The dehydration of the hydrated rare earth chlorides was accomplished first at ordinary pressures, when the process is slow; and second at reduced pressures, when the dehydration is rapid.

The melting points of some of the anhydrous rare earth chlorides were determined in an atmosphere of dry hydrochloric acid gas by use of the cooling curve method.

The densities of some of the anhydrous chlorides of the rare earths were determined by an air displacement method.

The hydrogen ion concentration of the aqueous solutions of some of the anhydrous rare earth chlorides was determined by electrometric measurement with a hydrogen electrode.

URBANA, ILLINOIS

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

GASEOUS SOLUTIONS

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There are two types of formulation of the properties of systems involving gaseous solutions, corresponding to the two types of formulation of the properties of liquid solutions. The one, recently used by Keyes,[1] requires, aside from a knowledge of the empirical constants of a selected equation of state, a knowledge of the change in the heat capacity and heat content of the gas or gases in the mixture with temperature and pressure. The other, used by Lewis and Randall,[2] determines the ratio of the fugacity of each gas in the mixture to the fugacity in a selected standard state at each temperature, and needs then only the change in the heat content of the gas in its standard state, with the temperature, to complete the ordinary thermodynamic formulation of the system.

Either type of formulation, if supplied with sufficient empirical constants, will give accurate results, but we believe that the second type leads to greater accuracy with fewer constants[3] and less labor. In this paper we shall elaborate the method of the latter authors and present the values of the fugacity of the constituents of gaseous mixtures in so far as they can be determined from the existing data. The rough regularities exhibited by these functions should be useful for estimating the values of similar functions in other undetermined systems.

In the absence of experimental information, Lewis and Randall[4] in

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[1] Keyes, THIS JOURNAL, **49**, 1393 (1927).

[2] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, Chap. XVII.

[3] See Randall, *Trans. Faraday Soc.*, **23**, 498 (1927), for a discussion of the significance of the activity coefficient.

[4] Ref. 2, p. 225.

1923 were forced to consider all gaseous solutions to be nearly perfect in the sense of their generalized statement of Raoult's law,[5] that "the fugacity of each constituent is proportional to the mol fraction of that constituent at every temperature, and at every pressure." They pointed out that it was reasonable to suppose that the solution of a given pair of substances would be more nearly perfect the less the density of the solution or, in other words, the greater the average distance between the molecules. We shall see that the deviations of such mixtures from the generalized Raoult's law are not as large as those in liquid mixtures, but that the same kinds of deviations are present.

In the case in which the solution is perfect we may write

$$f_2 = f_2^\circ N_2 \qquad (1)$$

where f_2 is the fugacity in the mixture, f_2° the fugacity of the pure constituent at the same temperature and same total pressure and N_2 the mole fraction of the constituent chosen as solute. In any case the laws of the dilute solution require that this law will be the limiting law which is approached when the mole fraction of the constituent is nearly unity. These laws also require

$$f_2 = k_2^\circ N_2 \qquad (2)$$

as the limiting law in the infinitely dilute solution, where k_2° is a constant which at a given temperature and total pressure is dependent upon the nature of the solute and solvent. The constant k_2° in the case of solutions is known as the Henry's law constant. The difference in the numerical value of f_2° and k_2° is greater the greater the divergence of the solution from the perfect solution. The validity of these laws has been amply proved in many cases of liquid mixtures and of solutions of gases in liquids.

Gaseous Solutions Above the Critical Temperatures of the Constituents

Gillespie[6] used the gaseous perfect solution rule and showed that the data for the ammonia equilibrium at different pressures obtained by Larson and Dodge[7] were approximately in accord with the rule. Keyes[1] assumed that for mixtures of gases the constants of his equation of state were additive, except the pressure correction term which was taken as a square root function. He also corrected for the "aggregation" of the molecules into condensed species. By laborious calculations he showed that the above data of Larson and Dodge and also of Larson[8] were in agreement with his assumption. He states that the data obtained by Burks[9] for mixtures of methane and nitrogen are also in agreement with his assumption.

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[5] Lewis, THIS JOURNAL, **30**, 668 (1908); Lewis and Randall, ref. 2, p. 222.

[6] Gillespie, *ibid.*, **48**, 28 (1926).

[7] Larson and Dodge, *ibid.*, **45**, 2918 (1923).

[8] Larson, *ibid.*, **46**, 367 (1924).

