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

A COMPUTATION OF THE FREE ENERGY AND FUGACITY IN GASEOUS MIXTURES OF ETHYLENE AND ARGON

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Introduction and Discussion of Results

The determination of the fugacity or free energy of a gas in a mixture is of considerable practical and theoretical interest. Lewis and Randall[1] consider it likely that almost any gaseous solution would be nearly perfect, that is, at a given temperature and total pressure the fugacity of any constituent would be proportional to its mole fraction or partial pressure.[2]

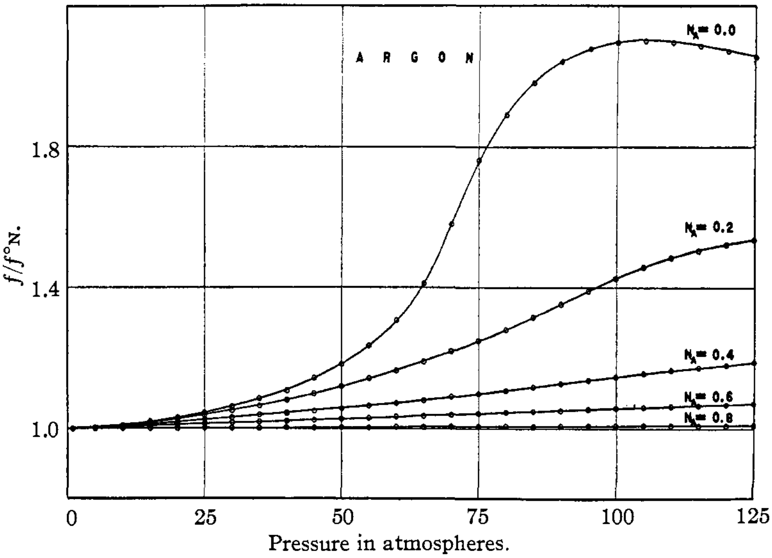

Fig. 1.—Deviation of argon in ethylene-argon mixtures from the rule of Lewis and Randall.

The partial pressure here is defined as the product of the mole fraction and the total pressure. The only data available in the literature for an accurate calculation of the fugacities in a gaseous mixture are those of Masson and Dolley,[3] who determined the isotherms of gaseous mixtures of varying composition of argon and ethylene at pressures from 30 to 125 atmospheres

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

[2] In a recent article by Lurie and Gillespie [THIS JOURNAL, 49, 1154 (1927)] this rule is found to hold fairly well for the Haber equilibrium at pressures up to about 13 atm. The deviations from Dalton's law are too small, however, at these pressures for an adequate test of the rule.

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

at 24.95°. The fugacities of both constituents have been calculated from these data and the results are shown graphically in Figs. 1 and 2. Details of the calculation will be given in the next section. In Fig. 1 (2) the ratios of $f/f^\circ\text{N}$ for argon (ethylene) are plotted as ordinates for various mole fractions, against the pressure in atmospheres as abscissas. Here f is the fugacity of the component under consideration, f° the fugacity of the pure component at the pressure of the mixture and N its mole fraction. The graphs show clearly the deviations of these mixtures from the perfect solution represented by the horizontal line $f/f^\circ\text{N} = 1$. In the limiting case, that of argon at zero concentration and about 100 atmospheres, the fugacity is nearly twice the value calculated on the assumption of a perfect solution. Thus the error made in calculating the partial molal free energy on the assumption of a perfect solution is given by the difference $RT \ln f - RT \ln f^\circ\text{N}$, which in this extreme case for argon is about 440 calories. Up to about 50 atmospheres the rule of Lewis and Randall is very closely obeyed, the maximum deviation for argon at zero concentration at this pressure being about 96 calories.

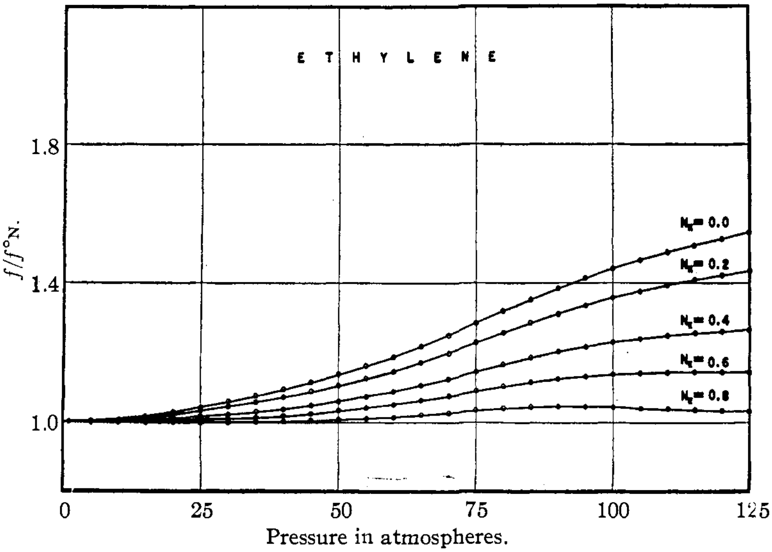

Fig. 2.—Deviations of ethylene in ethylene-argon mixtures from the rule of Lewis and Randall.

