Summary

The excess of iodine formed when pentavalent vanadium is reduced by iodide ion to the tetravalent state in the presence of oxygen of the air, has been shown to be appreciable (from 1.0 to 2.5%) in solutions having approximately the following concentrations: of iodide, from 0.6 to 2.0 *N;* sulfuric acid, from 1 to 4 *N;* vanadate, from 0.053 to 0.062 *N* (corresponding to 0.0772 to 0.136 g. of vanadium pentoxide used in these experiments).

From these results, and those obtained by others who have studied the iodimetric method for determining vanadium, it is concluded that under no conditions of acid, iodide and vanadium concentrations so far studied is the catalytic effect of pentavalent vanadium on the oxidation of iodide ion by oxygen negligible, and that therefore the iodimetric method of determining vanadium will not give accurate results under these conditions, when carried out in the presence of oxygen.

A simple and rapid method for carrying out the iodimetric determination of vanadium with oxygen excluded has been developed. The results obtained by this method have been shown to agree within 0.1% of those given by recognized standard methods for determining vanadium. The time required for a complete determination by this method is approximately 15 minutes.

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EQUILIBRIUM PRESSURES OF A GAS IN A MIXTURE, ESPECIALLY OF AMMONIA MIXED WITH NITROGEN

By Eli Lurie and Louis J. Gillespie

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Introduction

A knowledge of the equilibrium pressures of individual gases in mixtures of gases and a method for the calculation of these pressures from the composition, pressure and temperature of the mixture are of theoretical and practical importance, the term equilibrium pressure of a gas in a mixture being defined as the pressure of the pure gas in equilibrium with the mixture through a semi-permeable membrane, the entire system being at constant temperature.

In Fig. 1, the pressure, p_1, of pure ammonia in Compartment I, when equilibrium subsists, is the equilibrium pressure of ammonia in the mixture. If we had a real membrane semi-permeable to ammonia we could easily determine by means of this apparatus the composition of different mixtures (under different total pressures, P) in Compartment II which have the same equilibrium pressure of ammonia. The constancy of the pressure p_1, would be secured by suitable adjustment of the piston A.

Lacking a real membrane we can, nevertheless, reach the same objective[1] by making use of the fact that the decomposition pressure of a univariant system is fixed by the temperature. We can, therefore, use such a system as $BaCl_2 + BaCl_2.8NH_3$, to impose on different gaseous mixtures of ammonia and nitrogen the same equilibrium pressure of ammonia. The value of this pressure is determined by an experiment in which only ammonia is present in the gas phase.

We have determined the compositions and total pressures of various mixtures of ammonia and nitrogen in equilibrium with $BaCl_2 + BaCl_2.8NH_3$ at a temperature of 45° from a mixture of 15 mole % of ammonia and a pressure of 60 atm. down to pure ammonia and the decomposition pressure of 7 atm.

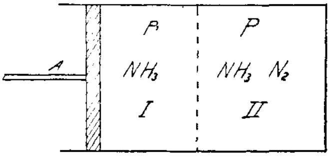

Fig. 1.

The constant value of the equilibrium pressure of ammonia in the mixtures will later be regarded as the measured equilibrium pressure for the mixtures studied and will be compared with values of the equilibrium pressure calculated thermodynamically by the use of several hypotheses.

The foregoing treatment requires a small correction which, of course, was made in all calculations, namely, the equilibrium pressure of ammonia over $BaCl_2 + BaCl_2.8NH_3$ is not quite the same in contact with the different gaseous mixtures, but varies slightly with the total pressure in the same way that the vapor pressure of a solution varies with the external pressure.

Recently, two experimental papers[2,3] have appeared in which the composition of a mixed vapor over a liquid in equilibrium with the vapor was determined; and still more recently the experiment actually proposed has been described by McHaffie,[4] evidently without knowledge of a previous publication.[1] He observed experimental anomalies so striking that neither he nor we have ventured to interpret them.

The work of Pollitzer and Strebel and of Larson and Black shows that the equilibrium pressure of a real gas in a mixture may be far from equal to the product, mole fraction times total pressure. Furthermore, this product is always greater than the equilibrium pressure, even when the latter is corrected for the effect of total pressure upon vapor pressure.

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[1] Gillespie, This Journal, **47**, 305 (1925).

[2] Pollitzer and Strebel, *Z. physik. Chem.*, **110**, 768 (1924).