[9] Burks, "Thesis," Massachusetts Institute of Technology, Cambridge, Mass., **1924.**

The extent to which the generalized Raoult's law applies is shown in Fig. 1, in which the ratio of the fugacity of the constituent in the mixture, f, to the fugacity of the pure gas at the same total pressure, f° (or the activity referred not to the gas at unit fugacity but to the fugacity of the gas at the given total pressure), is plotted against the mole fraction. The data are taken from the computations of Gibson and Sosnick[10] from the data of Masson and Dolley,[11] for mixtures of argon and ethylene. As is to be expected the least dense gaseous mixtures at one atmosphere follow the straight diagonal lines, or lines for perfect solutions. The deviation, as shown, is greater as the total pressure is increased. The curves appear in every way to be similar to those obtained with mixtures of liquids of nearly the same polarity.[12]

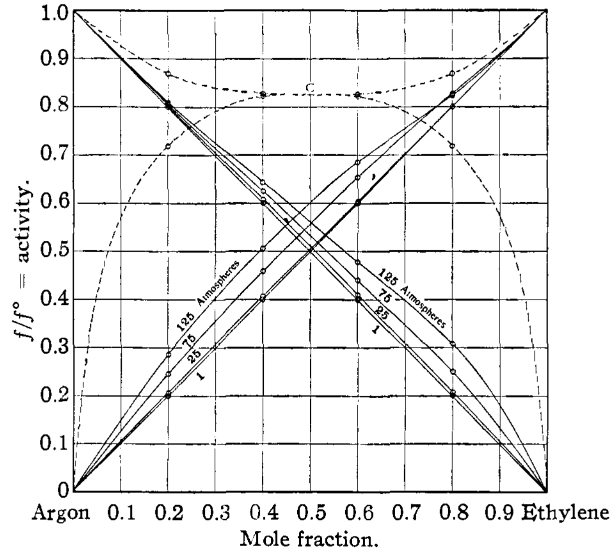

Fig. 1.—Activity of argon and ethylene in mixtures at 25°.

The deviations are better shown in Fig. 2, in which the logarithm of the activity coefficient, γ, defined as the quotient of the activity by the mole fraction, $f_2/f_2^\circ N_2$, is plotted against the mole fraction. Again it is evident that the deviations are larger the more dense the gas; but above about 100 atmosphere in solutions containing a small amount of the given constituent there is a marked decrease in the rate of increase of the deviations with pressure, and in fact an actual decrease[13] in some cases.

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[10] Gibson and Sosnick, THIS JOURNAL, **49**, 2172 (1927).

[11] Masson and Dolley, *Proc. Roy. Soc.* (*London*), **103A**, 524 (1923).

[12] See Hildebrand, "Solubility," Chemical Catalog Co., New York, **1924**, Chap. 5.

[13] See Figs. 1 and 2 of ref. 10.

The individual curves of Fig. 2 resemble those of typical pairs of liquids as shown by Hildebrand.[12] He has shown[14] that practically all such curves for liquid solutions may be represented by an equation of the form

$$\ln \gamma = \ln(f_2/f_2^\circ N_2) = 1/RT(bN_1^2 + cN_1^3 + \ldots) \quad (3)$$

in which the constants b, c, etc., are independent of the temperature, but vary with the pressure. In many cases an equation with the single term in b is sufficient to represent the data, but our curves cannot be fitted by a single constant equation.

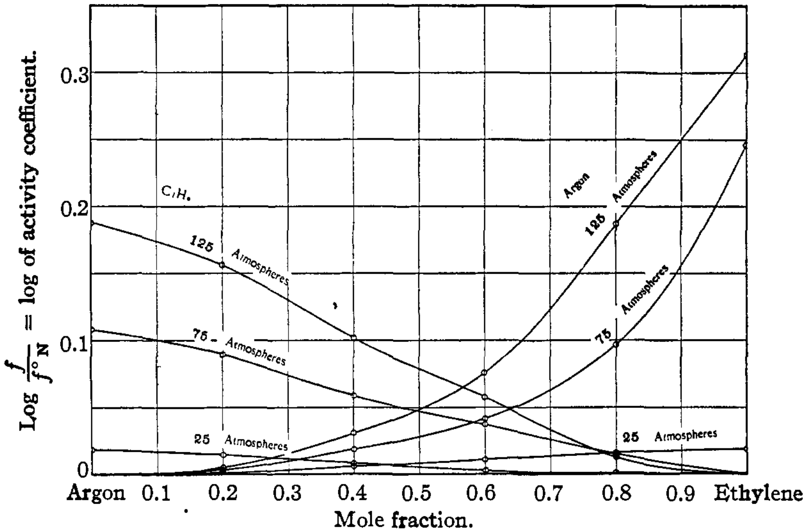

Fig. 2.—Logarithm of activity coefficient of argon and ethylene in mixtures at 25°.

Continued increase of the deviations with increase in pressure would lead to a curve such as the dotted curve of Fig. 1, which has a horizontal portion at C. In the case of liquids the point C is the critical mixing point. The dotted curve corresponds to a single constant equation with a value of b = 1185 cal. per deg. Further increase in the value of b at this temperature would then lead to the mathematical condition for the separation into two gaseous phases. However, we note in Fig. 2 that there is a falling off in the rate of increase of log γ (there is an actual decrease in some cases) as the pressure is increased and consequently a decrease in the value of b. A continued increase in the value of log γ is necessary for the coexistence of two gaseous phases in equilibrium, which, in accordance with the ordinary ideas of a gaseous phase, cannot occur.