Theory of the Calculation of the Fugacities from the Isotherms of Binary Mixtures

Consider a system consisting of n_1 moles of component I and n_2 moles of component II. Let its volume at total pressure P and absolute temperature T be V. The partial molal volume, $\bar{v}_1$, of constituent I is defined by the equation

$$\bar{v}_1 = \frac{\delta V}{\delta n_1} \tag{1}$$

and similarly for $\bar{v}_2$. The change in free energy in removing one mole of constituent I from a mixture at pressure P to a mixture of the same concentration at pressure P' is given by

$$\Delta F = \int_P^{P'} V\mathrm{d}P \tag{2}$$

The ratio of the fugacities is then given by the equation

$$\ln\frac{f'}{f} = \frac{\Delta F}{RT} = \frac{1}{RT}\int_P^{P'} \bar{v}\mathrm{d}P \tag{3}$$

The arbitrary constant in the fugacity is determined by making the fugacity of a perfect gas equal to its pressure. From these equations it is possible to calculate the fugacity of the constituents, when the total volume is known as a function of pressure and composition. Equation 3 is, however, not of convenient form for actual computation, and for this purpose may be transformed as follows. Defining the quantity α by the equation

$$\alpha = \frac{RT}{P} - \bar{v} \tag{4}$$

and noting that at zero pressure $f = \mathrm{N}P$, we obtain by substitution

$$RT \ln f = RT \ln \mathrm{N}P - \int_0^P \alpha\mathrm{d}P \tag{5}$$

or substituting base ten logarithms for natural logarithms, we obtain with $R = 82.07$ cc. atmos. per degree

$$\log f = \log \mathrm{N}P - \frac{1}{189.07T}\int_0^P \alpha\mathrm{d}P \tag{6}$$

In Equation 6, f and P are expressed in atmospheres and α in cubic centimeters. In order to obtain α we must first calculate $\bar{v}$, and here again the basic equation, Equation 1, is not in a convenient form for computation. We have, therefore, made use of the method described in the note of Sosnick.[4] For partial molal volumes, Sosnick's equation becomes

$$\bar{v}_1 = v_1 + \Delta + \mathrm{N}_2\frac{\mathrm{d}\Delta}{\mathrm{dN}_1}, \tag{7}$$

where v_1 is the molal volume of pure constituent I and Δ is defined by the equation

$$\Delta = v - (\mathrm{N}_1 v_1 + \mathrm{N}_2 v_2) \tag{8}$$

where $v = V/(n_1 + n_2)$ is the molal volume of the mixture and v_1 and v_2 are the molal volumes of the pure constituents.

The calculation thus resolves itself into the computation of N_1, N_2, v_1, v_2 and v from the data of Masson and Dolley,[3] the graphical evaluation of $\bar{v}_1$ and $\bar{v}_2$, using Equations 7 and 8, and the evaluation of the fugacity by graphical integration, using Equations 4 and 6.

[4] Sosnick, Note, THIS JOURNAL, 49, 2255 (1927).

Calculation of the Fugacities in the Mixtures of Ethylene and Argon From the Data of Masson and Dolley

Masson and Dolley[3] express their results in terms of "density D" which they define by

$$D = \frac{\text{sum of separate volumes at 1 atm.}}{\text{volume of mixture at } P \text{ atm.}} \tag{9}$$

The composition is expressed as percentage by volume of the separate constituents at one atmosphere. In order to calculate the mole fraction N from the volume per cent. V.P. we first obtain the molal volumes v_1 and v_2 of argon and ethylene, respectively, from the liter weight L of these gases, namely, $L_A = 1.781$ g. per liter at 0° and 1 atm.[5] and $L_{C_2H_4} = 1.2609$ g. per liter at 0° and 1 atm.,[6] and then employ the equations

$$N_1 = 1 - N_2 = (\text{V.P.})_1/v_1 \Big/ \left(\frac{(\text{V.P.})_1}{v_1} + \frac{100 - (\text{V.P.})_1}{v_2}\right) \tag{10}$$

The molal volumes, v, of the mixture are now obtained from the equation

$$v = \frac{N_1v_1 + N_2v_2}{D} \tag{11}$$

and are given in Table I.

