46): C (graph), 1.3 e. u.; 0.5 H_2, 15.615 e. u.; 0.5 Cl_2, 26.62 e. u.; 0.5 Br_2, 16.3 e. u.; 0.5 I_2, 13.3 e. u.; and 0.5 F_2, 34.48 e. u.[31]

The molal free energies of formation of these compounds from their elements appear in the last column of the table. For the most part the accuracy of these values was limited by the accuracy of the combustion data employed, so that they were valid to about 3 or 4%.

The author wishes to express his appreciation to Dr. F. D. Rossini for making available the isomeric hexanes used in the work.

Summary

The construction and operation of a calorimeter suitable for determining specific heats together with heats of transition and fusion of organic compounds over the temperature range 100 to 320°K. has been described. The apparatus possesses the advantage of not employing a vacuum, and requiring only a 5- or 6-ml. sample.

The following compounds have been measured by this method: toluene, carbon tetrachloride, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, and the five isomeric hexanes. Two anomalies were brought to light. The specific heat of n-hexane showed a "hump" in the liquid state. The solid state of 2,2-dimethylbutane showed a large heat of transition some 50° below its melting point.

BALTIMORE, MARYLAND

RECEIVED JULY 29, 1937

(31) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., N. Y., 1923, p. 464.

The Fugacities in Gas Mixtures

BY I. R. KRICHEVSKY

Much time will be required before the slowly accumulating data on the $P-V-T$ relation of gas mixtures of different composition will permit computing the fugacity of the components of a gas mixture in accordance with the thermodynamic equation[1]

$$RT \ln f_i = RT \ln P + RT \ln N_i + \int_0^l \left(\overline{V}_i - \frac{RT}{P}\right) \mathrm{d}P \quad (1)$$

In this equation (1) f_i—is the fugacity of the component of the gas mixture, p—the total pressure, N_i—the mole fraction of the component in the mixture and $\overline{V}_i$—the partial molal volume of the component.

When solving thermodynamical problems dealing with high pressure, we shall still have to use for a long time approximate methods in computing the fugacity in gas mixtures.

The best of all known approximative methods is certainly the combination of constants in some proved equation of state; for instance those of Beattie–Bridgeman, Beattie[2] and Gillespie[3] have acquired in this field considerable success, and it is improbable that any other approximate method could compete for accuracy with this one.

Among other methods the approximate method of calculation of the fugacity in gas mixtures, known as the Lewis–Randall rule,[4] has been adopted widely. This rule is quite simple and is based, as Gillespie[5] has shown, on the law established by Amagat[6] with regard to the additive property of volumes. Representing an exact equation in the case of a component whose mole fraction is insignificantly or, to be more exact, infinitesimally differing from a unit, the rule of Lewis–Randall did not withstand experimental check,[7,8] when applied to other concentrations.

Randall and Sosnick[9] in a very important paper have pointed out the limitations of 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 pressure for the solute gas below its critical temperature."[9]

Apart from the Amagat law, other "laws" are known for the determination of the $P-V-T$ relation in gas mixtures, such relations being known for pure gases. For the determination of the

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(1) Gillespie, THIS JOURNAL, **48**, 28 (1926).

(2) Beattie, *ibid.*, **51**, 19 (1929); Beattie and Ykehara, *Proc. Am. Acad. Arts Sci.*, **64**, 127 (1930).

(3) Gillespie, *Phys. Rev.*, **34**, 352 (1929).

(4) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

(5) Gillespie, *Phys. Rev.*, **34**, 352, 1605 (1929).

(6) Amagat, *Ann. chim. phys.*, [5] **19**, 384 (1880); *Compt. rend.*, **127**, 88 (1898).

(7) Merz and Whittaker, THIS JOURNAL, **50**, 1522 (1928).

(8) Gibson and Sosnick, *ibid.*, **49**, 2172 (1927).

(9) Randall and Sosnick, *ibid.*, **50**, 967 (1928).

fugacity of gas mixtures these laws have not yet been used.