Hildebrand[14] obtained the expression

$$(db)/(dP) = (\bar{V}_2 - v_2)N_1^2 \quad (4)$$

for the change of value of b in the single constant equation, when the

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[14] Hildebrand, *Proc. Nat. Acad. Sci.*, 13, 267 (1927).

pressure on a liquid mixture was varied at constant temperature and composition. While we are unable to make a quantitative application of this equation in the case of gases, we note that the above results are in qualitative agreement. Even when the difference in the partial molal volume of the gas and its molal volume decreases, the value of b decreases, as in the case of the argon at 125 atmospheres. The difference between the partial molal volume and the molal volume of a gas in a mixture increases as the pressure is increased but at high pressures this is no longer the case.[10] It is true that the percentage difference in these two quantities increases with pressure, but the absolute difference is smaller than at lower pressures. This again points to a value of b which will always be below that necessary for the coexistence of two gaseous phases in equilibrium.

The Fugacity of Supercooled Vapors

In the previous examples the temperature of the mixtures was above the critical points of the pure constituent gases. Before proceeding to a consideration of the vapor pressure of liquids and solids in the presence of inert gases we will study the form of the fugacity–pressure ratio of supercooled vapors. As an example we will assume that ammonia vapor obeys approximately the equation of van der Waals. The same general conclusions would be obtained by the use of the Keyes[15] equation of state, providing the constants are such as to give the critical temperature and pressure. The Keyes equation is inconvenient for calculating the ratio of the fugacity to the pressure, as we are unable to integrate the analytical expression for Vdp. A satisfactory equation of state, which would lead to an expression for Vdp which could be integrated, is much needed. An equation from which values of V could be directly calculated from those of P would enable us to utilize the graphical method of Lewis and Randall.[2] We have calculated values of P from selected values of V at 500, 405.1, 401 and 375°K., using $a = 4.1635 \times 10^6$ and $b = 37.11$ as the constants in the van der Waals' equation, which gives 405.1°K. and 112 atmospheres for the critical temperature and pressure, respectively, and at 318.1, 293.1, 273.1 and 253.1°K. from the Keyes equation[6]

$$P = 82.058\,(t + 273.13)/(V - 135.7 \times 10^{-63.24/V}) - 8.5408 \times 10^6/(V + 33.93)^2 \quad (4)$$

We have plotted the values of $\alpha = RT/P - V$ against the pressure in Fig. 3. The values of $\log (f/P)$ are given by the equation,[2]

$$\log (f/P) = -\text{area}/189.0T \qquad (5)$$

where the area is taken under the curve from $P = 0$ to the given pressure. Above the critical temperature the values of α gradually increase, but at very high pressures decrease, and at still higher pressures become slightly negative. At the critical temperature the values of α rapidly increase

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[15] Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

as the pressure nears the critical pressure, at which point $d\alpha/dP$ is infinity. Beyond this point α again increases, less rapidly, reaches a maximum, then rapidly decreases and finally becomes slightly negative at the higher pressures. Below the critical temperature (Curves C and D) the value of α increases with the pressure, more rapidly in the range of supercooled vapor, until the maximum in the P-V isotherm is reached and continues to increase (dotted part of curve) as the pressure decreases with smaller molal volumes in the unstable portion. If negative pressures are not attained as we proceed along the P-V isotherm to the minimum, we find a "turning point" in the α-P curve, beyond which the curve represents the difference between the ideal molal volume of the gas and the superheated liquid. At lower temperatures (Curves E to H), where for accuracy we have used the Keyes equation, the value of α reaches infinity at $P = 0$. The negative values of $(RT/P-V)$ are meaningless until P again equals zero as we follow along the curve, and there is another branch starting at infinity for zero pressure of superheated liquid and following above the curve.

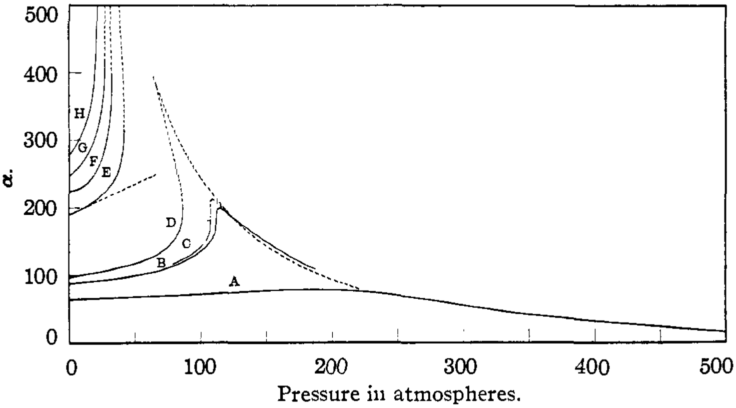

Fig. 3.—Alpha function for ammonia vapor. A at 500°, B at 405.1° (critical temperature), C at 401°, D at 375°, E at 318.1°, F at 293.1°, G at 273.1° and H at 253.1°K.