Table I

Molal Volumes

P (atmos.)	Mole fractions of C_2H_4 0.0000	0.2490	0.5017	0.6007	0.7091	0.9014	1.0000
1	24478	24425	24371	24350	24327	24286	24265
5	4882						4729
10	2431						2291
15	1615						1477
20	1208						1070
25	962.6						824.5
30	800.2	781.6	749.0	738.1	721.4	681.2	658.7
35	684.3	665.5	636.3	621.65	607.9	563.2	538.3
40	597.0	578.5	549.3	534.5	517.5	474.15	446.7
45	529.5	511.0	481.8	466.8	449.2	403.9	374.2
50	475.6	457.1	427.6	412.7	394.6	347.4	313.8
55	431.3	413.1	383.8	368.7	349.9	300.3	262.5
60	394.6	376.6	347.3	332.0	312.5	260.3	216.75
65	363.5	345.6	316.5	300.9	280.9	226.3	174.8
70	336.8	319.2	290.1	274.4	251.7	197.1	141.3
75	313.9	296.3	267.4	251.55	230.7	171.9	118.6
80	293.9	276.2	247.6	231.7	210.9	151.0	105.9
85	276.1	258.8	230.2	214.35	193.5	134.55	98.36
90	260.4	243.2	214.8	199.3	178.2	122.1	93.435
95	246.4	229.2	201.2	185.45	165.0	112.6	90.00
100	233.8	216.9	189.1	173.4	153.5	105.5	87.25
105	222.4	205.8	178.2	162.9	143.4	100.1	85.02
110	212.1	195.7	168.5	153.6	134.7	95.92	83.24

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[5] Watson, *J. Chem. Soc.*, **97**, 833 (1910).

[6] Stahrfoss, *Arch. sc. phys.*, **28**, 304 (1908).

TABLE I (*Concluded*)

P (atmos.)	Mole fractions of C_2H_4 0.0000	0.2490	0.5017	0.6007	0.7091	0.9014	1.0000
115	202.7	186.6	159.8	145.4	127.1	92.52	81.76
120	194.1	178.3	152.0	137.9	120.7	89.68	80.375
125	186.3	170.6	145.0	131.3	115.2	87.30	79.22

The partial molal volumes calculated from Equation 7 are given in Table II.

TABLE II

PARTIAL MOLAL VOLUMES

P (atmos.)	Mole fractions of $C_2H_4(N_2)$ 0.0		0.2		0.4		0.6		0.8		1.0	
	v_1	$\bar{v}_2$	$\bar{v}_1$	$\bar{v}_2$	$\bar{v}_1$	$\bar{v}_2$	$\bar{v}_1$	$\bar{v}_2$	$\bar{v}_1$	$\bar{v}_2$	$\bar{v}_1$	v_2
1	24478											24265
5	4882											4729
10	2431											2291
15	1615											1477
20	1208											1070
25	962.6											824.5
30	800.2	735.1	802.8	718.4	814.0	692.5	829.6	677.2	863.5	662.2	888.6	658.7
35	684.3	619.9	687.1	601.2	697.8	576.7	716.2	558.9	752.3	544.0	797.7	538.3
40	597.0	534.3	600.6	512.3	610.6	489.3	626.0	474.9	678.5	453.7	724.1	446.7
45	529.5	465.4	532.0	447.9	542.9	422.8	559.4	405.7	616.0	383.6	676.2	374.2
50	475.6	412.0	478.8	391.6	489.0	367.8	506.1	351.6	565.4	327.1	667.6	313.8
55	431.3	368.4	433.9	351.5	445.4	324.4	465.2	304.8	528.6	279.9	669.9	262.5
60	394.6	332.0	397.0	316.2	409.3	288.0	432.8	264.9	498.9	238.9	707.1	216.8
65	363.5	298.4	365.7	285.2	378.7	256.7	401.1	234.4	474.8	205.4	801.5	174.8
70	336.8	273.9	339.1	259.4	353.0	229.7	383.4	201.2	447.1	174.5	996.8	141.3
75	313.9	249.8	316.3	236.1	328.9	208.8	354.8	182.7	435.6	161.2	726.9	118.6
80	293.9	229.8	296.2	215.9	307.8	190.6	335.9	162.5	424.7	128.7	576.9	105.9
85	276.1	214.8	278.3	200.2	290.7	173.0	319.2	144.6	411.2	109.5	456.1	98.4
90	260.4	201.2	262.8	184.8	274.8	157.7	302.8	130.3	395.6	94.2	372.4	93.4
95	246.4	187.3	248.6	171.7	260.7	144.5	288.3	117.1	376.9	82.8	306.4	90.0
100	233.8	173.6	235.6	161.0	248.3	133.3	274.0	106.5	354.9	75.0	256.8	87.3
105	222.4	162.3	224.4	149.6	237.1	122.1	262.3	96.8	321.1	72.2	222.4	85.0
110	212.1	154.3	214.2	140.3	226.1	113.5	250.0	89.5	290.6	71.2	192.3	83.2
115	202.7	145.5	205.1	131.0	216.4	105.8	239.3	83.0	264.3	70.9	172.7	81.8
120	194.1	138.8	196.4	124.4	207.8	98.5	227.7	78.1	243.1	70.2	158.4	80.4
125	186.3	130.6	188.1	118.9	199.2	93.4	216.5	74.5	223.8	69.9	144.7	79.2

