − 80° C. was negligible, and no trace of water could be detected in the air after passage through the filters, in tests carried out both at high and low pressures.

In the low-temperature experiments sufficient air was passed through the apparatus to deposit 50–100 mg. ice in the ice filters; at higher temperatures up to 200 mg. ice was collected in each experiment. It was found by experience that a slow stream of dry air flowing for about 20 min. was sufficient to evaporate all the water from the ice filters. In the actual experiments the air was allowed to flow for 30 min.

Theoretical

In deciding the effect of superimposed pressure on the water concentration in the vapour phase the compressibility of the inert atmosphere must be taken into account at high pressures.

The compressibility factor K is defined by the expression:

$$P_sV_s = KRT_s$$

in which the subscript s refers to the compressed inert gas. The gas, when expanded to atmospheric pressure, may be assumed to obey the perfect-gas laws, and the effect of water vapour on the compressed volume may be neglected.

The relation between the volumes of gas before and after expansion is thus

$$\frac{P_sV_s}{P_0V_0} = \frac{KT_s}{T_0}$$

If pressures are expressed in atmospheres (absolute) and $P_0 = 1$ atm.

$$V_s = \frac{KT_s\,V_0}{P_sT_0}$$

and the concentration of water vapour in the compressed gas is

$$x = \frac{M}{V_s} = \frac{M\,P_sT_0}{KT_s\,V_0}$$

in which x is the weight (mg.) of water per litre of compressed gas at temperature T_s, M is the weight (mg.) of water collected and V_0 is the measured volume of gas after expansion to 1 atm. (absolute) at temperature T_0.

The effect of the superimposed gas pressure on the concentration of water in the vapour phase may be expressed by the ratio x/x_0, in which x_0 is the concentration of water in the vapour phase at a temperature T_s above pure water (or ice) under its own vapour pressure, in mg./l. Values of K and x_0 have been obtained from published data.[7, 8]

Results

The results and the calculated vapour-pressure factors are given in Table I. Each of the factors is derived from the average of six experimental determinations of x which showed a standard deviation of less than 2% in the experiments carried out at 0° C. and at 15° C., and of less than 4% in the experiments carried out at the lower temperatures. A column has been included showing the factors obtained by Pollitzer and Strebel, who studied the effect of air pressure on the vapour pressure of water at 50° C. The figures given in brackets at the foot of Table I show the factors at 200 atm. calculated from the Poynting relation.

Table I

Factors (x/x_0) found by experiment

Temperature x_0*	− 35° C. 0·2052	− 20° C. 0·8866	0° C. 4·849	+ 15° C. 12·80	+ 50° C.† 82·77
Pressure, atm.	Factor (= x/x_0)				
25	—	—	—	1·10	—
50	1·60	1·36	1·24	1·19	1·14
75	—	—	—	1·29	—
100	2·17	1·82	1·48	1·36	1·28
150	2·92	2·24	1·78	1·58	1·42
200	3·14	2·39	2·01	1·77	1·56
200 (Poynting)	(1·20)	(1·19)	(1·17)	(1·16)	(1·14)

* x_0 is expressed as mg./l. water in saturated vapour in the absence of air pressure. Calculation is assisted by the fact that the vapour pressure of water in mm. of mercury is numerically equal to the concentration of water expressed as mg./l. at 16° C. and 760-mm. pressure.

† The results at 50° C. are those of Pollitzer and Strebel.[4]

Graphs showing the relation between the experimentally determined vapour-pressure factors and the superimposed air pressure at the different experimental temperatures are given in Fig. 4.

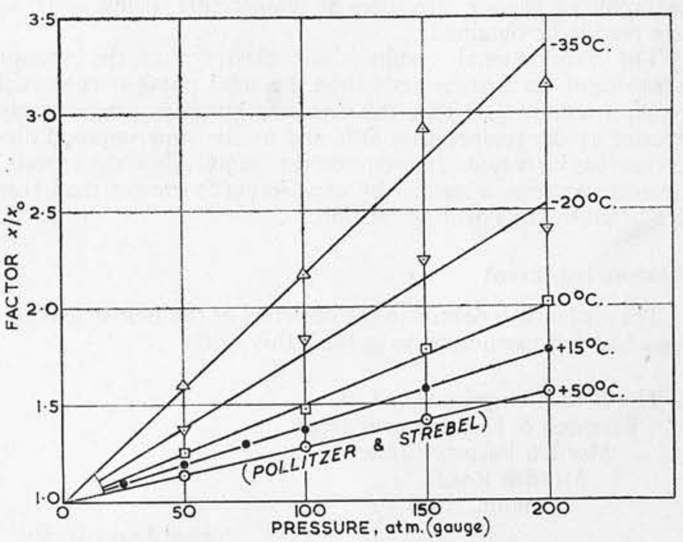

FIG. 4. *Relation between water vapour pressure and superimposed pressure*

Graphs showing the plot of the logarithm of the vapour pressure against the reciprocal of the absolute temperature at different pressures are given in Fig. 5; the values on which these graphs are based were taken from Fig. 4. Inert-gas pressures are given in atmospheres (gauge), and the water vapour pressure p is defined by

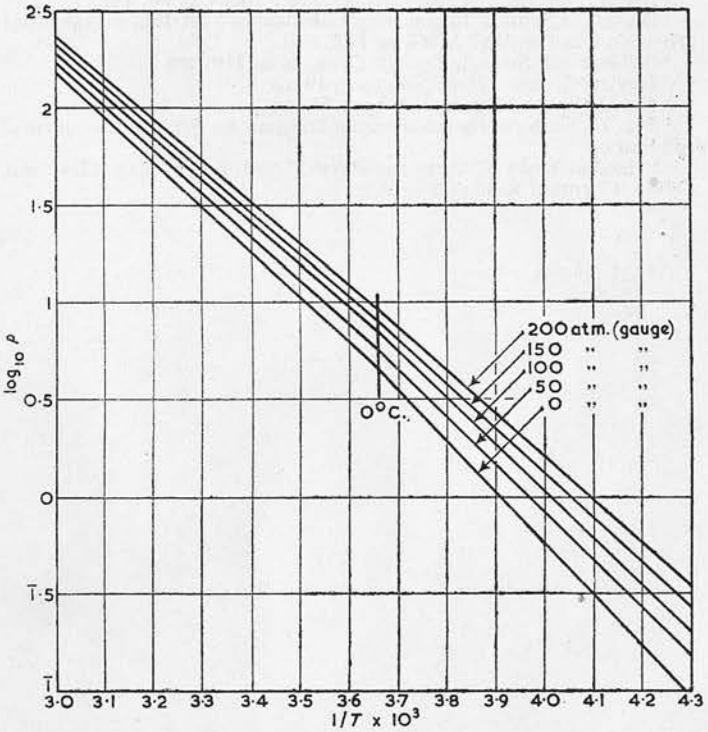

FIG. 5. *Relation between water vapour pressure and temperature at different total pressures*

$$p = \frac{x}{x_0}\cdot p_0$$

where p_0 is the normal vapour pressure of water or ice.

Straight lines are obtained when the logarithm of the actual vapour pressure at temperature T, computed from the values in Fig. 4, is plotted against the reciprocal of the absolute temperature at particular pressures. By extending these lines extrapolated vapour pressures at temperature below − 35° C. can readily be obtained.

The experimental results show clearly that the vapour pressure of ice is increased when the solid phase is subjected to air pressure and that this increase becomes progressively greater as the temperature falls and as the superimposed air-pressure is increased. In each case the magnitude of the vapour-pressure increase obtained by experiment is greater than that predicted by the Poynting relation.

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