# METHODS FOR THE THERMODYNAMIC CORRELATION OF HIGH PRESSURE GAS EQUILIBRIA WITH THE PROPERTIES OF PURE GASES[1]

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## I. THE GENERAL LIMIT METHOD

The general limit method is an exact thermodynamic method, but requires a knowledge of the properties of gas mixtures, as well as of pure gases.

Ordinary thermodynamics gives us partial differential equations for the variation of thermodynamic functions with pressure or volume at constant temperature and composition. By integration of such equations we can determine the value of any desired function at a finite pressure in terms of an integration constant, which represents its value when the system is in the initial state. If we take this initial state at infinite volume and assume that the system at infinite volume has the properties of ideal gases, we can eliminate the constant of integration, thus arriving at a formal solution of the problem.

For an understanding of this method it is necessary to know that when we calculate the relative value of a thermodynamic function by means of integration with respect to several variables the order of the integrations makes no difference in the final result, and we can choose the most convenient order. This is to make the pressure or volume integration at constant temperature and composition, and to make it last in the sequence.

We know that a system of real gases at infinite volume does not in all respects resemble a system of ideal gases. For instance, the volume change on mixing real gases at constant temperature and pressure does not in general approach the ideal gas value—zero—at zero pressure, but a finite value. Since the entropy and the two free energies become infinite like the volume, a similar finite difference between the ideal gas and the infinitely expanded real gas might reasonably be feared in these cases also. In any event, the limit method sketched above leads immediately to "in-

finite" integrals[2] which must be eliminated before any actual calculation can be made.

Van der Waals (45) used the limit method to calculate the Helmholtz free energy of a mixture of van der Waals gases. Van Laar in 1901 (29) stated what changes are necessary in the expression for the entropy of a mixture of ideal gases, in order to obtain an equation for substances in any state of aggregation, and proceeded to deduce a general mass-action law. It is obvious now that his formal expression could have been justified by the use of the limit method, leaving only the infinite entropies and integrals to be discussed. In his paper with Lorenz in 1925 (31), however, he applied the limit method only to the energy, and obtained the entropy expression by correcting the ideal gas expression for the "free volume" of the gas mixture, stating that a rigorous derivation of the entropy expression would be published in full elsewhere.

So far as the writer can discover, none of the immediate successors of van der Waals has brought the general limit method into a form suitable for actual calculation, nor has removed the difficulty of the infinite entropy or eliminated the infinite integrals and their partial derivatives.

This seems to have been done first by the writer in 1925 (19), by means of the assumption that the equilibrium pressure, $p_1$, of a gas in a mixture[3] becomes equal to the product of the total pressure, $p$, by the mole fraction, $x_1$, of the gas, as the pressures are indefinitely reduced at any temperature. This must of course be understood to mean that the ratio $p_1/px_1$ approaches unity at zero pressure. Indeed, according to the very logical development of J. A. Beattie (8), this ratio should be expressible as unity plus a power series in $p$ beginning with the first power of $p$ and having bounded coefficients, i.e., not infinite. With the aid of this assumption the following general equation was deduced for the fugacity, $f_e$, of a gas in a mixture

$$RT \ln f_e = \int_0^p (\bar{v}_1 - v_1)\, dp + RT \ln f_p + RT \ln x_1 \qquad (1)[4]$$

where $\bar{v}_1$ is the partial molal volume of gas 1 in the mixture at the variable pressure $p$, $v_1$ its molal volume at $p$, and $f_p$ is the fugacity of gas 1 at the upper limit,—the pressure of the mixture for which $f_e$ is calculated. This isothermal relationship, taken together with the treatment of fugacity by Lewis and Randall, solves in principle mass-action problems at constant

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[2] Whose integrand, or one of whose limits becomes infinite.

[3] The pressure of the pure gas when in equilibrium with the mixture through a semipermeable membrane.

[4] In accordance with a statement in the paper (19), zero has been placed in the lower limit instead of the $p^*$ originally printed.

temperature. With the aid of certain thermal data, problems involving change of temperature may also be solved.