Bartlett's[10] rule may be regarded as a modification of Dalton's[11] law on the additive properties of pressures: "At a constant temperature the pressure exerted by one constituent in a gas mixture equals the product of its mole fraction and the pressure it would exert as a pure gas at a molal concentration equal to the molal concentration of the mixture."

In accordance with Bartlett's rule, the total pressure of a gas mixture is represented by the equation

$$P = P_1^0 N_1 + P_2^0 N_2 \qquad (2)$$

where P, P_1^0 and P_2^0 are, respectively, the total pressure of the gas mixture and the pressures of pure components, all of them being taken of the same molal volume.

In principle, Bartlett's rule enables us to compute the fugacity of the component of a gas mixture. When using equation (2), we should be able to calculate the volumes of a gas mixture at different pressures and of different composition and then, on the basis of these data, to find the partial molal volumes of the component and, at last, to compute in accordance with equation (1) the fugacity of component. But such a method would be too complex and rather inconvenient for practical purposes. The problem consists in deducing such an equation as would render it possible to compute quickly the fugacity in a gas mixture subordinate to Bartlett's rule.

Preliminarily we shall give a new aspect to the well-known equation deduced for the fugacity of a pure gas[4]

$$RT \ln f = RT \ln P + \int_0^P (V - V_{\text{id}})\,\mathrm{d}P \qquad (3)$$

where V is the molal volume of the gas and V_{id} the volume of the ideal gas. Integrating by parts, we find that

$$RT \ln f = RT \ln P + PV - RT - \int_\infty^V P\,\mathrm{d}V - \int_0^P V_{\text{id}}\,\mathrm{d}P$$

On the other hand we have

$$\int_0^P V_{\text{id}}\,\mathrm{d}P = RT \ln P - RT \ln P^*$$

where P^* is the infinitesimal pressure.

From Clapeyron's equations it results that

$$RT \ln P^* = RT \ln RT - RT \ln V_\infty$$

where V_∞ is the infinitely great volume. Hence

$$RT \ln f = PV - RT - RT \ln V_\infty + RT \ln RT - \int_0^V P\,\mathrm{d}V$$

By adding and subtracting $\int_\infty^V P_{\text{id}}\,\mathrm{d}V$ from the right-hand part of this latter equation and by simplifying it, we obtain the ultimate equation for the fugacity of pure gas

$$RT \ln f = RT \ln RT - RT \ln V + PV - RT - \int_\infty^V (P - P_{\text{id}})\,\mathrm{d}V \qquad (4)$$

We may then proceed with the computation of the fugacity in a gas mixture subordinate to Bartlett's rule.

By the method of intercepts the partial molal volume of the component is provided by the equation

$$\overline{V}_2 = V + N_1 \left(\frac{\partial V}{\partial N_2}\right)_P$$

V being the molal volume of the gas mixture.

The differentiation of equation (2) at constant pressure gives the relation

$$(\partial V/\partial N_2)_P = (P_1^0 - P_2^0)(\partial V/\partial P)_{N_2}$$

Hence

$$\overline{V}_2 = V + N_1(P_1^0 - P_2^0)(\partial V/\partial P)_{N_2}$$

By introducing the meaning of the partial molal volume of the component in equation (1) and by using the method applied in deducing equation (4) we arrive at the following result

$$RT \ln f_2 = RT \ln RT - RT \ln V + PV - RT + RT \ln N_2 - \int_\infty^V [P - N_1(P_1^0 - P_2^0) - P_{\text{id}}]\,\mathrm{d}V$$

By expressing the total pressure of the gas mixture in the latter equation according to Bartlett's rule and simplifying the equation, this latter will read

$$RT \ln f_2 = RT \ln RT - RT \ln V + PV - RT - \int_\infty^V (P_2^0 - P_{\text{id}})\,\mathrm{d}V + RT \ln N_2$$

The addition and subtraction of $P_2^0 V$ from the right-hand part of the equation gives

$$RT \ln f_2 = RT \ln RT - RT \ln V + P_2^0 V - RT - \int_\infty^V (P_2^0 - P_{\text{id}})\,\mathrm{d}V + RT \ln N_2 + (P - P_2^0)V$$

The first five members of the right-hand part of this equation simply represent the fugacity of the pure component, determined at the same volume as that of the gas mixture. Thus, finally

$$RT \ln f_2/N_2 = RT \ln f_2^0 + (P - P_2^0)V \qquad (5)$$

We must once more point out that in equation (5) the fugacity f_2 of the component in the mixture, as well as the fugacity of the pure com-

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[10] Bartlett, Cupples and Tremearne, THIS JOURNAL, **50**, 1275 (1928).