[3] Larson and Black, This Journal, **47**, 1015 (1925).

[4] McHaffie, *Phil. Mag.*, [7] **1**, 561 (1926).

Since there is a greater concentration of evaporated gas in the gas mixture than is found when evaporation takes place into a vacuum, the inert gas is said to have a solvent effect. Only positive solvent effects have been observed (except for the anomalous results of McHaffie). Unless the experimental conditions are especially chosen for the purpose, it is very difficult to give numerical interpretations of such experiments. We have attempted below to do so only for our own experiments and for one series described by Pollitzer and Strebel.

Theoretical Considerations

Very little theory has been brought to bear on this topic. All experimenters have applied the Poynting relation for the effect of external pressure on vapor pressure, thus accounting for only a fraction of the observed effects. The use of this relation when the vapor (or decomposition) pressure is due to more than one condensed phase has been justified by brief reference[1] to the Gibbs theory.

Gibbs considered the problem[5] of equilibrium pressures of real gases in mixtures and suggested a modification of Dalton's law which could possibly hold for real gases, since it placed no thermodynamic restriction on the equations of state of the (pure) gases involved. In brief, the suggestion is: the sum of the equilibrium pressures of the individual gases in a mixture is equal to the total pressure, in which case Gibbs shows that the density of any one of the pure gases in equilibrium with the mixture through a semi-permeable membrane must be equal to its "density" in the mixture (that is, the number of moles of the gas in question divided by the total volume). We describe below a test of this suggestion made by the use of our data.

Gibbs evidently perceived a proposition which he did not state, and which has escaped the observation of subsequent writers. This proposition is: if Dalton's law holds (for various values of the variables) in the form, the equilibrium pressure of any gas in a mixture equals the product of its mole fraction times the total pressure, then the laws of Boyle and of Avogadro must hold for the pure gases present in the mixture.[6]

To show this proposition we note first that the sum of the equilibrium pressures is equal to the total pressure.

Therefore Gibbs' proof[5] can be used to show that the density of the pure gas on one side of the semi-permeable membrane is equal at equilibrium to the "density" of the same species in the mixture.

[5] Gibbs, "Thermodynamics," Longmans, Green and Co., New York, **1906**, p. 157.

[6] From a kinetic standpoint this may appear obvious. One should note, however, that the converse proposition is not true, in consequence of which the laws of Boyle and of Avogadro do not express enough of the ideal gas laws to permit a derivation of the mass-action law.

Let now the gas mixture whose pressure and volume are P and V be made up of n'_1, n'_2, n'_3, etc., moles of various gaseous species and be contained in a vessel with appropriate semi-permeable membranes denoted by broken lines in Fig. 2. Let n_1 moles of pure gas 1 under a pressure p_1 in a volume v_1 be in equilibrium across the membrane with the n'_1 moles in the mixture, and similarly for the other species. The temperature is the same, and constant throughout. We have then

$$p_1 = Pn'_1/\Sigma n'_1 \qquad (1)$$

$$v_1/n_1 = V/n'_1 \qquad (2)$$

$$p_1v_1/n_1 = PV/\Sigma n'_1 \qquad (3)$$

Equation 3 must hold for equilibrium variations of the variables not excluded by these equations. A possible equilibrium variation is a change in n'_1 compensated by such variations of the moles of the other gases in the mixture as will leave $\Sigma n'_1$ unchanged. P and V are held constant. The relation between the pressure and the volume is then

$$p_1v_1/n_1 = \text{constant} \qquad (4)$$

Since none of Gas 1 has crossed the membrane, this must be the relation for a gas confined in an ordinary cylinder. Equation 4 includes, therefore, the law of Boyle. Furthermore, the constant of the right-hand side of 4 is evidently independent of the identity of Gas 1. Therefore, Equation 4 includes the law of Avogadro.

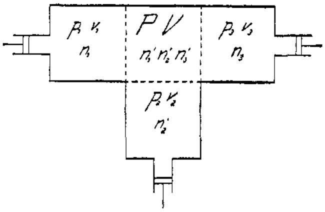

Fig. 2.

It follows that the hypothesis $p_1 = Px_1$, where x_1 is written for mole fraction, is thermodynamically inconsistent with all equations of state except the perfect gas law.