Starting with the above assumption and the second assumption that the *energy* of a pure gas is expressible at any temperature as a similar power series in the pressure—both are isothermal assumptions—Beattie (8) has given a very complete and logical treatment of the thermodynamics of gases and gas mixtures along classical lines, which includes a theoretical basis for the determination of thermodynamic temperature by gas thermometry.

It is known that the integral of equation 1 is not infinite or zero (22). With regard to the possible finite difference between the infinite entropy of mixtures of real gases and of ideal gases at infinite volume, it can be proved (23) from equation 1 that the entropy and also the free energy changes on mixing real gases at constant temperature and pressure are the same in the limit at zero pressure as for ideal gases (8). Equation 1 can be applied without further hypothesis in case there are enough data relating to the volumes of gaseous mixtures.

The thermodynamically equivalent relation (2)

$$RT \ln f_e = \int_0^p (\bar{v}_1 - RT/p) \, dp + RT \ln px_1 \tag{2}$$

was later derived by the writer (21), by Gibson and Sosnick (18), and also by van Lerberghe (35) (except that the infinite integral was not yet removed), and was applied empirically by Gibson and Sosnick to the extensive data of Masson and Dolley (38) on the volumes of mixtures of ethylene and argon. Similarly Merz and Whitaker (39) applied equation 2 to the data of Bartlett (1).

These calculations were not really wholly empirical, as in the absence of complete data these authors assumed that the integrand was not only finite but also zero at zero pressure, which is not the case for the given mixtures, according to the writer (22). As there was no immediate chemical application for the fugacities thus calculated, the calculations represent in a sense one-half a typical thermodynamic correlation.

The methods now to be discussed are special methods, which, containing hypotheses about gaseous mixtures, do not require for their application any gas-mixture data, and are the methods promised in the title.

## II. THE METHOD OF GIBBS

Gibbs showed (17) that the law of Dalton in the comprehensive form given by Gibbs and its thermodynamic consequences are consistent and possible for a mixture of gases which are not ideal gases and indeed without any limitation in regard to their individual thermodynamic properties.

His proposition—that the chemical potential of a gas in a mixture will be equal to the potential of the same gas when pure and at the temperature and concentration which it has in the mixture—gives a solution of the problem. This solution is very convenient in certain cases, but implies that the Gibbs-Dalton law holds throughout the pressure range. Using the general limit method, and assuming that this law holds at infinite volume, the author (24) showed that it will apply at all pressures if the pressures are additive at constant volume.

This method of Gibbs has been applied only in a few examples of what we may call the vapor pressure problem: by Lurie and Gillespie (37) to their data on mixtures of nitrogen and ammonia in equilibrium with barium chloride ammine, and essentially by Cupples (11), who developed independently by means of interesting physical reasoning a method of calculation—which is the same as the Gibbs method—and applied it to the data of Larson and Black (33) on mixtures of ammonia, hydrogen, and nitrogen in equilibrium with liquid ammonia. The writer (24) compared the calculated with the measured values of the mole fraction of ammonia in the equilibrium gas mixtures, for both sets of experiments, and stated that the deviations of the Gibbs-Dalton law are in all cases smaller than those of the ideal gas form, but the improvement is not in most cases impressive.

Gerry and Gillespie (15) found in the calculation of the normal vapor pressure of iodine from the data of the gas-stream method that the errors of the Gibbs method are of the same order of magnitude and in general slightly greater than for the common assumption that the vapor pressure, corrected for the effect of total pressure, equals $px_1$ at the experimental pressures.

In terms of fugacities, the Gibbs-Dalton law states that the fugacity, $f_e$, of a gas in a mixture equals the fugacity of the pure gas at the temperature and concentration of the gas in the mixture. This is evident because the chemical potentials are then equal. The limit method gives the general equation

$$RT \ln f_e = \int_{\infty}^{V} (dp_1/dn_1 - dp/dn_1) \, dV + RT \ln f_{1c} \qquad (3)$$

where the first derivative is for the pure gas at the molal volume $V/x_1$ and the second is for the mixture at the average molal volume $V$; the upper limit is the average molal volume of the mixture at the pressure and temperature for which $f_e$ is calculated. The derivatives are partial, being taken at constant volume and temperature, and without variation of any mole numbers except for gas 1.

