Application of the Theory of Regular Solutions to Binary Phase Equilibria. I. Method of Application to Binary Liquid Equilibria

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Accurate prediction of phase relationships over a wide range of temperatures from some data determined at several temperatures is difficult in general. It seems that if the theory of strictly regular solutions developed by Guggenheim[1] is applicable to mixtures for most binary systems, the behavior of solutions may be more satisfactorily interpreted by the theory than by the semi-empirical equations according to van Laar or Margules. However, exceedingly few systems satisfy all the conditions for forming regular mixtures in which the molecules are assumed to be sufficiently alike in size and shape to be interchangeable on a lattice or quasi-lattice.

The author has shown that the theory of regular solutions can apply to a much wider class of mixtures by assuming the formation of stable 'clusters' consisting of each component in its liquid phases[2]. This paper will be concerned with the derivation of the relationship between the compositions in two conjugate liquid phases on which the application of the theory of regular solutions is based and with the method of representing the solubility curves for most binary systems symmetrically. Detailed consideration referring to the estimation of interchange energy from mutual solubility data and its dependency upon temperature will be given in a subsequent paper.

1. Thermodynamic Aspects on the Coexistence Curve of Binary Liquid Mixtures

The rigorous thermodynamic equations of the form

$$\ln(a_{\rm I}/a_{\rm II})=\ln(x_{\rm I}/x_{\rm II})+\ln(\gamma_{\rm I}/\gamma_{\rm II}) \qquad (1,1)$$

are applicable to any binary mixtures, where a's, x's and γ's denote activities, mole fractions and activity coefficients of the component designated by subscripts I and II at a given temperature, respectively. (The pure component is taken as standard state). When the solution is separated into two liquid phases by the increase of the deviation from Raoult's law, designating the I-component rich phase by one prime and the II-component rich phase by two primes,

$$a_{\rm I}'=a_{\rm I}'',\ a_{\rm II}'=a_{\rm II}'' \text{ and } x_{\rm I}'=1-x_{\rm II}'.$$

It therefore follows

$$\ln\{(1-x_{\rm II}')/x_{\rm II}'\}-\ln\{(1-x_{\rm II}'')/x_{\rm II}''\}=\ln(\gamma_{\rm I}''\gamma_{\rm II}'/\gamma_{\rm I}'\gamma_{\rm II}'') \qquad (1,2)$$

In cases where mutual solubilities are not so great, both values of $\gamma_{\rm I}'$ and $\gamma_{\rm II}''$ are near unity.

The temperature dependence of the activity coefficient can be related to the heat of mixing by the following equation

$$\frac{\mathrm{d}\ln\gamma_{\rm I}}{\mathrm{d}T}=-\frac{\Delta\overline{H}_{\rm I}}{\boldsymbol{R}T^2} \qquad (1,3)$$

where $\Delta\overline{H}_{\rm I}$ is the partial molal heat of solution of component I, $\boldsymbol{R}$ the gas constant and T the absolute temperature. Then, Eq. 1, 2 may be transformed into

$$\frac{\mathrm{d}\ln\{(1-x')/x'\}}{\mathrm{d}T}-\frac{\mathrm{d}\ln\{(1-x'')/x''\}}{\mathrm{d}T}=-\frac{\Delta H}{\boldsymbol{R}T^2} \qquad (1,4)$$

where

$$\Delta H=\Delta\overline{H}_{\rm I}''-\Delta\overline{H}_{\rm II}''-(\Delta\overline{H}_{\rm I}'-\Delta\overline{H}_{\rm II}') \qquad (1,5)$$

In Eq. 1, 4 $x_{\rm II}$ is represented as x for the sake of simplicity.

For most binary liquid mixtures with a few exceptions, it is observed that the solubilities of one component in one phase increase as the corresponding values in the other conjugate phase decrease with changing temperatures, and then the signs of $(\Delta\overline{H}_{\rm I}''-\Delta\overline{H}_{\rm II}'')$ and $(\Delta\overline{H}_{\rm I}'-\Delta\overline{H}_{\rm II}')$ are opposite. The absolute values of these two quantities are equal in particular systems where the solubility curves are symmetrical with respect to the mole fraction as it is for a regular mixture. If the absolute value of the latter of these two quantities is m times the former and m is assumed to be independent of temperature, then

$$\Delta\overline{H}_{\rm I}'-\Delta\overline{H}_{\rm II}'=-m(\Delta\overline{H}_{\rm I}''-\Delta\overline{H}_{\rm II}'') \qquad (1,6)$$

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[1] E. A. Guggenheim, "Mixtures", Oxford University Press, London (1952).

[2] K. Ishida, *Nature*, **184**, 814 (1959).