It is obvious from the curves of Fig. 3 that it is impossible to calculate the fugacity of a pure supercooled vapor above the pressure corresponding to the maximum in the P-V isotherm.

Gaseous Solutions Below the Critical Temperature of One of the Gases

Lurie and Gillespie[16] have measured the composition of mixtures of nitrogen and ammonia in equilibrium with a mixture of barium chloride and barium chloride octa-ammine at 45°. Col. 1 of Table I gives the total pressure, Col. 2 the mole fraction of ammonia in the vapor phase and Col.

[16] Lurie and Gillespie, This Journal, **49**, 1146 (1927).

3 the fugacity of the ammonia in equilibrium with the solids. We have assumed the difference in molal volumes of the solids to be 20 cc. as taken by Lurie and Gillespie and have calculated the change in activity of the solids with the pressure in the usual manner.[17] The fugacity of the ammonia vapor, given in Col. 4 for the various pressures in Col. 1, was calculated by means of Equation 5, using the plot of α against P in Fig. 3. The values in brackets for the two highest pressures were obtained by using a value of α indicated by the broken line in Fig. 3. Col. 5 gives the fugacity of the ammonia according to the rule of Lewis and Randall.

TABLE I

ACTIVITY FUNCTIONS OF AMMONIA VAPOR IN MIXTURES WITH NITROGEN AT 45°

P (atmos.)	$N_2(NH_3)$	f_2	$f_2°$	$f_2°N_2$	k_2	$k_2/f_2°$	k_2/P
7.123	1.000	6.759	6.759	6.759	6.759	1.000	0.952
10.133	0.7040	6.774	9.40	6.615	9.62	1.022	.949
11.716	.6393	6.783	10.73	6.86	10.61	0.990	.906
13.272	.5655	6.791	12.02	6.88	12.05	1.003	.905
23.695	.3313	6.845	19.75	6.54	20.67	1.046	.872
32.818	.2478	6.894	25.45	6.26	27.80	1.078	.846
47.912	.1743	6.974	(32.65)	(5.69)	40.00	(1.225)	.835
60.864	.1484	7.043	(37.09)	(5.50)	47.45	(1.279)	.780

By referring to Equations 1 and 2 it is evident that the number, k, by which we multiply N_2 to obtain f_2, varies continuously from $f_2°$, the fugacity of the pure ammonia at the given temperature and pressure, to $k_2°$, the limiting value at infinite dilution, corresponding to the Henry's law constant for liquid solutions. For small mole fractions this number, k_2, will not differ appreciably from $k_2°$. The values of k_2 are given in

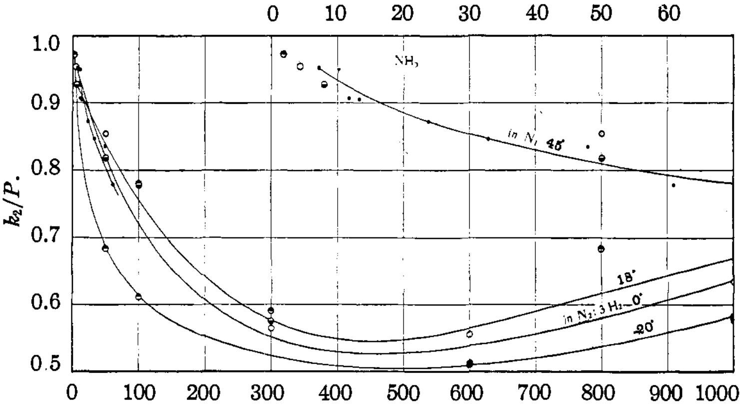

Fig. 4.—Activity function of ammonia vapor in mixtures. ● in N_2 at 45°, ◒ in N_2: 3 H_2 at −20°, ○ in N_2: 3 H_2 at 0°, ◓ in N_2: 3 H_2 at 18°.

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[17] See Lewis and Randall, ref. 2, p. 198.

Col. 6, and the ratio $k_2/f_2°$, given in Col. 7, is a measure of the departure of the gaseous solution from the law of the perfect solution. This ratio, $k_2/f_2°$, is defined as the activity coefficient in Equation 3, or is the number by which we multiply the mole fraction to give the activity referred to the activity of the pure gas at the same temperature and pressure as unity, and is in this sense analogous to the ordinary activity coefficient in solutions. The last column gives the ratio of k_2/P, which we shall find useful in studying these systems at still higher pressures. The values of k_2/P are plotted in Fig. 4.

