run for a longer time than is customary, it can be made more sensitive for potassium than zirconium sulfate solution.

4. With dilute solutions of potassium sulfate—0.5 mg. of potassium—a comparison blank test with water and zirconium sulfate was needed. When sodium was present, a blank using sodium sulfate and zirconium sulfate was used for comparison with the solution tested.
5. Dilution of the zirconium sulfate solution to 10.48%, or one-half strength, had little or no effect upon its sensitiveness for potassium in the absence of sodium and increased the sensitiveness for potassium from 1.76 mg. of potassium to 0.7 mg. of potassium in the presence of sodium. No deposit in the blank test was formed.
6. To detect potassium with zirconium sulfate, add to the solution to be tested an equal volume of zirconium sulfate solution. If a deposit does not form at room temperature, cool in ice water. With small amounts of potassium a comparison with a blank is necessary.

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[Contribution from the Fertilizer and Fixed Nitrogen Laboratory of the United States Bureau of Chemistry and Soils]

THE FREE ENERGY AND FUGACITY IN GASEOUS MIXTURES OF HYDROGEN AND NITROGEN

By Albert R. Merz and Colin W. Whittaker

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Knowledge concerning the free energies and fugacities of gases in mixtures is very meager. Lewis and Randall[1] assumed, *in the absence of theoretical or experimental investigations on the subject,* that every gaseous solution is a perfect solution and therefore that at a given temperature and total pressure the fugacity of each constituent is proportional to its mole fraction or to its partial pressure. This assumption was based on the supposition "that the solution of a given pair of substances will be more nearly perfect when the density of the solution is less" and by reason of the fact that "even among liquids numerous cases occur where there is a close approach to the perfect solution."

Lurie and Gillespie,[2] applying this rule to the calculation of the equilibrium pressures of ammonia, in mixture with nitrogen, over $BaCl_2 + BaCl_2{\cdot}8NH_3$, found in the region where it could be applied that it gave results in fair agreement with the observed equilibrium pressures. This region, however, was limited to pressures of less than 17 atmospheres.

Gibson and Sosnick,[3] using the experimental results of Masson and

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

[2] Lurie and Gillespie, This Journal, **49**, 1154 (1927).

[3] Gibson and Sosnick, *ibid.*, **49**, 2172 (1927).

Dolley,[4] have recently calculated the fugacities and free energies of ethylene and argon in their mixtures up to pressures of 125 atmospheres. The rule of Lewis and Randall was found to be closely obeyed at low pressures. At about 50 atmospheres it was in error by 0 to 20%, according to the mole fraction, while for argon at zero concentration and about 100 atmospheres the fugacity is nearly twice the value calculated on the assumption of a perfect solution.

The experimental results of Bartlett[5] make possible the calculation of the fugacities of hydrogen and nitrogen in mixtures at 0° and under pressures ranging up to 1000 atmospheres. A full description of the method of calculation of fugacities from the isotherms of binary mixtures has already been given by Gibson and Sosnick[3] and need not be repeated here. Bartlett reports his values in terms of "density D," expressed in grams per liter. Division of the density D_p at pressure P of a given mixture by density, D_1, of the same mixture at 1 atmosphere, gives the volume of gas at 1 atmosphere compressed to 1 liter at P atmospheres. We assume, as did Bartlett, that at 1 atmosphere the sum of the separate volumes equals the volume of the mixture. The result of the division, therefore, also gives the "density D" of Masson and Dolley. The mole fraction was calculated from the volume per cent., V.P., by first obtaining the molal volumes v_1 and v_2 of hydrogen and nitrogen, respectively, from the liter weight L of these gases, namely, $L_{H_2} = 0.898$ g. per liter at 0° and 1 atm. and $L_{N_2} = 1.2507$ g. per liter at 0° and 1 atm., and then employing the equation

$$N_1 = 1 - N_2 = (V.P.)_{1/v_1} \frac{(V.P.)_1}{v_1} + \frac{100 - (V.P.)_1}{v_2} \tag{1}$$

The molal volumes, v, of the mixture as obtained from the equation

$$v = \frac{N_1 v_1 + N_2 v_2}{D_p / D_1} \tag{2}$$

are given in Table I.

TABLE I

MOLAL VOLUMES OF MIXTURES OF HYDROGEN AND NITROGEN

	Mole Fractions of N_2									
P (atmos.)	0.0000	0.1152	0.2464	0.4495	0.5415	0.6595	0.7404	0.8633	0.9391	1.000
1	22449.9	22444.2	22437.6	22427.7	22423.1	22417.2	22413.2	22407.1	22403.3	22400.3
50	464.1	463.2	460.9	457.5	456.3	452.9	450.6	446.3	443.8	441.1
100	239.4	238.4	237.4	234.6	233.2	230.5	228.6	225.0	222.9	220.5
200	127.8	126.8	126.6	125.2	123.9	122.5	121.0	119.0	117.7	116.4
300	90.5	90.3	90.0	89.6	88.7	87.8	87.3	86.2	85.6	85.0
400	72.0	72.1	72.3	72.3	72.0	71.5	71.3	70.9	70.8	70.5
600	53.4	53.9	54.6	55.4	55.5	55.9	56.1	56.7	56.9	56.9
800	44.1	44.8	45.8	47.1	47.4	48.2	48.7	49.5	49.9	50.5
1000	38.5	39.4	40.5	42.1	42.7	43.5	44.1	45.2	45.8	46.4

The partial molal volumes, calculated by means of Sosnick's[6] equation, are contained in Table II.