Putting the integrand of equation 3 equal to zero can be shown equivalent to announcing additivity of pressures. This equation is given only to

show an analogy with the Lewis and Randall fugacity rule; other analogies have been given elsewhere (24).

In applying the method, the pressure of a pure gas must be determined for the same concentration as it has in the mixture. Since this concentration, in the case of the vapor pressure problem, often exceeds the concentration at the normal vapor pressure, a certain degree of extrapolation into a metastable region is required. This is however much less than for the next method.

### III. THE METHOD OF LEWIS AND RANDALL

This is based on a suggested rule (36) that the fugacity of a gas in a mixture equals its fugacity when pure, and at the temperature and total pressure of the mixture, multiplied by its mole fraction in the mixture. They stated that the rule implies the additivity of volumes at constant pressure and the additivity of heat content. Using the general limit method, and assuming that this rule holds at infinite volume, the author (19) showed that it will hold at all pressures if the volumes are additive. A little consideration of equation 1 supplies the proof.

The method is particularly convenient in studying the variation of the equilibrium constant with pressure. The first real test of the rule by chemical data was by the author (21), in which the Haber equilibrium data of Larson and Dodge (34) were correlated with the pressure data for the pure gases with the aid of the Keyes equation of state. It was concluded that the Lewis and Randall rule is verified excellently to 50 atmospheres and well at 100. Available constants in the Keyes equation of state were sufficient to determine the last two coefficients in the very simple equation

$$\log K_p = A/T - B - Cp/T + Dp/T^2 \qquad (4)$$

The first two coefficients reproduce the absolute value of $\log K_p$ at zero pressure over the temperature range, and had been determined empirically by the author (20).

The results of this simplified equation were substantially identical with the results obtained by exact integrations with the aid of the complete Keyes equation of state. Furthermore, different values for the equation of state constants as obtained by different authors led to equally satisfactory agreement with the experimental data. It is evident that "the danger of the use of an equation of state of imperfect accuracy for calculations of such functions as $\gamma$"—the ratio of the fugacity to the pressure—as feared by Newton (40) can easily be overestimated.

Newton and Dodge (41) have recently applied the Lewis and Randall

rule again to the Haber equilibrium data, using for the pure gases the fugacity graphs of Newton (40) with good results.[5]

The practical significance of the success of the Lewis and Randall rule is twofold. First, the enormously important effect of pressure upon the yield of a chemical reaction can be calculated reasonably accurately at pressures not too high. Second, as pointed out already (21), such success means that the equilibrium constant will not vary greatly with composition at constant temperature and pressure, and hence not much improvement of yield can be expected in the use of unstoichiometrical ratios of reactants.

On the other hand, success in the calculation of the equilibrium constant does not prove the accuracy of the separate fugacities found for the several gases involved in the reaction, since compensation of errors can and does occur in this calculation, and the writer (19) therefore proposed to study simpler systems in which no compensation is possible, such as barium chloride ammine in equilibrium with ammonia admixed with an inert gas.

In the application of the method to the vapor pressure problem the integral of $(v - RT/p)dp$ has to be determined from zero to the total pressure of the mixture. If the phase emitting the vapor is a compound the method can be applied without extrapolation, until the total pressure reaches the normal vapor pressure. As thus applied by Lurie and Gillespie (37) to their data it gave good results. On the other hand, if the phase emitting the vapor is a practically pure liquid or solid, vaporizing without decomposition, a serious degree of extrapolation will be required. Gerry (14) found the results of the method "extremely bad for cases of condensible substances at small mol fractions," as illustrated by the case of iodine vapor mixed at 1 atmosphere with air, hydrogen, or carbon dioxide. The errors here were from 3 to 8.7 per cent, much worse than the ordinary ideal gas treatment—whose errors were from $-0.7$ to $+2.4$ per cent—as judged by the equation of state method.

## IV. EQUATIONS OF STATE FOR GASEOUS SOLUTIONS

The contributions of van der Waals to our problem included not only a suggestion of the general limit method and his equation of state for pure gases, but also an important attempt toward an equation of state for gaseous solutions.