Larson and Black[18] have studied the approximate composition of mixtures of ammonia and 1 to 3 mixtures of nitrogen and hydrogen up to 1000 atmospheres' total pressure in equilibrium with liquid ammonia at various temperatures between −22 and 20°. We have interpolated their results to −20, 0 and 18° and summarize our studies in Table II.

TABLE II

ACTIVITY FUNCTIONS OF AMMONIA VAPOR IN MIXTURES WITH 1:3 NITROGEN HYDROGEN MIXTURES

P (atmos.)	f_2 (−20°)	N_2 (−20°)	k_2/P (−20°)	f_2 (0°)	N_2 (0°)	k_2/P (0°)	f_2 (18°)	N_2 (18°)	k_2/P (18°)
v. p.	1.833	1.0000	0.972	4.045	1.0000	0.954	7.351	1.0000	0.927
50	1.946	0.0570	.683	4.271	0.1000	.854	7.716	0.1885	.818
100	2.071	.0339	.611	4.533	.0581	.780	8.174	.1050	.778
300	2.655	.0150	.590	5.753	.0340	.564	10.309	.0597	.575
600	3.858	.0126	.510	8.219	.0246	.555	14.608	.0476	.512
1000	6.344	.0109	.582	13.239	.0209	.634	23.241	.0403	.577

The vapor pressure of ammonia was taken as 1.88 at −20°, 4.24 at 0° and 7.93 atmos. at 18°, and the molal volume as 25.84 at −20°, 26.69 at 0° and 27.74 cc. at 18°. The solubility of the gases in the liquid ammonia was neglected. The fugacities of the pure ammonia at its vapor pressure were taken by aid of the curves of Fig. 3. Obviously any attempt to calculate the fugacity of pure "supercooled" ammonia vapor at the measured total pressures is meaningless. The values of k_2/P are also plotted in Fig. 4.

The recent measurements of Bartlett[19] on liquid water and compressed gases enable us to examine more accurately the limiting value of the activity coefficient in dilute gaseous solutions at higher pressures. The activity of the water is not constant at the several pressures, but can be calculated from the molal volume of the water at varying pressures.[17] The amount of gas dissolved by the water was estimated to be insufficient to lower the activity of the water by more than a few per cent.

The activity of the liquid water at the several temperatures and pressures used by Bartlett (neglecting the lowering by dissolved gases) is

[18] Larson and Black, THIS JOURNAL, **47**, 1015 (1925).

[19] Bartlett, *ibid.*, **49**, 65 (1927).

shown in Cols. 2 to 4 of Table III. The volumes were taken from the work of Bridgman.[20] The fugacity of the liquid water at atmospheric pressure is 0.03125 at 25°, 0.06372 at 37.5° and 0.1219 at 50°. The fugacity of the liquid water at the several pressures is shown in Cols. 5 to 7 of Table III.

TABLE III

FUGACITY OF LIQUID WATER AT VARIOUS TEMPERATURES AND PRESSURES

P (atmos.)	$a(25°)$	$a(37.5°)$	$a(50°)$	$f_2(25°)$	$f_2(37.5°)$	$f_2(50°)$
1	1	1	1	0.03125	0.06372	0.1219
100	1.0757	1.0728	1.0703	.03362	.06836	.13047
200	1.1576	1.1515	1.1461	.03618	.07337	.13971
300	1.2454	1.2356	1.2270	.03892	.07873	.14957
400	1.3394	1.3254	1.3132	.04186	.08445	.16009
500	1.4402	1.4214	1.4050	.04501	.09572	.17127
600	1.5481	1.5240	1.5029	.04838	.09711	.18320
700	1.6637	1.6336	1.6072	.05199	.10409	.19592
800	1.7874	1.7506	1.7184	.05586	.11155	.20947
900	1.9200	1.8755	1.8367	.06000	.11951	.22389
1000	2.0618	2.0089	1.9628	.06443	.12701	.23927

TABLE IV

ACTIVITY FUNCTION OF WATER VAPOR IN MIXTURES WITH HYDROGEN AND WITH NITROGEN AT 50°

P (atmos.)	N_2 in H_2	k_2 in H_2	k_2/P in H_2	N_2 in N_2	k_2 in N_2	k_2/P in N_2
100	0.1391	93.8	0.938	0.1576	82.8	0.828
200	.0785	178.0	.890	.1001	139.6	.698
300	.0582	257.1	.857	.0796	188.0	.627
400	.0473	338.7	.847	.0684	234.1	.585
500	.0408	420.0	.840	.0623	275.0	.550
600	.0364	504.0	.840	.0584	318.0	.530
700	.0334	586.5	.838	.0551	355.6	.508
800	.0312	671.5	.839	.0527	397.4	.497
900	.0294	761.0	.845	.0505	443.0	.492
1000	.0282	849.0	.849	.0486	493.0	.493

