to use equation (9) for the purpose of integrating equation (6).

It may be pointed out that our use of Raoult's law necessitates the independence of $\bar{v}_2$ from N_2.[6]

Equation (8) can also be applied to calculate the mixed solubility of slightly soluble gases, such as the solubility in water of a 3:1 mixture of hydrogen and nitrogen. In such a case in equation (8) f_2 is the fugacity of one of the gases, N_2 is its mole fraction in solution and P is total pressure. Having no experimental data about the mixed solubility of gases, we are unable to verify equation (8) by concrete examples.

Equation (8) can be used also to solve the inverse problem of calculating the fugacity of pure and mixed gases.

Summary

1. A thermodynamical equation is given which allows the calculation of the solubility of slightly soluble gases in solvents with small vapor pressure.

2. · The deduced equation is verified in examples of solubilities of nitrogen and hydrogen in water at a pressure up to 1000 atmospheres and temperatures from 0 to 100°.

3. Partial molal volumes of nitrogen and hydrogen in their water solutions are calculated.

4. The possibility of calculation of the fugacity of gases on account of their solubility is shown.

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[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 222.

[CONTRIBUTION FROM THE D. I. MENDELEYEFF CHEMICAL-TECHNOLOGICAL INSTITUTE]

Partial Molal Quantities in an Infinitely Dilute Solution

BY I. R. KRICHEVSKY AND J. S. KASARNOVSKY

The partial molal quantities g_1 and g_2 and the composition of a binary solution, expressed in mole fractions, N_1 and N_2, are connected with each other by a well-known equation, which it will be convenient for the purpose of further argumentation to set forth as follows

$$\frac{\partial \bar{g}_1}{\partial N_2}\bigg/\frac{\partial \bar{g}_2}{\partial N_2} = -\frac{N_2}{N_1} \qquad (1)$$

This equation has been submitted by Lewis and Randall for the case of an infinitely dilute solution to a special analysis. "In an infinitely dilute solution of X_2 in X_1, where we may write $N_2/N_1 = 0$, it is evident that either $\partial \bar{g}_1/\partial N_2$ is zero, or $\partial \bar{g}_2/\partial N_2$ is infinite. In other words, when N_2 is zero either the curve $\bar{g}_1$ becomes horizontal, or the curve of $\bar{g}_2$ becomes vertical."[1]

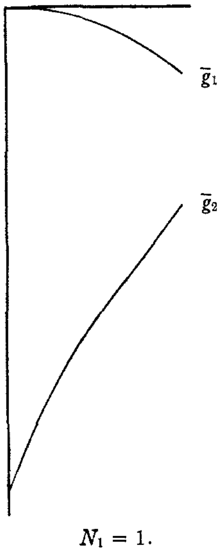

Fig. 1.

The analysis given by Lewis and Randall does not exhaust the question, inasmuch as mathematically (equation (1) is not a thermodynamical one) three other cases are possible: (1) $\partial \bar{g}_1/\partial N_2$ is zero and $\partial \bar{g}_2/\partial N_2$ is zero; (2) $\partial \bar{g}_1/\partial N_2$ is zero and $\partial \bar{g}_2/\partial N_2$ is infinite; (3) $\partial \bar{g}_1/\partial N_2$ is infinite and $\partial \bar{g}_2/\partial N_2$ is infinite.

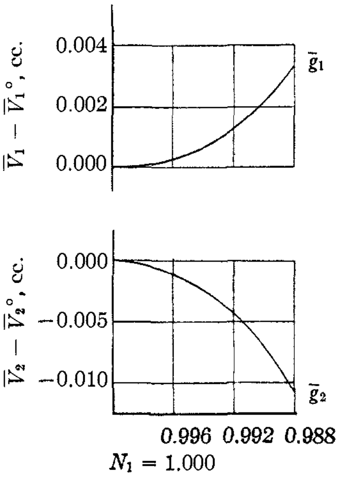

Fig. 2.—Partial molal volumes of water and ethyl alcohol at 40°.

Notwithstanding the fact that, if such allowances are made, the left part of equation (1) turns into indefiniteness, the latter at $N_2 = 0$ may have for its limit zero.

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

When $\partial\bar{g}_1/\partial N_2$ is tending to attain zero as the first degree of N_2, then at $N_2 = 0$, $\partial\bar{g}_2/\partial N_2$ differs from zero, as it is to be seen from equation (1) (Fig. 1).[2] This is one of the two cases pointed out by Lewis and Randall.

