

Equilibria in Solutions

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The voluminous careful vapor pressure data for binary solutions of Zawidski¹ led Dolezalek² to seek a quantitative explanation of positive and negative deviations from Raoult's law in terms of depolymerization and compound formation. Relatively few applications of this procedure have since been made.³ It appears to be impossible to apply such calculations to all systems involving deviations from Raoult's law,⁴ but there are other systems where the consistency of the results seems to justify the procedure.⁵ The possibility of obtaining equilibrium constants for any system, over a range of composition, might be accepted as a sufficient a posteriori criterion of the applicability of Dolezalek's hypotheses. Or, the procedure might equally well be accepted as arbitrary, applicable only to some systems. This has the advantage of bringing vapor pressure data into conformity with Raoult's law with the aid of a single constant which is deducible from the data. Regardless of the point of view, the procedure remains the same.

The solubility of sulfur dioxide in acetone and in methyl acetate⁶ conforms neither to Raoult's law nor to Henry's law. These two systems show large negative deviations from Raoult's law and will be treated here as though a one-to-one compound exists in each case and as though this compound formation were entirely responsible for the observed deviations. Symbols used below are defined as follows:

n'_1, n'_2 = experimental mol number of solvent and solute

n_1, n_3 = equilibrium mol numbers of solvent and compound

p_1^0, p_2^0, p, p_2 = vapor pressure of solvent, solute, solution and partial vapor pressure of solute

$K = n_3/n_1p_2$ = equilibrium constant

For convenience in the computations the basis $n'_1 + n'_2 = 1$ is chosen.

From the application of Raoult's law and the equilibrium relation above it follows that

$$n_3 = (-b \pm [b^2 - 4ac]^{1/2})/2a,$$

where $b = p_2^0 + 2p_1^0 + (p_2^0 - p_1^0)n'_2 - 2p,$

$$a = p - p_1^0 - p_2^0,$$

$$c = p_1^0 - p + n'_2(p_0 - p_1^0).$$

¹ Zawidski, Z. physik. Chem., **35**, 129 (1900).

² Dolezalek, Z. physik. Chem., **64**, 727 (1908).

³ Bein, Z. physik. Chem., **66**, 257 (1908), Hildebrand, Trans. Am. Electrochem. Soc., **22**, 319 (1912), Sameshima, J. Amer. Chem. Soc., **40**, 1482 (1918).

⁴ Schmidt, Z. physik. Chem. **99**, 71 (1921).

⁵ Sameshima, loc. cit.

⁶ Horiuti, Sci. Papers Inst. Phys. Chem. Research (Tokyo), **17**, 125 (1931).

$$p_2 = p - p_1^0(1 - n_2' - n_3) / (1 - n_3),$$

$$n_1 = n_1' - n_3.$$

For the usual binary liquid system the experimental vapor pressures may be used with sufficient reliability for the purpose. In the present instance, however, since gas pressures as high as four atmospheres are involved, it becomes necessary to employ the fugacity of the solute throughout. The following simple device of Lewis and Randall⁷ was adopted:

$$f/p = p/p_1.$$

The computed results are tabulated. It is apparent that the equilibrium constants are sufficiently consistent to justify the procedure adopted. The treatment of the system sulfur dioxide-acetone must be regarded as strictly empirical since Sameshima⁸ reports self-consistent evidence for the trimerisation of acetone in the liquid state. It is apparent, therefore, that since the method adopted here is sufficiently flexible to handle such a system, caution must be exercised in forming any conclusions from the constancy of the equilibrium constants.

Summary

The solubility of sulfur dioxide in acetone and in methyl acetate at 25° can be brought into conformity with Raoult's law if the systems be treated as though compound formation occurred between solvent and solute.

TABLE I.—Sulfur dioxide-Methyl acetate.

n_2'	p_{mm}	n_3	p_2	(10)°K
0.000	213.4	0.000		...
0.143	324.4	0.093	143.0	852
0.254	456.7	0.156	298.8	882
0.336	602.5	0.190	467.2	858
0.406	754.4	0.214	633.5	890
0.456	894.3	0.223	780.0	889
0.497	1038.5	0.219	924.5	834
1.000	2902	0.000	2902	...

TABLE II.—Sulfur dioxide-Acetone.

n_2'	p_{mm}	n_3	p_2	(10)°K
0.000	229.2	0.000		...
0.160	310.9	0.118	122.8	133
0.294	451.6	0.201	303.4	131
0.372	576.6	0.240	452.0	137
0.445	740.1	0.265	634.3	144
0.483	856.3	0.269	756.6	143
0.519	994.3	0.266	896.0	138
1.000	2902	0.000	2902	138

⁷ Lewis and Randall, *Thermodynamics*, **63**, (1925), New York.

⁸ Sameshima, *loc. cit.*