TABLE V

ACTIVITY FUNCTION OF WATER VAPOR IN MIXTURES WITH 3:1 HYDROGEN–NITROGEN AT 25, 37.50 AND 50°

P (atmos.)	N_2 (25°)	k_2 (25°)	k_2/P (25°)	N_2 (37.5°)	k_2 (37.5°)	k_2/P (37.5°)	N_2 (50°)	k_2 (50°)	k_2/P (50°)
100	0.0385	87.3	0.873	0.0768	89.0	0.890	0.1451	89.9	0.899
200	.0234	154.7	.773	.0449	163.3	.817	.0846	165.0	.825
300	.0183	212.5	.708	.0341	230.9	.770	.0631	237.1	.790
400	.0157	266.8	.667	.0287	294.1	.735	.0521	307.2	.768
500	.0140	321.5	.643	.0254	377.0	.724	.0460	372.5	.745
600	.0128	377.8	.630	.0231	420.0	.700	.0417	439.5	.732
700	.0120	433.0	.619	.0214	487.0	.696	.0386	508.0	.726
800	.0113	494.5	.618	.0200	558.0	.697	.0362	579.0	.724
900	.0108	556.0	.618	.0189	632.0	.702	.0344	651.0	.723
1000	.0104	620.0	.620	.0181	702.0	.702	.0328	729.0	.729

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[20] Bridgman, *Proc. Am. Acad. Arts Sci.*, **47**, 439 (1912).

The various values of N_2, of k_2 found by dividing f_2, from Table I, by N_2 and of k_2/P are given in Tables IV and V for the various gases studied by Bartlett.

Since the attempt to calculate the fugacity of the supercooled water vapor at the pressures used by Bartlett is meaningless, as was shown in the case of ammonia vapor, we cannot calculate the activity coefficient referred to the pure supercooled gas. We show the values of k_2/P in Fig. 5 for the various mixtures at different pressures. The curves necessarily begin at the activity coefficient (f/P) of the pure gas at its vapor pressure. The value of k_2/P depends upon the added gas, decreases with increase in pressure, less rapidly in the region of a few hundred atmospheres, remains about constant for a considerable range and then slowly increases.

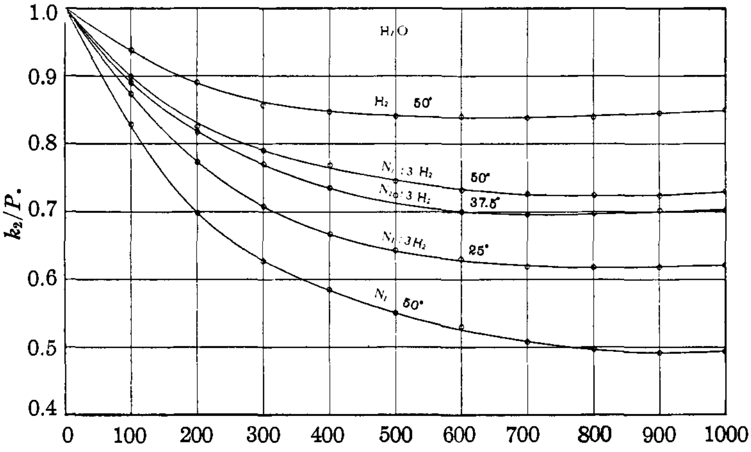

Fig. 5.—Activity function of water vapor in mixtures.

The curves of Figs. 4 and 5 also represent approximately the quotient of the limiting value k_2° by P. It is significant that the value of k_2/P reaches a minimum value in every case, corresponding, perhaps, to the limiting value of log γ for argon in Fig. 2. The values of k_2/P are not far different from what we would expect for the ratio of Raoult's and Henry's law constants for mixtures of liquids of similar likeness.

The considerations of this section limit the application of the Lewis and Randall rule to vapors above their critical point, and to a limited extent below the critical point. The values of the ratio k_2/P, however, for any given pressure, show how the fugacity of the gas depends upon the chemical nature of the added gases, and these ratios furnish an excellent means of estimating the effect for other temperatures, pressures and other gases.[21]

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[21] k_2/P is in a sense an activity coefficient, for it represents the number by which we multiply the product of the mole fraction and the total pressure of the gases to obtain the actual fugacity or activity of the gaseous constituent.

It is possible to make a rough estimate of the value of $f_2°$ for high pressures and for temperatures below the critical point by extrapolating the values of $f_2°$ for a given pressure obtained at higher temperatures to the lower temperature. This, in effect, partially leaves out of consideration the effect of the attraction terms in the equation of state. As a matter of fact we should not expect the attraction between atoms of the same kind in these dilute solutions to be a function of the attraction between their own molecules so much as of that between the solute and solvent molecules. In fact, the highest temperature for the formation of a liquid phase is usually lowered by the addition of a gas with a lower critical point.[22] The calculations of Lurie and Gillespie,[16] in effect, take this into consideration.