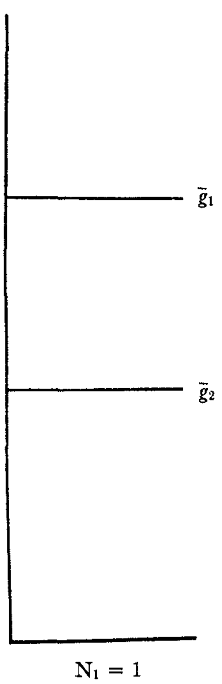

Fig. 3.

When $\partial\bar{g}_1/\partial N_2$ is tending to attain zero as the higher degree of N_2, then $\partial\bar{g}_2/\partial N_2$ is likewise tending to attain zero, but the left part of the equation (1) has for its limit zero (Fig. 2).

Figures 1 and 2 correspond to such partial molal quantities, as for instance the volume (or heat capacity or heat content). According to Fig. 1 in the infinitely dilute solution only the partial molal volume of the solvent is constant. According to Fig. 2 in the infinitely dilute solution the partial molal volumes both of the solvent and solute remain constant. Hence it is natural to turn to such a case, when this constancy extends into the field of finite concentrations (Fig. 3).

As the temperature is rising, *i. e.*, when the abnormality of the solutions is decreasing, it may be expected that the trend will be from Fig. 1 via Fig. 2 to Fig. 3.

The partial molal volumes for the system water–ethyl alcohol[1] (apparently for the temperature 20–25°) calculated by Lewis and Randall correspond to Fig. 1. The calculations made by us of the partial molal volumes for 40° are given in Fig. 2.

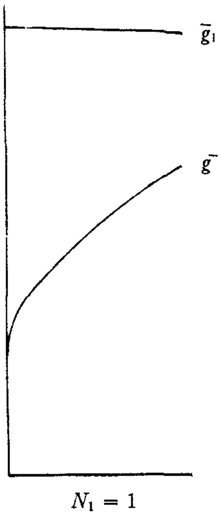

Fig. 4.

With a further rise of temperature it is likely that we shall arrive at Fig. 3.

When $\partial\bar{g}_1/\partial N_2$ is approaching zero as N_2 in a degree below one, then at $N_2 = 0$, $\partial\bar{g}_2/\partial N_2$ is infinite (Fig. 4). The partial molal volumes of the system water–strong electrolyte[3] correspond to this case.

The third case when at $N_2 = 0$, $\partial\bar{g}_1/\partial N_2$ and $\partial\bar{g}_2/\partial N_2$ are infinite, is apparently of no practical value.

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[2] Figure 1 corresponds to Fig. 7 of Lewis and Randall.

[3] Redlich and Rosenfeld, *Z. Elektrochem.*, **37**, 705 (1931).

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Amides Obtained from Benzenesulfinic Acid

By L. Chas. Raiford and Stewart E. Hazlet

A large number of aryl sulfinic acids have been prepared[1] but few of them have been converted into the corresponding acid chlorides, while the behavior of the latter toward amino compounds has received very little attention.

Hilditch and Smiles[2] obtained benzenesulfinyl chloride in rectangular plates that melted at 38°. Braun and Kaiser[3] may have obtained this product as a solid, but they recorded no melting point. Although they used specially purified starting material, Whalen and Jones[4] could not duplicate Hilditch and Smiles' results, and they did not obtain crystals when they followed Braun and Kaiser's directions. Their product was an oil with a boiling range of 85–90° at 3 to 4 mm.

In the present work, the purpose of which was to test further the action of benzenesulfinyl chloride on amino compounds, the "crude" acid chloride was obtained in nearly quantitative yield by treatment of benzenesulfinic acid[5] with thionyl chloride at room temperature. Distillation, when successful, gave about 83% of a yellow oil at 80–85° and 2 mm. Often rapid and violent decomposition of material took place. Comparison of products obtained by the action of "crude" chlo-

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[1] Gattermann, *Ber.*, **32**, 1136 (1899); Knoevenagel and Kenner, *ibid.*, **41**, 3315 (1908); Claasz, *Ann.*, **380**, 303 (1911).

[2] Hilditch and Smiles, *Ber.*, **41**, 4115 (1908); *J. Chem. Soc.*, **97**, 2585 (1910).

[3] Braun and Kaiser, *Ber.*, **56**, 552 (1923).

[4] Whalen and Jones, This Journal, **47**, 1355 (1925).

[5] Prepared as directed by Gattermann, "Praxis des organischen Chemikers," 18th Auflage, Walter de Gruyter, Berlin, 1923, p. 268.