He concluded that the equation of state of a mixture of van der Waals gases is itself a van der Waals equation whose constants or parameters can be calculated by relations such as the following for a binary mixture:

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[5] No stress should be laid on the fact that their results at 300 atmospheres are better than those of the writer, as the contrary is the case at 100 atmospheres, and their deviations are changing sign between 100 and 600 atmospheres.

$$b = b_1 x_1^2 + 2b_{12} x_1 x_2 + b_2 x_2^2$$
$$A = A_1 x_1^2 + 2A_{12} x_1 x_2 + A_2 x_2^2 \tag{5}$$

in which the interaction constants $b_{12}$ and $A_{12}$ are not predicted by theory and may have to be determined from data as adjustable constants. Various authors have used simplifying assumptions such as the relations 6 and 7:

$$b = b_1 x_1 + b_2 x_2 + b_3 x_3 + \ldots \ldots \tag{6}$$
$$A^{1/2} = A_1^{1/2} x_1 + A_2^{1/2} x_2 + A_3^{1/2} x_3 + \ldots \ldots \tag{7}$$

which enable the calculation of the constants or parameters of the mixture equation, for any number of components, from the equations of the pure gases, without the introduction of arbitrary constants.[6]

For an account of the early work on these suggestions reference is made to the paper of Beattie and Ikehara (9). They state "because of the failure of van der Waals' equation to give even an approximate representation of the compressibility of pure gases over a wide range of temperature and density, it has never been applied to compressibility data on gas mixtures except[7] at relatively low pressures."

It has already been emphasized (19) that a determination of the mixture equation, taken together with the general limit method, will bring with it a complete solution of the mass-action law for compressed gases.

For convenience, the relations 6 and 7 will be designated hereafter as linear combination of parameters, in spite of the fact that the combination rules are theoretically derived from the quadratic relations 5.

F. G. Keyes suggested (see Gillespie (19)) that the equation of state of a mixture of Keyes gases is of the Keyes form, and that the constants for the mixture can be determined by applying equation 7 to the $A$ constant and equation 6 to the remaining constants.

As will be mentioned later, Lurie and Gillespie (37) applied this suggestion in connection with the general limit method to their equilibrium data on mixtures of ammonia and nitrogen with very good results and also to the previous equilibrium data of Pollitzer and Strebel (42) on mixtures of nitrogen and carbon dioxide with very good results to 80 atmospheres at 0°C. and to 50 atmospheres at −51.6°C. More recent tests by means of equilibrium data will be discussed later.

Keyes and Burks (28) measured the compressibility of mixtures of nitrogen and methane to about 300 atmospheres and from 0° to 200°C. and found that the constants in the Keyes equation for the mixtures could be satisfactorily calculated by means of this combination of parameters.

[6] Relations 6 and 7 imply that $b_{12}$ is the arithmetic mean of $b_1$ and $b_2$ and that $A_{12}$ is the geometric mean of $A_1$ and $A_2$.

[7] See, for instance, Trautz and Emert (43), Trautz and Narath (44), and Eucken and Bresler (13).

Beattie (5) found that the pressures of the nitrogen–methane mixtures of Keyes and Burks are well represented by the Beattie–Bridgeman equation of state when the $A$ constant is calculated by equation 7 and the others by equation 6.

For other methods of attack on the problem of equations of state for gas mixtures, which have not yet been applied extensively to chemical data, reference will be made only to the paper of Beattie and Ikehara (9).

## V. THE CALCULATION OF VAN LAAR

In discussing the experimental work of Bartlett (1), who found very much more water vapor in a mixture of nitrogen and water vapor in equilibrium at high pressures with liquid water than can be explained by the long-known effect of pressure on vapor pressure as given by the Poynting relation, van Laar (30) states in 1929 "we have repeatedly given the exact solution of this problem, the last time in 1928 in this journal."[8]

He assumes as in 1901 that the constant-volume heat capacity of the gas is constant at infinite constant volume. For thermodynamic correlations over an extended temperature range this should undoubtedly be replaced with a series expansion in the temperature, and there is no objection to this on the basis of the general limit method. The thermodynamic derivations of van Laar are based on the van der Waals equation with constant $A$ and $b$, but in the application of the resulting equations the $A$ constant, which alone enters the final result, is recognized as variable with temperature and pressure, and a value is used for the experimental temperature and pressure.[9] These distinguishing features of the calculation are retained in other papers by van Laar and appear characteristic of his method of attack.