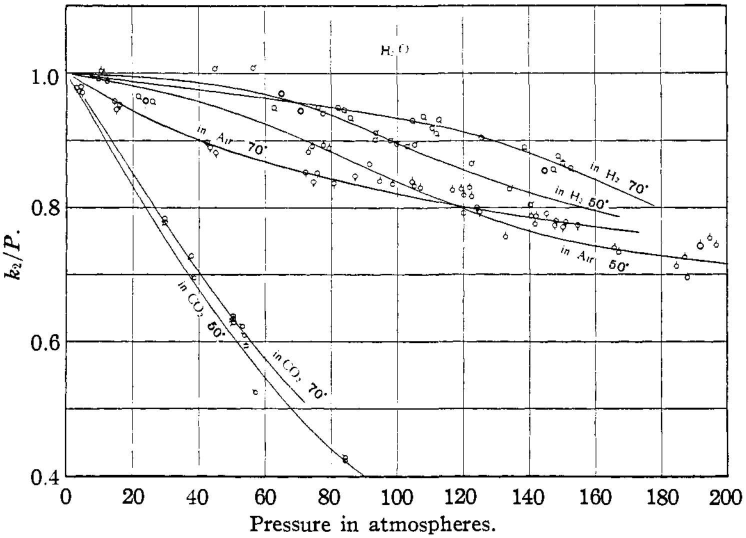

Fig. 6.—Activity function of water vapor in mixtures.

Pollitzer and Strebel[23] determined the concentration of water vapor in the presence of air, of hydrogen and of carbon dioxide up to about 200 atmospheres at 50 and 70°. Their method was less accurate than that of Bartlett, but from their results the same conclusions can be drawn. In the case of the solutions in carbon dioxide, a small correction was made for the effect of the solubility of the carbon dioxide in the liquid phase. This amounted to less than 2% in the largest case. We shall not reproduce our calculations but give in Fig. 6 the values of k_2/P plotted against P as in Fig. 4. As we might predict from the imperfectness of carbon dioxide as a gas at these temperatures the effect upon the activity of the water vapor is much larger than that of the other more perfect gases.

[22] See Caubet, "Liquefaction des Mélanges Gazeux," Hermann, Paris, **1901**.

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

Pollitzer and Strebel[23] also determined the composition of mixed gases in equilibrium wth liquid carbon dioxide at 221.5 and 273.1°K. The compressibility of liquid carbon dioxide was assumed to be negligible, and the solubility of the nitrogen or hydrogen in the liquid was neglected. These assumptions involve a small error in the activity of the liquid. The molal volume was taken as 38 cc. at 221.5° and 48 cc. at 273.1°. The activity of the liquid is given in Col. 5 of Table VI. The vapor pressure of the liquid at 221.5°K. is about 6.6 atmospheres and at 273.1°K. is about 34.3 atmospheres. The vapor pressure was taken as the geometrical mean of the fugacity and the theoretical pressure calculated by the gas law.[24] Using the values 2522 cc. and 458 cc. for molal volumes of saturated gaseous carbon dioxide at 221.5 and 273.1°, respectively, we find the fugacity of the liquid referred to the gas at unit

TABLE VI

ACTIVITY FUNCTION OF CARBON DIOXIDE IN NITROGEN AND IN HYDROGEN

Temp., °K.	Gas	P	N_2	a_2 (1)	a_2/N_2	f_2/N_2	k_2/P
221.5	N_2	40.6	0.222	1.086	4.89	29.55	0.728
		60.5	.182	1.133	6.22	37.60	.621
		74.6	.176	1.167	6.63	40.07	.537
		78.4	.176	1.176	6.68	40.35	.515
		92.9	.179	1.212	6.77	40.90	.440
		108.4	.188	1.252	6.66	40.25	.371
		122.0	.200	1.289	6.44	38.93	.319
		125.8	.205	1.299	6.33	38.28	.304
		139.9	.230	1.338	5.82	35.13	.251
		143.2	.237	1.347	5.68	34.34	.240
		146.6	.248	1.357	5.47	33.05	.225
		148.6	.256	1.364	5.33	32.19	.216
		153.4	.270	1.376	5.10	30.80	.201
	H_2	78.4	.120	1.176	9.80	59.15	.755
		95.3	.105	1.218	11.60	70.08	.736
		100.6	.101	1.232	12.20	73.7	.733
		112.8	.094	1.264	13.45	81.2	.720
		157.3	.084	1.387	16.50	99.8	.634
273.1	N_2	53.7	.744	1.12	1.50	36.0	.67
		63.9	.668	1.12	1.68	40.3	.63
		65.1	.665	1.15	1.73	41.5	.64
		68.2	.642	1.16	1.81	43.4	.64
		75.8	.616	1.17	1.90	45.6	.60
		76.5	.615	1.18	1.92	46.1	.60
		81.9	.603	1.19	1.98	47.4	.58
		88.6	.594	1.21	2.04	48.9	.55
	H_2	78.4	.594	1.18	1.99	47.8	.61
		92.4	.534	1.22	2.29	54.9	.60
		103.0	.503	1.24	2.47	59.3	.58
		122.0	.458	1.30	2.84	68.1	.56