We note further that no special explanation needs to be invented to account for the fact that the concentration of vapor over a liquid is not the same in the presence of an "inert" gas as would be expected if the inert gas acted only as a piston to apply increased pressure upon the liquid. This fact is a necessary consequence of the fact that the laws of Boyle and of Avogadro fail at the experimental pressures.

Gibbs' general treatment furnishes differential equations which can be applied to calculate equilibrium pressures, or mass-action expressions, if we assume simple limiting equilibrium conditions, and if we have data or assumed relations for the pressure-volume-temperature behavior of gaseous mixtures. Thus, assuming that at sufficiently low pressures the equilibrium pressure of a gas in a mixture approaches the mole fraction-total pressure product the following equation has been deduced:[1]

$$RT\ ln\ f_e = \int_0^P (\partial V/\partial n_1 - v_1)dP + RT\ ln\ f_{P}x_1 \qquad (5)$$

where f_e = fugacity of Gas 1 in the mixture, P = total pressure of the mixture, v_1 and f_P are the molal volume and fugacity of the pure gas 1 at the pressure and temperature of the mixture, and x_1 = mole fraction of Gas 1 in the mixture.

In order to apply this equation, it is necessary to know or assume something as to the partial volume $\partial V/\partial n_1$ of the gas 1 in the mixture at the pressure P. An equation of state for mixtures would contain sufficient information; such equations are, however, not yet known. The fact seems to be that the effect of pressure on chemical equilibrium may be calculated with considerable accuracy by the use of an assumption regarding $\partial V/\partial n_1$ only approximately true.

The simplest assumption is that $\partial V/\partial n_1 = v_1$. This means that the volumes of real gases are additive at constant pressure and temperature (which is known to be inexact) and leads at once to Equation 6, which expresses a rule given by Lewis and Randall.[7]

$$f_e = f_P x_1 \qquad (6)$$

The application of this rule requires an equation of state for the pure gas holding approximately up to the pressure of the mixture. This means a very severe extrapolation when the system is one containing an evaporating liquid, as the total pressure is always greater than the vapor pressure. In our experiments, dealing with a compound as condensed phase, it was possible to apply the rule at the lower pressures without such extrapolation, and a test of the rule is described below.

Keyes and Burks[8] have found that the pressures of gaseous mixtures of methane and nitrogen can be calculated with considerable success by writing a Keyes equation for the mixture, in which equation the constants are obtained by averaging the individual constants for the pure gases, weighting the latter constants according to the mole fractions. [In the case of the cohesive pressure constant, A, the square root of A is naturally taken for averaging, since A is per (mole)^2.] A test of this principle is described under the heading "Test of an equation of state for mixtures."

Preparation of Materials

Liquid ammonia that had been standing over sodium for several months was fractionally distilled thrice. After each distillation the ammonia was frozen by means of liquid air and evacuated by means of oil and mercury diffusion pumps. The middle fraction from the final distillation was stored in a steel bomb as liquid ammonia.

The nitrogen[9] was prepared from ammonium sulfate and sodium nitrite, fractionally distilled twice, and stored in a large glass reservoir.

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[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 226.

[8] Burks, *Thesis*, Massachusetts Institute of Technology, **1924.**

[9] Maverick, *Thesis*, University of Geneva, **1923.**

C. P. barium chloride was recrystallized from distilled water thrice, and dried at 110° for a week.

Experimental Procedure

The apparatus used in this investigation is shown in Fig. 3.

About 1 g. of dry barium chloride was placed in the steel reaction bomb F, and the entire system evacuated. Then the reaction bomb was connected through the steel stopcocks C and E, with the liquid ammonia reservoir H, for two days. In this manner the octa-ammine of barium chloride was prepared. Then enough ammonia was withdrawn to have present a small amount of uncombined barium chloride,[10] and nitrogen from the glass reservoir J was admitted into the bulb K and displaced by mercury into the reaction bomb, which was immersed in liquid nitrogen.