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

[5] Bartlett, THIS JOURNAL, **49,** 1955 (1927).

[6] Sosnick, *ibid.*, **49,** 2256 (1927).

TABLE II

PARTIAL MOLAL VOLUMES OF HYDROGEN AND NITROGEN IN THEIR MIXTURES

	Mole Fractions of N_2											
	0.0		0.2		0.4		0.6		0.8		1.0	
P (atmos.)	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	22449.9	...	...	...	...	...	...	...	...	...	...	22400.3
50	464.1	457.1	465.0	451.0	466.4	447.5	468.9	444.6	475.5	441.9	481.6	441.1
100	239.4	236.6	239.9	229.9	241.3	226.7	243.9	224.1	249.4	221.6	253.6	220.6
200	127.8	124.2	128.1	122.7	129.1	120.3	131.4	118.0	113.6	116.7	136.4	116.4
300	90.5	88.6	90.6	88.0	91.1	86.9	92.1	85.9	93.5	85.3	94.9	85.0
400	72.0	73.9	72.1	72.8	72.5	71.8	73.1	71.2	73.9	70.7	74.8	70.5
600	53.4	59.2	53.6	57.7	53.6	57.3	53.8	57.3	54.2	57.0	54.6	57.0
800	44.1	50.0	44.0	50.3	43.9	50.6	44.0	50.6	44.1	50.5	44.0	50.5
1000	38.5	45.9	38.5	46.0	38.3	46.4	38.5	46.4	38.4	46.4	38.5	46.4

The values of $\alpha = RT/P - \bar{v}$ were calculated from Table II and plotted against P for various mole fractions. Graphical integration of these curves gave the values of $\int_0^P \alpha \, dP$ and by use of the equation

$$\log f/\mathrm{N}P = \frac{1}{2.3026 \times 82.07 \times 273.1} \int_0^P \alpha \, dP$$

the values of $f/\mathrm{N}P$ and of $\log f$ were obtained.

The free energies given in Table III were obtained by multiplying these values of $\log f$ by 1250.45 = 2.3026 RT, R here being expressed in calories per degree.

TABLE III

FREE ENERGY OF HYDROGEN AND NITROGEN

	N_{N_2}											
	0.0		0.2		0.4		0.6		0.8		1.0	
P (atmos.)	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2
1	1		−120	−881	−276	−498	−497	−278	−873	−122		0
50	2155		2035	1243	1880	1619	1662	1837	1289	1992		2112
100	2551		2432	1623	2278	1997	2062	2210	1697	2363		2483
200	2966		2846	2020	2696	2387	2482	2595	2128	2744		2861
300	3223		3104	2271	2957	2632	2745	2836	2397	2983		3099
400	3418		3299	2465	3154	2823	2943	3025	2597	3171		3283
600	3714		3597	2776	3454	3129	3245	3330	2901	3474		3587
800	3948		3831	3035	3689	3388	3480	3589	3137	3732		3844
1000	4146		4029	3268	3887	3622	3677	3823	3336	3967		4079

TABLE IV

DEVIATION OF HYDROGEN AND NITROGEN IN THEIR MIXTURES FROM THE PERFECT GAS LAW $f/\mathrm{N}P = 1$

	N_{N_2}											
	0.0		0.2		0.4		0.6		0.8		1.0	
P (atmos.)	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2
1	1.002	0.999	1.002	0.999	1.002	0.999	1.002	0.999	1.002	0.999	1.002	0.999
50	1.058	.997	1.060	.987	1.063	.986	1.066	.981	1.074	.979	1.078	.978
100	1.096	1.020	1.101	.993	1.105	.989	1.113	.976	1.137	.969	1.153	.965
200	1.176	1.081	1.179	1.031	1.193	1.013	1.208	.990	1.258	.977	1.297	.971
300	1.261	1.152	1.266	1.091	1.285	1.061	1.307	1.031	1.375	1.011	1.426	1.002
400	1.353	1.241	1.358	1.170	1.384	1.131	1.412	1.093	1.493	1.073	1.555	1.055
600	1.556	1.476	1.568	1.383	1.605	1.325	1.638	1.278	1.739	1.250	1.863	1.231
800	1.796	1.796	1.808	1.672	1.855	1.600	1.895	1.546	2.015	1.508	2.159	1.485
1000	2.069	2.205	2.086	2.052	2.141	1.969	2.185	1.902	2.325	1.858	2.489	1.828

The ratios of $f/\text{N}P$ are given in Table IV. These values show the deviations from the perfect gas law $f = \text{N}P$ of hydrogen and nitrogen, respectively, in their mixtures.