From Table II the values of $\alpha = RT/P - \bar{v}$ (Equation 4) were calculated and are plotted against P for various mole fractions in Fig. 3. The values of $\int_0^P \alpha dP$ were obtained by graphical integration of these curves, and thence by Equation 9 the values of $\log f$ from which the curves of f/f°_N plotted in Figs. 1 and 2 were derived. The free energies given in Tables III and IV were obtained by multiplying the values of $\log f$ by 1364.9 = (2.3026RT).

TABLE III

FREE ENERGY OF ARGON

P (atmos.)	$N_{C_2H_4}$ 0.0	0.2	0.4	0.6	0.8
1	0	−132	−302	−543	−954
5	954	822	652	412	2

TABLE III (*Concluded*)

P (atmos.)	$N_{C_2H_4}$ 0.0	0.2	0.4	0.6	0.8
10	1364	1231	1063	825	415
15	1602	1470	1304	1067	658
20	1771	1639	1474	1239	832
25	1901	1769	1606	1372	969
30	2007	1876	1714	1482	1082
35	2097	1966	1805	1575	1180
40	2174	2043	1884	1656	1266
45	2242	2112	1953	1728	1344
50	2303	2173	2016	1793	1416
55	2358	2228	2072	1851	1482
60	2408	2278	2124	1906	1544
65	2454	2325	2172	1956	1603
70	2496	2367	2216	2004	1659
75	2535	2407	2257	2048	1713
80	2572	2444	2296	2090	1765
85	2607	2479	2332	2130	1816
90	2639	2511	2366	2167	1865
95	2670	2542	2399	2203	1911
100	2699	2572	2430	2237	1956
105	2727	2600	2459	2270	1997
110	2753	2626	2487	2301	2034
115	2778	2652	2514	2330	2067
120	2802	2676	2540	2359	2098
125	2825	2699	2564	2386	2126

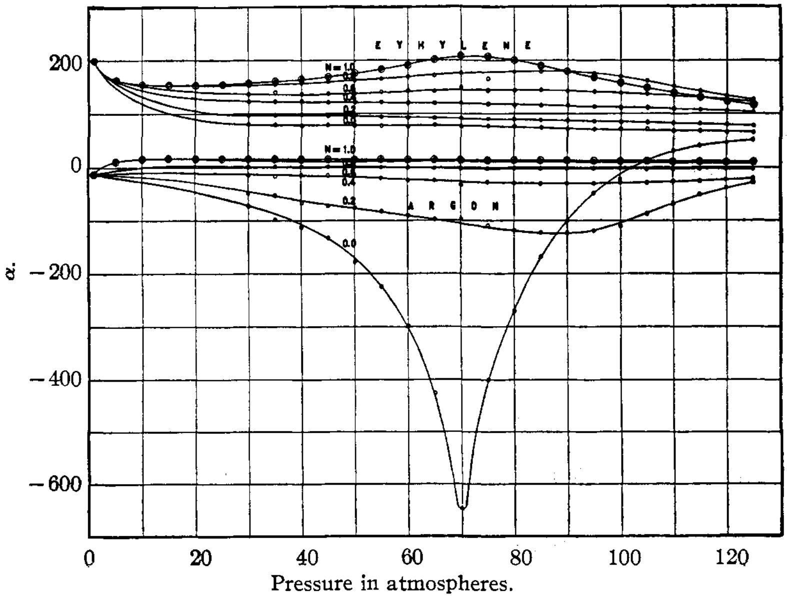


Fig. 3.—Graph of α as a function of P.