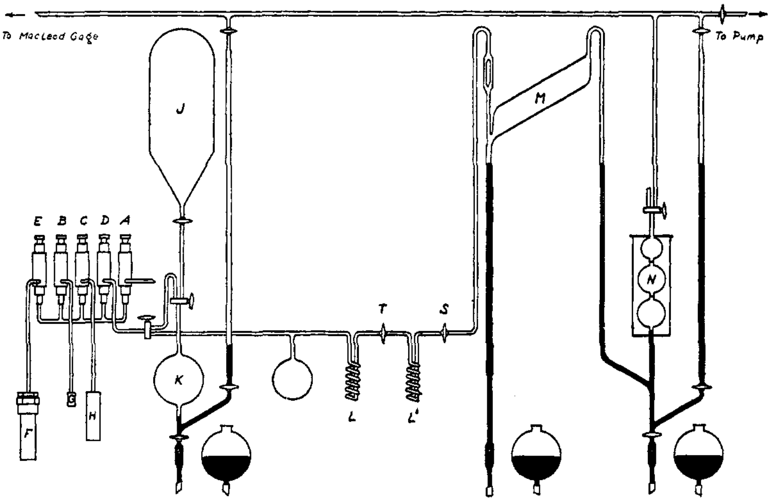

Fig. 3.

After the reaction bomb was loaded, it was placed in a thermostat, the temperature of which was constant to ±0.02.° The pressures were determined by a piston gage connected to the reaction bomb through the steel stopcocks A and E.

When equilibrium, determined by the constancy of the pressure measurements, was reached, Stopcocks A and E were closed, and the entire glass system and the connecting tubing between the steel stopcocks were evacuated. Then a portion of the gas mixture in the reaction bomb was blown off into the small steel bomb G, having a volume of about 1 cc., by opening the stopcocks B and E.

[10] Pressure-composition diagrams by Hüttig and Martin [*Z. anorg. Chem.*, **125**, 269 (1922)] show no other compound between ammonia and barium chloride.

The withdrawn sample of the gas mixture was analyzed in the following manner. The stopcocks E, T and S were closed, the coils L and L′ were immersed in liquid air, and stopcock D was opened. Thus the ammonia was frozen out of the mixture in the coil L; then by means of the air pump M, the nitrogen was transferred into the water-jacketed volume meter N and its temperature and pressure measured over mercury. After the nitrogen had been determined, the system was evacuated, the liquid air around the two coils removed, and the ammonia determined in a similar manner, the bomb G and the steel and glass leads up to the stopcock S being heated with a gas flame in order to recover adsorbed ammonia. Ammonia was completely frozen out in the first coil as was shown by the absence of any gas in the coil L′ after the nitrogen and liquid air about the coil L′ had been removed.

As during the analysis of the gas mixture the pressure of ammonia was never greater than 120 mm., and that of nitrogen never greater than 500 mm., the perfect gas law was used in the calculation of the moles of each gas in the sample analyzed. The error due to the use of the perfect gas law was estimated by the van der Waals equation, with Keyes' constants for b and A, and found to be less than the experimental error.

Experimental Results

For all determinations of the equilibrium pressures of ammonia in mixtures of ammonia and nitrogen the temperature was 45.00° ± 0.02°, and was determined by a mercury thermometer calibrated against a platinum-resistance thermometer.

The dissociation pressures of the system[11] $BaCl_2$-$BaCl_2.8NH_3$-NH_3, which had been determined between 38 and 50°, are represented over this range by the equation

$$\log p = -2031.39/T + 10.1191 \qquad (7)$$

with an average deviation of ±0.1%. From this equation, the dissociation pressure of the above system at 45.00° is 5414 mm., or 7.123 atm.

This value would be the equilibrium pressure of ammonia in the presence of an inert gas but for the fact that the excess pressure has a small effect on the dissociation pressure. However, if the pressure-volume relationships for gaseous ammonia and the two solid phases are known, the effect of external pressure on the dissociation pressure can be calculated by means of the Poynting relationship,

$$\int_{P_e}^{P'_e} v\,dp_e = \int_{P_e}^{P} \bar{v}\,dP \qquad (8)$$

where v = molal volume of ammonia gas, $\bar{v}$ = partial molal volume of ammonia in the solids, P_e = dissociation pressure of the system when

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[11] To be published.

the total pressure is P_e, P'_e = dissociation pressure of the system when the total pressure on the solids is P, and P = the total pressure.

In integrating Equation 8, the Bureau of Standards equation of state for ammonia[12] was used, and it was assumed that barium chloride and $BaCl_2.8NH_3$ are incompressible and that the partial molal volume of ammonia in the ammine is equal to 20 cc. per mole, a value found for $CoCl_2.6NH_3$ and a number of other hexammines.[13,14] It is not necessary to know the value of the partial molal volume of ammonia with great accuracy, for a 10% error in the latter will cause but a 0.4% error in the calculated dissociation pressure. The dissociation pressures so calculated will be called the observed equilibrium pressures of ammonia in mixtures of ammonia and nitrogen.