[11] Dalton, *Gilberts Ann. Physik*, **12**, 385 (1802); **15**, 1 (1803).

ponent f_2^0, and the total pressure of the gas mixture, P, as well as the pressure of the pure component, P_2^0, apply to the same molal volume.

It is of importance to point out that equation (5) is not confined to the case of a binary gas mixture, but is also applicable to gas mixtures of any composition whatsoever.

In the case of mixtures containing several components the partial molal volume of a component is given by the equation

$$\overline{V}_2 = V + N_1(\partial V/\partial N_2)_{N_3.\, N_i.\, N_k} + N_3(\partial V/\partial N_2)_{N_1,\, N_i.\, N_k} + \ldots + N_k(\partial V/\partial N_2)_{N_1,\, N_3.\, N_i} \quad (6)$$

The molal volume of the gas mixture and the partial molal volumes of the components are related to one another by the equation[4]

$$V = N_1\overline{V}_1 + N_2\overline{V}_2 + N_3\overline{V}_3 + \ldots N_i\overline{V}_i + N_k\overline{V}_k \quad (7)$$

By differentiating equation (7) in respect to N_2 at the expense of N_1 we arrive at

$$(\partial V/\partial N_2)_{N_3.\, N_i.\, N_k} = \overline{V}_2 - \overline{V}_2 + N_1\left(\frac{\partial \overline{V}_1}{\partial N_2}\right)_{N_3.\, N_i.\, N_k} + N_2\left(\frac{\partial \overline{V}_2}{\partial N_2}\right)_{N_3.\, N_i.\, N_k} + \ldots N_k\left(\frac{\partial \overline{V}_k}{\partial N_2}\right)_{N_3.\, N_i.\, N_k}$$

The equation of Gibbs–Duhem yields[4]

$$N_1\left(\frac{\partial \overline{V}_1}{\partial N_2}\right)_{N_3.\, N_i.\, N_k} + N_2\left(\frac{\partial \overline{V}_2}{\partial N_2}\right)_{N_3.\, N_i.\, N_k} + \ldots + N_k\left(\frac{\partial \overline{V}_k}{\partial N_2}\right)_{N_3,\, N_i.\, N_k} = 0$$

Hence

$$(\partial V/\partial N_2)_{N_3,\, N_i.\, N_k} = \overline{V}_2 - \overline{V}_1$$

When using a similar method we get

$$(\partial V/\partial N_2)_{N_1.\, N_i,\, N_k} = \overline{V}_2 - \overline{V}_3$$
$$(\partial V/\partial N_2)_{N_1,\, N_3,\, N_i} = \overline{V}_2 - \overline{V}_k$$

The substitution in equation (6) of the values found for

$$(\partial V/\partial N_2)_{N_3.\, N_i,\, N_k}, \ \ldots \ (\partial V/\partial N_2)_{N_1.\, N_3.\, N_i}$$

results in identity, which proves that this equation is correct.

By Bartlett's equation for multi-component systems

$$P = P_1^0N_1 + P_2^0N_2 + P_3^0N_3 + \ldots + P_i^0N_i + P_k^0N_k$$

we obtain

$$(\partial V/\partial N_2)_{N_3,\, N_i.\, N_k} = (P_1^0 - P_2^0)\partial V/\partial P$$
$$(\partial V/\partial N_2)_{N_1.\, N_3,\, N_i} = (P_k^0 - P_2^0)\partial V/\partial P$$

We have thus for a partial molal volume of a component "2" the equation

$$\overline{V}_2 = V + (N_1P_1^0 - N_1P_2^0 + N_3P_3^0 - N_3P_2^0 + \ldots + N_kP_k^0 - N_kP_2^0)\partial V/\partial P$$

By substituting in equation (1) this value for the partial molal volume of the component and by performing the operations mentioned above, we once more arrive at equation (5).