Table IV

Free Energy of Ethylene

	$N_{C_2H_4}$				
P(atmos.)	0.2	0.4	0.6	0.8	1.0
1	−959	−548	−308	−137	−5
5	−22	389	629	799	932
10	373	781	1021	1191	1323
15	599	1005	1243	1413	1545
20	756	1160	1396	1565	1697
25	876	1277	1511	1679	1810
30	972	1370	1603	1768	1899
35	1052	1446	1677	1841	1972
40	1119	1511	1740	1901	2031
45	1177	1566	1793	1952	2081
50	1228	1614	1838	1995	2122
55	1273	1656	1878	2031	2157
60	1313	1693	1913	2063	2186
65	1349	1725	1943	2090	2210
70	1382	1755	1969	2113	2229
75	1412	1781	1992	2132	2244
80	1440	1806	2013	2149	2258
85	1465	1828	2032	2163	2270
90	1488	1848	2048	2176	2282
95	1510	1866	2063	2186	2293
100	1530	1883	2077	2196	2304
105	1549	1898	2089	2205	2314
110	1566	1912	2100	2214	2324
115	1583	1926	2111	2222	2334
120	1598	1938	2121	2231	2344
125	1613	1950	2130	2239	2354

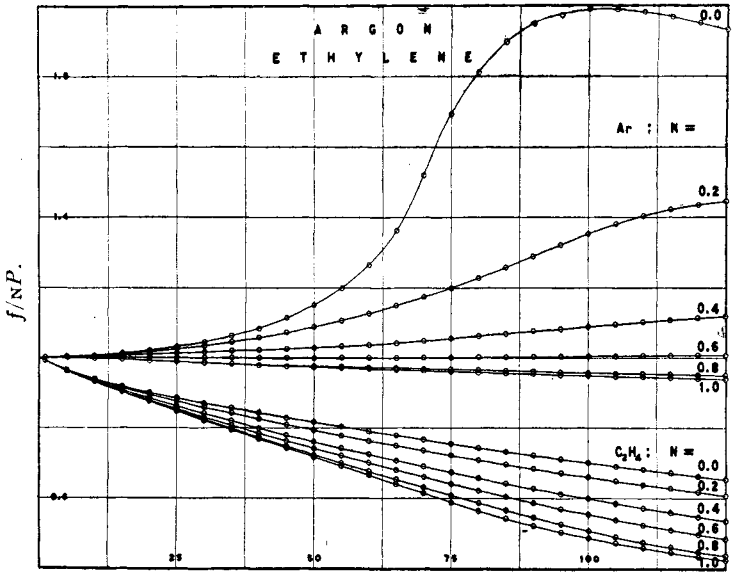
In order to show the deviations of the two gases from the ordinary perfect gas laws for mixtures, the values of f/NP have been calculated and are shown in Fig. 4.

It is difficult to give an estimate of the accuracy of the calculated fugacities. The errors introduced in the course of the calculations are certainly much less than the probable experimental error. Making reasonable but very liberal assumptions as to the experimental uncertainty, based on the irregularities in the curves of Δ (Equation 8) against N, we estimate the limit of error in the fugacities to be as follows.

1. The greatest errors occur in the values for argon at zero concentration, that is, for argon in pure ethylene. They range from a few hundredths of a per cent. at one atmosphere to a maximum of 7% at 125 atmospheres. With increasing mole fractions of argon the uncertainty in the fugacities at each pressure diminishes until in pure argon the error limit varies from a few hundredths of one per cent. at one atmosphere to 1.5% at 125 atmospheres.

2. For ethylene at zero concentration the error ranges from a few

hundredths of a per cent. at one atmosphere to 4.6% at 125 atmospheres, diminishing slightly with increasing mole fraction at each pressure. In pure ethylene the error ranges from zero to 3.5%.



Pressure in atmospheres.

Fig. 4.—Graphical representation of the fugacities and deviations from the perfect gas law $f = \text{N}P$ of ethylene and argon in their mixtures.

Summary

In order to test the rule of Lewis and Randall, that the fugacity of a constituent in a mixture of gases is the product of the mole fraction and the fugacity of the pure constituent at the pressure of the mixture, the fugacities of ethylene and argon were calculated from the experimental data of Masson and Dolley. The rule was found to hold fairly well at low pressures. At about 50 atmospheres, however, the error of the fugacity calculated by the rule ranges from zero to 20%, depending on the mole fraction. At 100 atmospheres the errors range from zero to about 100%.

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