In Table I are tabulated the determined total pressures (P) and the corresponding mole fractions of ammonia (x_1), the observed equilibrium pressures of ammonia (p_e), the Dalton partial pressures of ammonia (Px_1), and the percentage difference between the latter two.

TABLE I

OBSERVED DATA AND TEST OF DALTON'S PARTIAL PRESSURE AT 45°

P, atm.	x_1	p_e, atm.	Px_1, atm.	$(Px_1 - p_e)\ 100/p_e$
7.123	1.0000	7.123	7.123	
10.133	0.7040	7.141	7.275	1.87
11.716	.6393	7.150	7.490	4.76
13.272	.5655	7.160	7.506	4.83
23.695	.3313	7.220	7.852	8.76
32.818	.2478	7.273	8.133	11.83
47.912	.1743	7.363	8.350	13.41
60.864	.1484	7.440	9.030	21.38

In Fig. 4 the data are represented graphically, the first curve being a plot of the total pressure P against the Dalton partial pressure Px_1, and the second a plot of the total pressure P against the observed equilibrium pressure, p_e. The smoothness of the upper curve indicates that no change in the character of the solid phase occurs due to the presence of nitrogen.

Calculations and Discussion

Test of the Gibbs Modification of Dalton's Law.—From the last three columns of Table I it is apparent that application of Dalton's law of partial pressures in the usual form leads to results far from correct. It remains to be seen whether Dalton's law as modified by Gibbs[5] is a real improvement. Gibbs' hypothesis leads to an equation for the pressure of a gaseous mixture, which is given by adding the respective equations

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[12] *U. S. Bur. Standards Sci. Paper*, No. 501 (1925).

[13] Clark, Quick and Harkins, THIS JOURNAL, **42**, 2483 (1920).

[14] Biltz and Birk, *Z. anorg. allgem. Chem.*, **134**, 125 (1924).

of state for the pure gases, the volume of the pure gas in each individual equation of state being replaced by the volume of the mixture. That is,

$$P = p_{e_1} + p_{e_2} = f_1(T, V/n_1) + f_2(T, V/n_2); \quad p_{e_1} = f_1(T, V/n_1) \qquad (9)$$

where $p = f(T, V/n)$ is the equation of state for a pure gas. In the calculations of the equilibrium pressures of ammonia by this method, the Keyes equation of state for nitrogen and the Bureau of Standards equation of state for ammonia were used. It is necessary to evaluate the volume of the mixture by successive approximations, the equilibrium pressures being computed at the same time. The results are shown in Table II.

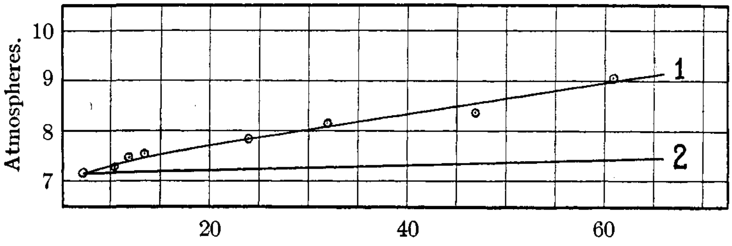

Fig. 4.—Px_1 (Curve 1) and P_t (Curve 2) as functions of the total pressure, P, in atmospheres.

Test of the Rule of Lewis and Randall.—As the vapor pressure of liquid ammonia at 45° is about 17 atm., only at the three lowest pressures can this rule be properly applied, and in the calculation made to test it the Bureau of Standards equation of state was used throughout. The calculated fugacities were then transformed into equilibrium pressures, using the same equation of state. The results are shown in Table II.