Equation (5) we will name Bartlett's rule.

Gibson and Sosnick's[8] computations and also those made by Merz and Whittaker[7] demonstrate that values computed according to the Lewis–Randall rule are not as good as those derived on the basis of the exact equation (1).

We will now prove that the fugacity value determined according to Bartlett's rule must always be better than the one obtained by the Lewis–Randall rule.

As already mentioned above, f_2^0 in equation (5) is the fugacity of a pure component, if the volume is V and the pressure is, consequently, P_2^0. According to the Lewis–Randall rule f_2^0 is the fugacity of a pure component at a pressure P. The relationship between these two fugacity values is expressed by the equation

$$RT \ln f^0_{2(P)} = RT \ln f^0_{2(P_2^0)} + \int_{P_2^0}^{P} V\mathrm{d}P$$

The right part of equation (5) differs from $RT \ln f^2_{0(P)}$ inasmuch as $(P - P^2_0)\ v$ is not equal to $\int_{P_2^0}^{P} V\mathrm{d}P$.

In the case of P being superior to P_2^0, the values $(P - P_2^0)\ V$ and $\int_{P_2^0}^{P} V\mathrm{d}P$ are positive. Inasmuch as the volume introduced in equation (5) corresponds to the lower pressure P_2^0, this volume represents the maximum volume within the pressure range from P_2^0 to P. Thus $(P - P_2^0)\ v$ will exceed $\int_{P_2^0}^{P} V\mathrm{d}P$ and the value of the fugacity determined in accordance with Bartlett's rule will exceed the one computed in accordance with the Lewis–Randall rule. In the case of P being smaller than P_2^0, the values $(P - P_2^0)\ V$ and $\int_{P_2^0}^{P} V\mathrm{d}P$ will be negative. In this case V already represents in equation (5) the smallest volume within the pressure range from P_2^0 to P and the absolute value of $(P - P_2^0)\ V$ must be less than $\int_{P_2^0}^{P} V\mathrm{d}P$. In this case the fugacity computed in accordance with Bartlett's rule will also exceed the value of the fugacity determined by the Lewis–Randall rule.

The rule of Bartlett has been checked by us on the argon–ethylene[8] mixture, where the Lewis–Randall rule yields very important errors.

The tests were made with solutions of ethylene in argon, where $N_{C_2H_4}$ = 0.0, 0.2, 0.4 and 0.6.

The test for the first two concentrations was made from 20 to 125 atm., the test for the third to 110 atm., and for the last to 90 atm.

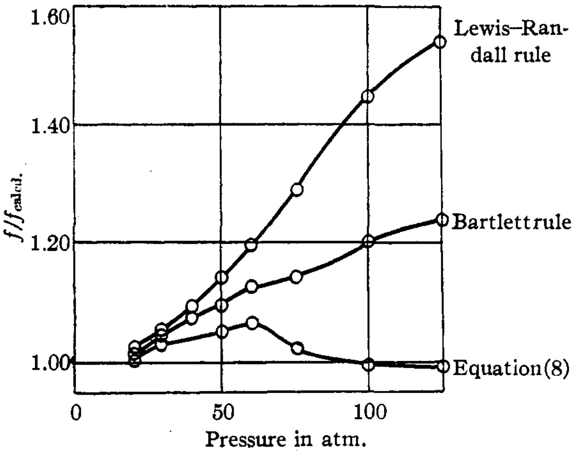

Fig. 1.—$N_{C_2H_4}$ = 0.0.