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[24] See ref. 2, p. 198.

activity to be 6 atmospheres at 221.5°K. and 24 atmospheres at 273.1°K. The constants in Col. 6 are those referred to the liquid at unit activity, while the ratios in Col. 7 are obtained by multiplying the ratios of Col. 6 by the fugacity of the liquid referred to the gas at unit activity. Col. 8, k_2/P, is obtained by dividing Col. 7 by the respective pressures.

The values of k_2/P from Table VI are plotted in Fig. 7. The solid circles are the values of the ratios of f_2/P at the vapor pressure of the pure liquid. The values of $f_2{}^\circ/P$ are smaller as the pressure increases, therefore a curve of $k_2/f_2{}^\circ$ would start at unity at the vapor pressure and remain nearly constant. The generalized Raoult's law appears to be of more general applicability in the case of the mixtures of carbon dioxide and nitrogen or hydrogen than in the case of mixtures of water vapor with these gases.

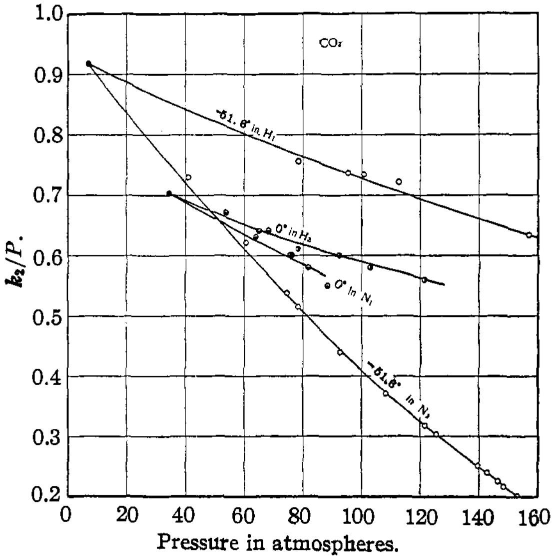

Fig. 7.—Activity function of carbon dioxide in mixtures.

Pollitzer and Strebel[23] also quote some experiments of Kölliker with mixtures of hydrogen and nitrogen in equilibrium with liquid nitrogen, but there are not sufficient data to make an interpretation on the basis here presented.

McHaffie[25] has defined a quantity, called by him the relative activity coefficient, f_p, by means of the equation

$$\log f_p = Pv_s/RT + \log c_0 - \log c_p \qquad (6)$$

in which P is the "partial pressure" of the indifferent gas, v_s the molal volume of the liquid in the condensed phase, c_0 the concentration of vapor when the liquid is under its own vapor pressure, and c_s the concentration

[25] McHaffie, *Phil. Mag.*, [7] **1**, 561 (1926); 3, 497 (1927).

of the vapor when the partial pressure of the indifferent gas is P. We have defined the activity coefficient as the number by which the mole fraction is to be multiplied to obtain the activity. Our definition conforms to the usual practice in the case of liquid or solid phases. The standard state of a liquid at each temperature is taken as the liquid under 1 atmosphere pressure. We have taken the standard state of the vapor as the vapor at unit fugacity, which is more useful for a consideration of the general problem of gaseous solutions.[26] The activity of the vapor in equilibrium with the liquid is not given by the first term on the right of Equation 6, nor is the concentration (moles per liter) of the vapor in the compressed phase its mole fraction. To call McHaffie's function an activity coefficient is, therefore, somewhat misleading. He measured quantities from which results similar to those of Bartlett can be calculated for mixtures of water vapor in equilibrium with liquid water or anhydrous and hexahydrated sodium sulfate and air to 100 atmospheres. His results are anomalous but in qualitative agreement with those of Bartlett.

Summary

The application of the generalized statement of Raoult's law to gaseous solutions has been elaborated. The deviations are found to be of the same nature but, in general, of less magnitude than those of typical liquid pairs of like polarity.

The fugacity of supercooled vapor has been investigated. It is shown that for pressures near that of the turning point of the pressure–volume curve, the fugacity of the pure constituent should not be used for the Lewis and Randall rule.

This latter rule has been shown to hold as an approximation and as a limiting law for gaseous solutions above the critical temperature of the gases, and for a limited range of total pressures for the solute gas below its critical temperature.

For solute gases below their critical temperature, values of "activity coefficients" have been calculated which enable rough quantitative predictions of values in other mixtures and at other temperatures to be made.

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[26] See Ref. 2, Chap. XXII, for a discussion of the definition of these quantities.