Test of an Equation of State for Mixtures.—Finally, Equation 5 which for convenience in these calculations may be written in the form

$$RT \ln f_e = \int_0^P (\partial V/\partial n_1 - v)\, dP + RT \ln f_m x_1 \qquad (10)$$

(where f_e = fugacity of Gas 1 in the mixture, f_m = fugacity of the mixture[15] at the total pressure P, x_1 = mole fraction of Gas 1 in the mixture, v = volume of one mole of the mixture at the variable pressure P and $\partial v/\partial n_1$ = partial molal volume of Gas 1 in the mixture, at the variable pressure P) was used for the calculation of the fugacity of ammonia in mixtures of ammonia and nitrogen. In order to evaluate the separate terms of this equation, it is necessary to have an equation of state for binary mixtures of ammonia and nitrogen, and the equation of state for mixtures of Keyes and Burks[8] was used.

$$P = RT\,\Sigma n_1/(V - 10^{-(\Sigma\alpha_1 n_1)/V}\Sigma n_1\beta_1) - (\Sigma n_1\sqrt{A_1})^2/(V + \Sigma n_1 l_1)^2 \qquad (11)$$

The values of the constants used in the above equation are

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[15] By this we mean the fugacity calculated from the equation of state of the mixture, in this case from Equation 11.

	A	l	β	α
Ammonia[16]	8.5408×10^6	33.93	135.7	68.24
Nitrogen[8]	1.2651×10^6	7.005	46.43	13.74

R = 82.058 cc. atm./mole °.
$T = 273.13 + t°$.

In calculating an equilibrium fugacity two graphic integrations were necessary, details of which will not be given. If the pressures (or volumes) of the pure gases were given by algebraic expression permitting $p\mathrm{d}V$ integrations in terms of known functions, an equation of mixtures containing averaged constants would almost certainly permit explicit integration of $(\partial V/\partial n_1)\mathrm{d}P$, for this is equal to $-(\partial p/\partial n_1)_{tVn_1n_2\ldots}\mathrm{d}V$, since the integration is performed at constant temperature and composition.

The fugacities thus calculated were transformed into equilibrium pressures, using the Keyes equation of state for ammonia with the above constants.

In Table II the values of the equilibrium pressures of ammonia calculated by the above methods are compared with the observed values. All pressures are expressed in atmospheres.

TABLE II

OBSERVED AND CALCULATED EQUILIBRIUM PRESSURES AT VARIOUS TOTAL PRESSURES

P (total pressure), atm.	p_e obs., atm.	p_e atm., calculated by Eq. 1	Lewis and Randall rule	Method of Gibbs	Dalton's law
7.12	7.12				
10.33	7.14	7.14	7.07	7.14	7.28
11.72	7.15	7.30	7.20	7.32	7.49
13.27	7.16	7.26	7.11	7.30	7.51
23.69	7.22	7.33		7.51	7.85
32.82	7.27	7.37		7.60	8.13
47.91	7.36	7.28		7.90	8.35
60.86	7.44	7.76		8.46	9.03

Table II shows that Dalton's law, as usually stated and also as modified by Gibbs, is inaccurate at even relatively low pressures, but that equilibrium pressures calculated by means of Equation 1 and also by the Lewis and Randall rule, in the region of pressures where the latter can be applied, are in fair agreement with the observed equilibrium pressures.

Equations 10 and 11 were also applied to the data of Pollitzer and Strebel[2] on mixtures of nitrogen and carbon dioxide in equilibrium with liquid carbon dioxide, at 0° and at —51.6°. The total pressure-mole fraction products, (Px_{CO_2}), were plotted against the total pressures, P. From the curve drawn through these points were read off the values of Px_{CO_2} at approximately equal pressure intervals, and the calculations were made using these smoothed values of Px_{CO_2}. The following constants for carbon dioxide[17] were used.

[16] Lawrence, *Thesis*, Massachusetts Institute of Technology, **1924**.

[17] Keyes and Kenney, *Am. Soc. Refrigerating Eng. J.*, **3**, 17 (**1917**).

A	l	β	α
6.2325×10^6	-2.43	128.4	31.09

The experimental data at the two temperatures and the calculated fugacities of carbon dioxide are summarized in the graphs of Fig. 5. The graphs of Fig. 5 show that though the agreement between the calculated and observed fugacities of carbon dioxide is much better at both temperatures than that between the usual Dalton partial pressures and the observed pressures, it is not as good at —51.6° as that obtained for the ammonia-nitrogen mixtures. However, there must be taken into consideration the fact that the constants of the equation of state for carbon dioxide were obtained from measurements at specific volumes greater than the saturation specific volumes, whereas the calculated volumes of the nitrogen-carbon dioxide mixtures containing 1 g. of carbon dioxide were in most cases less than the saturation volume of 1 g. of carbon dioxide. Therefore, it is to be expected that the calculated values of the fugacities would show considerable deviations from the observed values, especially below 0°, as the data used in obtaining the carbon dioxide constants were all obtained above 0°.