He computes the $A$ constant for water from the heat of vaporization, corrects the $A$ value of nitrogen given by van der Waals for the difference of temperature and pressure, and combines these $A$ parameters according to equation 7. He is able to calculate essentially the mole fraction of water in the gas mixture in equilibrium with the liquid within about 2 per cent of the observed value at the one point studied,—50°C. and 1000 atm.

In conclusion, he states "And herewith we have indeed said everything which is to be said theoretically about this interesting problem." This need not be taken to indicate any estimate of the previous American work, particularly the calculations of Lurie and Gillespie on the data of Pollitzer

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[8] Z. physik. Chem. **137A**, 421 (1928); see also Z. anorg. allgem. Chem. **171**, 42 (1928).

[9] Instead of for some average value of the pressure. Really there would be an integration from zero to the final pressure, were the variation in $A$ introduced in the beginning.

and Strebel, as none of this work is mentioned by him. It refers probably to certain experimenters who did not realize that the $px_1$ product for a gas mixture in equilibrium with a condensed phase emitting the gas 1 need not theoretically be equal to the vapor pressure after this is corrected for the total pressure by the Poynting relation.

This theoretical lack of equality is shown by the calculations of van Laar. It had been shown in a general manner by Lurie and Gillespie that the lack of equality is a necessary consequence of the fact that the laws of Boyle and Avogadro fail at the experimental pressures. This follows from their proof[10] that these laws must hold if such equality holds for various values of $p$ and $x_1$ at any given constant temperature.

## VI. THE EQUATION OF STATE METHOD AND ITS APPLICATIONS

We have seen that the general limit method furnishes equations which need integration. An equation of state for mixtures, obtained by combination of parameters, permits the integration, either graphically—as in the case of the Keyes equation—or explicitly in terms of simple functions—as in the case of the Beattie–Bridgeman equation. Such integration of the equations of the limit method gives us what we may call the equation of state method. It is special, like those of Gibbs and of Lewis and Randall. The method of Gibbs involves addivity of pressures; that of Lewis and Randall, the additivity of volumes; and the equation of state method involves a kind of additivity of equation of state constants. It is of course true that additivity of pressures or of volumes furnishes at once the equation of state of mixtures in terms of the equations for the pure gases, but this circumstance need not be the occasion of any confusion in our use of the term "equation of state method," especially since it is only for this method that equations of state are indispensable.

The equation of state method furnishes useful if not indispensable aid in the empirical application of the general limit method. As a matter of fact, neither this latter method, nor the method of Lewis and Randall, can be applied purely empirically. There are integrals to be found—under curves that must be extrapolated from the experimental region to the axis of zero pressure—and for this extrapolation some hypothesis must be used, such as (1) that the limit intercept is zero, or (2) that the experimental curves should be continued to the axis without introduction of new curvature, or (3) that the limit intercept and its slope at the axis can be found for the general limit method by combination of parameters and for the Lewis and Randall method by the use of the individual equations of state. The first assumption was tacitly made by several authors, as mentioned above, but the writer showed (22) that in application this vio-

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[10] Later repeated more fully by the writer (24).

lated both the second and the third, which were together in agreement. A judicious use of equations of state is therefore recommended even to those aiming at pure empiricism in the treatment of data, whether for mixtures of gases or for pure gases.