Using these assumptions, Eq. 1, 4 may be written in the form

$$\frac{\mathrm{d}\ln\{(1-x')/x'\}}{\mathrm{d}T}-\frac{\mathrm{d}\ln\{(1-x'')/x''\}}{\mathrm{d}T}=(1+m)\frac{\mathrm{d}\ln(\gamma_{\mathrm{I}}''/\gamma_{\mathrm{II}}'')}{\mathrm{d}T} \qquad (1,7)$$

In the following Eq. 1, 8, which is obtained by setting the value of the first derivative of the molal free energy of mixing at a given temperature and pressure, $g(x)$, with respect to x equal to zero,

$$\ln(\gamma_{\mathrm{I}}/\gamma_{\mathrm{II}})=-\ln\{(1-x)/x\} \qquad (1,8)$$

values of x represent the mole fractions of component II along the coexistence curve in cases of symmetrical systems. However, in cases of ordinary unsymmetrical systems, values of x do not represent the mole fractions along the consolute curve, but they represent those at the extreme values on the $g(x)$ curve in the neighborhood of the compositions in mutual equilibrium of two phases such as x' and x'', which are the two points of contact of the common tangent on the $g(x)$ curve. If the dependency of the logarithms of mole ratio of two components at the compositions in two coexisting phases upon temperature is assumed to be scarcely different from that at the compositions corresponding to the extreme values on the $g(x)$ curve, the following simple relation can be obtained

$$\ln\{(1-x')/x'\}=-m\ln\{(1-x'')/x''\}+B \qquad (1,9)$$

for the values of x' and x'' on the coexistence curves, where B is a constant independent of temperature.

As will be clear from Figs. 1—3* in which plots are made of the logarithms of the mole ratios of two components in one phase against the corresponding values in the other conjugate phase for several systems described in the literature, fair straight lines whose slopes are near minus unity are obtained from these plots over the considerably wide range of temperatures not only for systems with virtually symmetrical solubility curves, but also for systems with extremely unsymmetrical ones. Even for the systems showing the closed solubility curve, the linear relationships between the functions $\log\{(1-x')/x'\}$ and $\log\{(1-x'')/x''\}$ hold for temperatures within 30° of a critical solution temperature, T_c. This fact indicates that the value of m is near unity for most systems and the deviations due to two assumptions involved in the derivation of Eq. 1, 9 from actual behavior of solutions are almost cancelled, and that when the logarithm of the mole ratio of two components in one phase increases with the change in temperature, the corresponding value in the other phase decreases in proportion to the increase of that in the former phase and the proportional factor is a constant over a wide range of temperature. It is clear that the form of Eq. 1, 9 is independent of whether weight, mole or volume fractions are used for the unit of concentration.

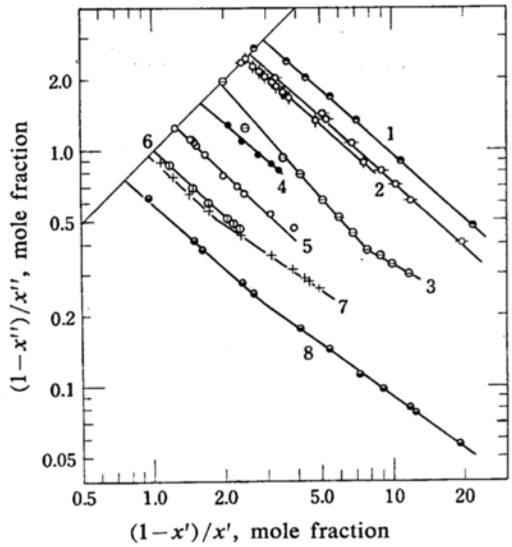

Fig. 1. Plot on double logarithmic coordinates of $(1-x'')/x''$ against $(1-x')/x'$.

No.	Symbol	Component I — II	Ref.
1	◓	Benzene—Perfluoromethylcyclohexane	3
2	-○-	Carbon tetrachloride—Perfluoromethylcyclohexane	3
	⌽	〃 〃	4
3	⊖	*n*-Butane—Perfluoro-*n*-butane	5
4	●	Silicon tetrachloride—Stannic iodide	6
5	○	Cyclohexane—Aniline	7
6	⦶	Isooctane—Stannic iodide	8
7	+	Cyclohexane—Methanol	9
8	◒	*n*-Heptane—Furfural	10

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* Estimated values of the compositions in coexisting phases from solubility curves are also included as points in these figures.

3) J. H. Hildebrand and D. R. F. Cochran, *J. Am. Chem. Soc.*, **71**, 22 (1949).

4) B. H. Zimm, *J. Phys. & Colloid Chem.*, **54**, 1306 (1950).

5) J. H. Simons and J. W. Mansteller, *J. Chem. Phys.*, **20**, 1516 (1952).

6) J. H. Hildebrand and G. R. Negishi, *J. Am. Chem. Soc.*, **59**, 339 (1937).

7) D. Atack and O. K. Rice, *J. Chem. Phys.*, **22**, 382 (1954); *Disc. Faraday Soc.*, **15**, 210 (1953).

8) M. E. Dice and J. H. Hildebrand, *J. Am. Chem. Soc.*, **50**, 3023 (1928).