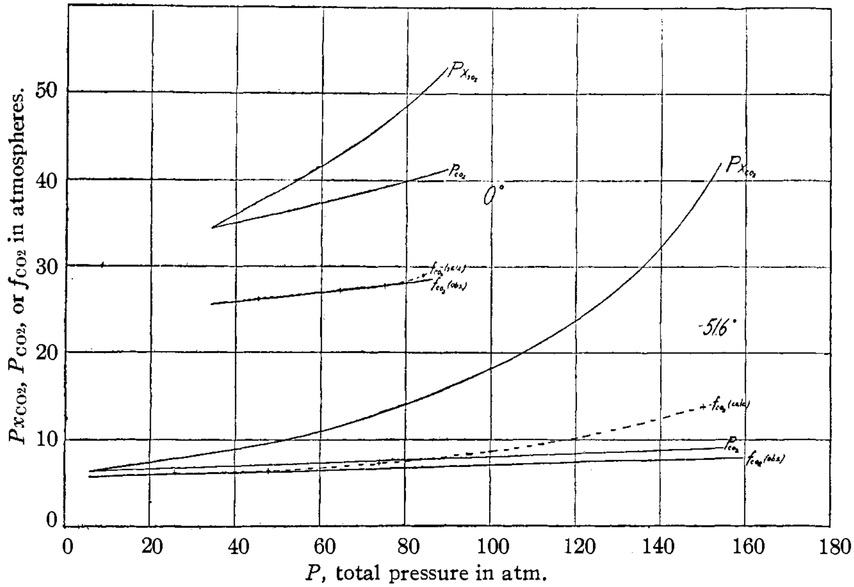

Fig. 5.—Plots from the data of Pollitzer and Strebel on the vapor pressure of carbon dioxide in the presence of nitrogen, comparing at various pressures Px_1 with the corrected vapor pressure P_{CO_2} and the observed fugacity (f_{CO_2}) with that calculated ($f_{calcd.}$) from Equation 1.

In the above discussion a free use has been made of fugacity, as this function was of great convenience in the actual calculations.

Summary

It has been proved that if the equilibrium pressure of each gas in a mixture equals its mole fraction-total pressure product for various values of the variables, then the laws of Boyle and of Avogadro apply to all the gases.

The system, $BaCl_2$-$BaCl_2.8NH_3$ has been used as the equivalent of a semi-permeable membrane for ammonia in the experimental determination of the equilibrium pressures of ammonia in mixtures of ammonia and nitrogen at 45° and over a pressure range from 10 to 60 atm.

The Dalton partial pressures were found to differ from the observed equilibrium pressures by 2 to 21%.

Several hypotheses were used for numerical calculation of the equilibrium pressures, and one of these was found to give values which do not differ greatly from the observed values over the whole pressure range to 60 atm. The deviations are possibly within the experimental error.

A similar calculation for the case of carbon dioxide and nitrogen, studied by Pollitzer and Strebel, was reasonably successful in spite of the fact that an equation of state was used at densities at which it is inexact.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VERMONT]

THE EQUILIBRIUM BETWEEN BENZENE, HYDROGEN AND CYCLOHEXANE

BY GEORGE H. BURROWS AND CARL LUCARINI

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Introduction

That cyclohexane may be synthesized from benzene and hydrogen in the presence of metallic catalysts, and that the reaction is a reversible one, have been known for some years through the work of Sabatier and Senderens,[1] and others. The first quantitative study to be published, from the standpoint of the reversibility of the reaction, is that of Taylor and Dougherty.[2] They measured the velocity of reaction between benzene and hydrogen at several temperatures, by measuring the changes of pressures undergone at constant volume. They also measured the extent of interaction, that is, the equilibria attained by means of the flow method. In their experiments the catalyst was nickel.

In the present work nickel was at first used as a catalyst. It led to erratic results through the usual but seemingly not invariable formation of side products. At the suggestion of Professor Taylor, platinum was substituted for nickel. With platinum, at the temperatures employed,

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[1] Sabatier and Senderens, *Compt. rend.*, **132**, 210 (1901).

[2] Taylor and Dougherty, *J. Phys. Chem.*, **27**, 533 (1923).