As mentioned above, the equation of state method was applied by Lurie and Gillespie to their data on mixtures of ammonia and nitrogen in equilibrium with barium chloride–barium chloride octammine. They found a good agreement of computed to experimental values, possibly within the uncertainty of the latter. They applied the method also to the previous data of Pollitzer and Strebel on the compositions and pressures of nitrogen and carbon dioxide in equilibrium with liquid carbon dioxide, with very good agreement at 0°C. to 80 atmospheres and at $-51.6$°C. to about 50 atmospheres. For these calculations they used the Keyes equation of state. Later calculations of Dr. Eli Lurie (unpublished) showed that when the Beattie–Bridgeman equation is used for mixtures linear combination must not be applied to the first power of the $c$ constant—because of its large value for ammonia—but may be applied to its square root.

Keyes (27) developed equations for chemical equilibria in non-ideal gases whose isometrics are linear, starting with an entropy expression derived from a consideration of the modifications of the ideal gas result necessary in such a case. As the entropy expression is consistent with that derived from the limit method the results are treated in this group. Comparison of the results with the experimental data of Larson and Dodge (34) and of Larson (32) showed tolerable agreement to 600 atmospheres, and agreement as to order of magnitude throughout.

Gillespie and Beattie (25) undertook to correlate all the Haber equilibrium data with respect to both temperature and pressure. Empirical equations for the heat capacities of the pure gases as functions of the temperature at infinitely low pressures were deduced from 1 atmosphere values by means of a relation given by Beattie (6), and the general limit-method was applied with the use of the Beattie–Bridgeman equation of state of mixtures. Instead of using the empirical two-constant equation of Gillespie (20) for $K_p$ at infinitely low pressure, a new equation was derived containing terms from the known heat capacities and two adjustable constants, determined from the whole body of data. They compared the experimental with the calculated percentages of ammonia in the equilibrium mixtures and found an agreement within the experimental error over the whole field of temperature and pressure. The deviations are small, and the deviation plot shows no significant trends in the deviations.

Newton and Dodge (41) have recently stated: "however, they do not strictly calculate the high pressure equilibrium constants from the low pressure ones, but rather leave two adjustable constants in their final equa-

tion and select their values to fit the data best." Without explanation, this statement may prove very misleading. It ought therefore be emphasized, that the two adjustable constants were used substantially in the same way as the two used by Newton and Dodge, not being used at all in the calculation of the pressure effects. Furthermore, a recent examination of the published papers shows that Gillespie and Beattie would not have found a less satisfactory agreement with the limited field of data considered by Newton and Dodge if they had in fact used the same empirical equation and constants as were used by the latter authors, but on the contrary a slight over-all improvement, which would have been gained at the expense of the agreement with the high temperature data of Haber.

The pressure effects were in fact calculated from existing equation of state constants without any use or benefit of arbitrary constants, and if, for example, the equilibrium constant is known at one temperature and pressure and the heat effect of the reaction similarly known at one point, then calculations similar to those of Gillespie and Beattie will reproduce the whole body of equilibrium data, which extend at 30 atmospheres from 325° to 952°C. and at some temperatures from 10 to 1000 atmospheres. The superior results given by their method over those given by the Lewis and Randall rule is not due to a better management of the two necessary adjustable constants, but to the known superiority of combination of parameters over the rule of additive volumes. Likewise, these results serve to verify the precision of the equilibrium data[11] and thus to show that the discrepancies introduced by this rule of additive volumes are real and of chemical significance.

Gillespie and Beattie further calculated the entropy constants of ammonia, nitrogen, and hydrogen, and the heat effect $(-\Delta H)$ of the Haber reaction as a function of pressure and temperature. With the aid of the papers of Beattie (4, 7, 8) all numerical values for any desired thermodynamic function can be calculated for these gases, severally or in mixtures.

Again, they calculated (26) the optimum hydrogen:nitrogen ratio for ammonia formation in the Haber equilibrium. At, for example, 500°C. and 1000 atmospheres the best ratio, when argon is absent, is not 3, as would be the case according to the ordinary mass-action law and according to the Lewis and Randall rule, but 2.91 in the initial reactant mixture and 2.68 in the final equilibrium mixture. When argon is introduced with the nitrogen in the usual amount, the ratio of hydrogen to (pure) nitrogen is not 3.036, as would be the case according to the ordinary mass-action law,

[11] Actually, their calculated percentages of ammonia agree better with the measured values than will percentages calculated from the $K_p$ values given by the experimenters, since these used an approximate relation for finding $K_p$ which has less precision than the data warrant.

but 2.92 in the initial and 2.72 in the final mixture. The corresponding improvement in yield that could be realized by the use of optimum rather than stoichiometrical ratios turns out however to be insignificant—only about 0.03 to 0.04 per cent ammonia, when the final mixture contains about 58 per cent ammonia. On the other hand, if the yield at a ratio of say 3 were to be calculated from the actual yield at a quite different ratio, the error of the ordinary mass-action law, even at constant temperature and pressure, might easily be important.