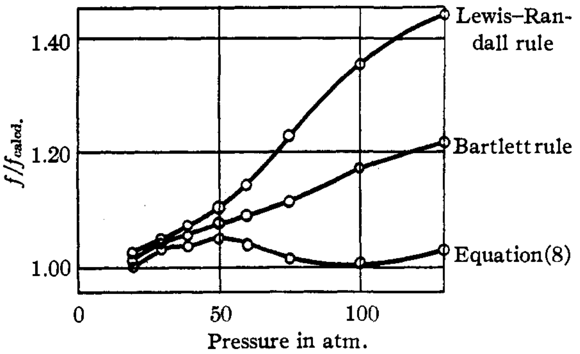

Fig. 2.—$N_{C_2H_4}$ = 0.2.

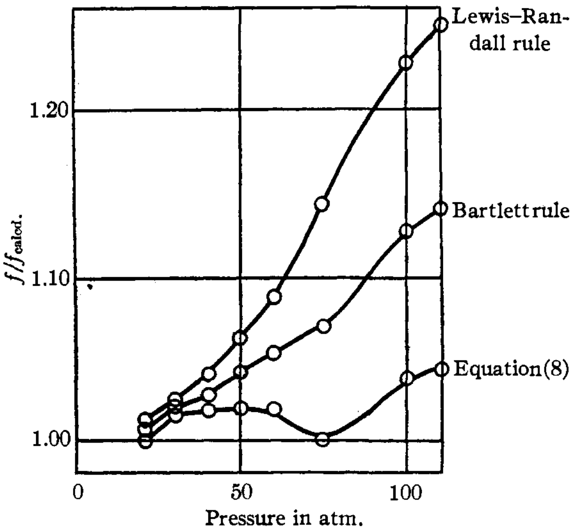

Fig. 3.—$N_{C_2H_4}$ = 0.4.

We were forced to diminish for the more concentrated solutions of ethylene the upper limit of pressure in order to avoid extrapolation of $P-V$ relation of argon, only known up to 125 atm.

As is to be seen from the curves reproduced in Figs. 1–4, Bartlett's rule gives much better results than the rule of Lewis–Randall.

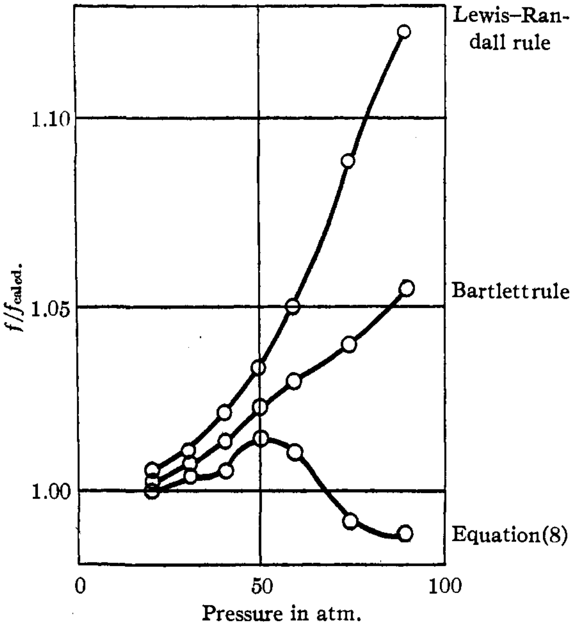

Fig. 4.—$N_{C_2H_4}$ = 0.6.

This was also confirmed by computing the fugacity of hydrogen in nitrogen–hydrogen mixtures at 0° at pressures of 1000 atm.[7] (Fig. 5).

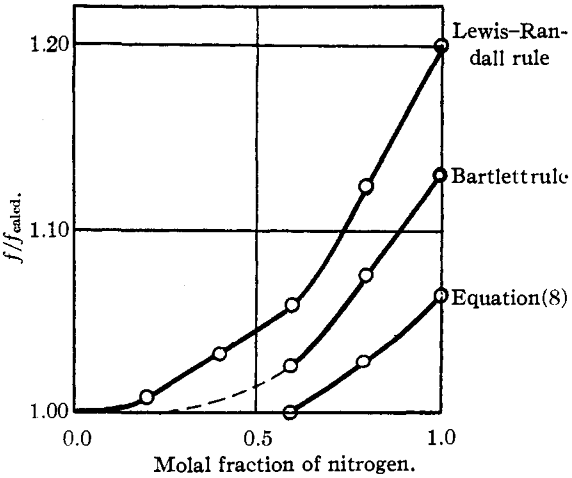

Fig. 5.—P = 1000 atm.