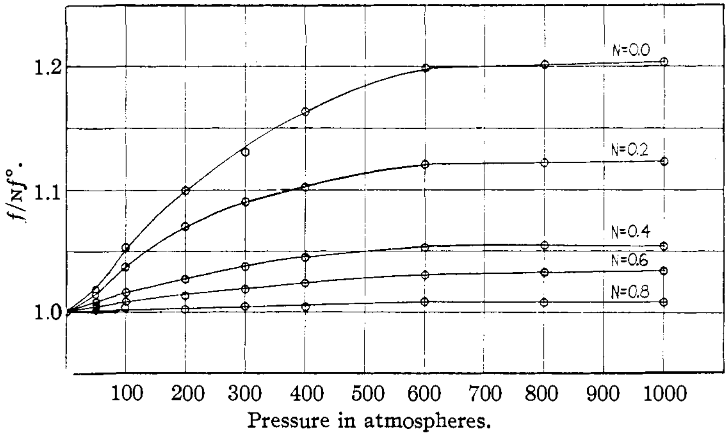

Fig. 1.—Deviation of hydrogen in hydrogen-nitrogen mixtures from the law of the perfect solution $f/\text{N}f^\circ = 1$.

The ratios of $f/\text{N}f^\circ$ for hydrogen are plotted in Fig. 1 against pressures for the different mole fractions and similarly for nitrogen in Fig. 2. It will be observed from these graphs that even at pressures around 1000 atmospheres the deviation from the law of the perfect solution $f/\text{N}f^\circ = 1$ is only about 20%. It is particularly noteworthy that near the limiting case for hydrogen at zero concentration and 1000 atmospheres the density of the solution is about six-tenths that of water.

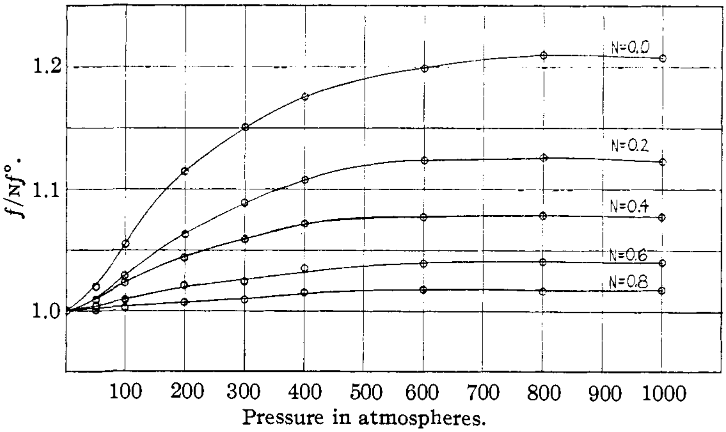

Fig. 2.—Deviation of nitrogen in hydrogen-nitrogen mixtures from the law of the perfect solution $f/\text{N}f^\circ = 1$.

The accuracy of the calculation of the fugacities is dependent primarily upon the determination of the slopes of the curves of Δ against N. These slopes in turn are dependent upon the magnitudes of Δ. With such small magnitudes of Δ as were found (the maximum $\Delta = 4.6$) it is estimated that the probability of a greater error than 1.5% is very slight. Independent calculations by both authors differed in most instances by less than 0.3% and in only two instances approached a difference of 1.5%.

Summary

The fugacities and free energies of hydrogen and nitrogen in their mixtures have been calculated from the experimental results of Bartlett. Maximum deviation from the Lewis and Randall assumption of a perfect solution does not exceed about 20% with pressures up to 1000 atmospheres.

WASHINGTON, D. C.

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

THE SOLUBILITY OF LEAD BROMIDE IN AQUEOUS SALT SOLUTIONS AND THE CALCULATION OF THE ACTIVITY COEFFICIENT FROM SOLUBILITY MEASUREMENTS[1]

BY MERLE RANDALL AND WILLIAM V. A. VIETTI

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Lewis and Randall[2] found that the activity coefficient of lead bromide was about the same as that of cadmium bromide, and was less than that of barium chloride, potassium sulfate and similar salts. Lead bromide must not, therefore, be considered a typically strong electrolyte. It is moderately soluble and its solubility can be accurately measured. A determination of the solubility of this salt in the presence of several strong and moderately strong electrolytes was undertaken, with the hope that the deviations of the activity coefficients from those predicted by the principle of the ionic strength would be large, and that we might thus find a further experimental basis for prediction as to the behavior of mixtures of electrolytes.

Solubility of Lead Bromide in Aqueous Salt Solutions at 25°

Lead bromide was prepared from dilute solutions of recrystallized lead nitrate and sodium bromide by metathesis. The salt was purified by recrystallization and was

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[1] Presented at the Joint Session of California Section of the American Chemical Society and the Pacific Division of the American Association for the Advancement of Science at Stanford University, California, June 26, 1924. Referred to by Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

[2] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 424.