In all these calculations the first power of the $c$ constant was combined linearly, instead of the square root, as is now believed better. (When the constants are small, or the temperature high, the difference is slight.) Professor Beattie has studied the differences made in the former calculations of the equilibrium constant when the root of $c$ is combined, and finds that they are small,—the recalculated values fit the data as well as the previous values, the deviations being simply distributed differently among the points.

In the determination of normal vapor pressures from the data of the gas-stream method it becomes necessary to make a correction for the failure of the ideal gas laws. When equation of state constants are available for all the substances concerned, the problem is like the vapor pressure problem previously discussed. In the case of iodine, there are no pressure–volume–temperature data from which such constants can be deduced. Braune and Strassman (10) obtained gas-stream data for iodine, using two different inert gases, hydrogen and carbon dioxide, and worked over a field of temperature and pressure. Gerry and Gillespie (15) showed that these data could be used to determine the constants $A_0$, $B_0$, and $c$ in the Beattie–Bridgeman equation of state, as simplified for low pressures, and the results in turn used to calculate the normal vapor pressure of iodine from the very accurate measurements of Baxter and his coworkers (2, 3). The effect of the correction for the failure of the ideal gas laws as applied at 1 atmosphere was found decidedly important, compared with the precision obtainable in the best measurements. A simple equation for the vapor pressure of iodine as a function of the temperature was given. This utilizes their pressure corrections and the temperature smoothing by Giauque (16) of the Baxter data by means of spectroscopic and specific heat data.

In most previous cases of a solid or liquid evaporating into a gas mixture, the experimenters have found more evaporated substance at equilibrium than they expected from the ordinary assumption that the vapor pressure (corrected for total pressure) is equal to the $px_1$ product, and they have therefore spoken of a solvent effect. In the case of iodine, the results for air and for carbon dioxide at the experimental temperatures were in this same sense, but the results for hydrogen were opposite.

## VII. CONCLUSION

Corresponding to a greater activity of experimenters in the study of chemical and physical equilibria involving gas mixtures at high pressures, and to renewed attacks on the equation of state problem, there has been in the last few years considerable progress in the thermodynamic correlation of the results of equilibrium studies with equations of state and thermal data. Much of this has been with the aid of equations of state for mixtures, deduced from equations for the pure gases by means of a rule for combination of parameters.

Although an exact solution of any of the problems is complicated, in many cases solutions are possible by means of simple equations, obtained by omission of terms of the higher orders.

The only very polar gas involved in a complete correlation is ammonia. Extension to the cases of other polar gases may introduce difficulties, especially at low temperatures. These difficulties appear already in the development of an equation of state for the pure gas. At present the limiting factor in future progress appears to be, not the linear combination of parameters, but the experimental inaccuracy of the equilibrium data and, in some cases, lack of suitable equations of state for the pure gases.

Newton (40) has recently presented fugacity values for a great variety of gases, obtained without equations of state, and some of these were used by Newton and Dodge (41) in connection with the Lewis and Randall rule, as mentioned above. In order to use them in connection with the Gibbs method it would be necessary to know the molal volumes of the pure gas at certain important pressures. In order to use such fugacity values in connection with corrections of the Lewis and Randall rule, found from linear combination of parameters, it would of course be necessary to have equation of state constants for the various pure gases. But it would not be necessary to have these with the same accuracy as would be necessary for calculation of the fugacity values themselves; and it may be that some approximate calculation of the constants—for instance, by van der Waals theory from critical data—will in some cases be good enough for the purpose of calculating the correction terms.

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