In computing the fugacity of gas mixtures by Bartlett's rule the error arrived at generally amounts to about half the error found when applying the Lewis–Randall rule. Still, the absolute value of this error is rather considerable.

Endeavoring to provide some more satisfactory agreement, we have found that satisfactory results are obtained when it is assumed that the fugacity computed according to Bartlett's rule is the geometrical mean of the true fugacity and the fugacity computed according to the Lewis–Randall rule

$$f:f_B = f_B:f_{L.R.} \qquad (8)$$

where f is the true value of the fugacity, f_B the fugacity computed by Bartlett's rule and $f_{L.R.}$ the one computed by the Lewis–Randall rule.

Equivalent to equation (8) are the following conditions: the volume of a gas mixture computed by Bartlett's rule is the arithmetical mean from the true volume and the volume computed according to the Amagat law

$$V - V_B = V_B - V_A$$

where V is the true volume of the gas mixture, V_B and V_A, the volumes computed in accordance with Bartlett's and Amagat's rules, respectively.

As is to be seen from Figs. 1–5, compared to the rules of Lewis–Randall and Bartlett, the best results are obtained from equation (8).

The error of calculation of fugacity in gas mixtures by equation (8) makes mostly 2 to 5% and is often 10 times less than the error of the Lewis–Randall rule.

For ethylene and argon ($N_{C_2H_4} = 0.2$) Gillespie,[3] by combination of constants, has found better coincidence with the data of Gibson and Sosnick.[8] The error of calculation of fugacity was only 0.17% from 15–70 atm.

Although the combination of constants is the most exact of the approximate methods, nevertheless the methods proposed by us in view of their simplicity and sufficient accuracy can have scientific and engineering interest.

I am very indebted to J. S. Kasarnovsky for his help in making the calculations.

Summary

An equation is deduced for the computation of the fugacities in gas mixtures subordinate to the Bartlett rule. The examples of the systems argon–ethylene (to 125 atm.) and hydrogen–nitrogen (1000 atm.) prove that the Bartlett rule gives half the error of the Lewis–Randall rule.

For these systems an agreement with errors from 2 to 5% with the true fugacity values is attainable, if it be assumed that the fugacity computed in accordance with Bartlett's rule is the geometrical mean of the true fugacity and the fugacity computed in accordance with the Lewis–Randall rule.

MOSCOW, U. S. S. R. RECEIVED APRIL 7, 1937

NOTES

The Thermal Decomposition of Gaseous Hydrogen Peroxide

BY L. W. ELDER, JR.

In a recent note[1] commenting on the kinetics of the thermal decomposition of gaseous hydrogen peroxide, Kistiakowsky and Rosenberg have erroneously concluded that the data published by Elder and Rideal[2] correspond to a pressure increase of "about 1000%" instead of the theoretical 50%. This conclusion is apparently based on the assumption that the pressure readings as tabulated, *e. g.*, page 548, are total pressures. Actually these are manometer readings representing the pressure increase only, *i. e.*, based on a zero setting of the manometer at the start of the reaction. It is regretted that these pressures were not more explicitly identified in the tabulation as incremental pressures; however, this distinction is clearly shown by the coördinates of the curve (Fig. 2). On the other hand, the figures shown on page 547, involving total pressure readings, lead to an average pressure increase of 52%. This is as close to theoretical as could be expected in view of uncertainties regarding the initial concentrations after evacuating the charge at room temperature. No attempt was made to keep the initial concentrations at any predetermined value, since the "infinity" readings were used in every case for calculation of the rate constants.

GENERAL FOODS CORPORATION
BATTLE CREEK, MICHIGAN
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(1) Kistiakowsky and Rosenberg, THIS JOURNAL, **59**, 422 (1937).

(2) Elder and Rideal, *Trans. Faraday Soc.*, **23**, 545 (1927).