9) E. L. Eckfeldt and W. W. Lucasse, *J. Phys. Chem.*, **47**, 164 (1934).

10) E. N. Pennington and S. J. Marwil, *Ind. Eng. Chem.*, **45**, 1371 (1953).

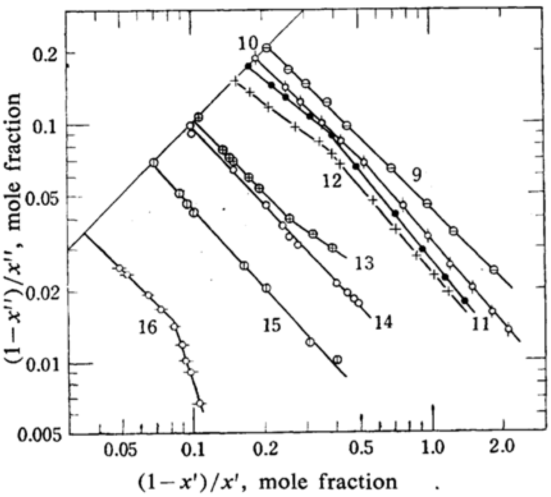

Fig. 2. Plot on double logarithmic coordinates of $(1-x'')/x''$ against $(1-x')/x'$.

No.	Symbol	Component I II	Ref.
9	⊖	Ethylbenzene— Liquid ammonia	11
10	⦶	Mesitylene—Liquid ammonia	11
11	●	Propylbenzene— Liquid ammonia	11
12	+	1-Methylnaphthalene— Liquid ammonia	11 11
13	⊕	Methyldiethylamine—Water	12
14	○	Phenol—Water	13
15	⦶	2, 6-Dimethylpyridine—Water	14
16	-○-	Palmitic acid— Liquid propane	15

It is reasonable that Eq. 1, 9 holds for temperatures within 30°C of a critical solution temperature for most binary liquid systems, since this formula is immediately derived from the empirical relations 1, 10 shown by Cox and Herington[14].

$$T-T_c=[A'\log\{(1-x')/x'\}+B']^3 \qquad (1,\ 10a)$$

$$T-T_c=[A''\log\{(1-x'')/x''\}+B'']^3 \qquad (1,\ 10b)$$

2. Method of Representing the Solubility Curve Symmetrically

At the critical solution temperature T_c, the two coexisting phases become identical having the composition $x'=x''=x_c$. Eq. 1, 9 may be transformed into

$$\frac{1-x'}{x'}\cdot\frac{x_c}{1-x_c}=\left[\frac{1-x''}{x''}\cdot\frac{x_c}{1-x_c}\right]^{-m} \qquad (2,\ 1)$$

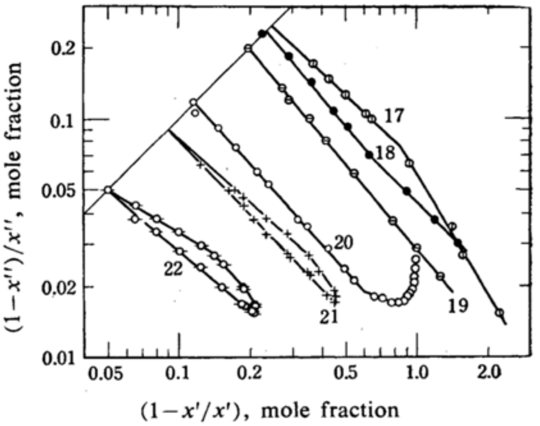

Fig. 3. Plot on double logarithmic coordinates of $(1-x'')/x''$ against $(1-x')/x'$.

No.	Symbol	Component I II	Ref.
17	⦶	Octene—Liquid sulfur dioxide	16
18	●	*m*-Xylene—Liquid ammonia	11
19	⊖	Isopropylbenzene— Liquid ammonia	11
20	○	*n*-Butanol—Water	13
21	+	1-Propoxypropane-2-ol— Water	17
22	-○-	Ethylene glycol *n*-butyl ether— Water	18

It is possible to represent the solubility curve for a binary liquid system symmetrically with respect to the composition by plotting properly selected units. When the following units φ, which are the variation of volume fractions, are used for the concentrations, the resulting solubility curve will be symmetrical with respect to φ as for regular binary mixtures, since $\varphi'+\varphi''=1$.

$$\varphi'=\frac{x'/x_c}{x'/x_c+(1-x')/(1-x_c)}$$

$$\varphi''=\frac{(x''/x_c)^m}{(x''/x_c)^m+\{(1-x'')/(1-x_c)\}^m} \qquad (2,\ 2)$$

Therefore, the interchange energy w between two kinds of cluster may be obtained from the theory of regular solutions by assuming that each component forms clusters consisting of each component in its liquid phase, the number of moles being $(1-x')x_c$ and $x'(1-x_c)$ respectively, and that two kinds of cluster are stable and sufficiently alike in size and shape to satisfy all the conditions for forming strictly regular solutions on mixing[2]. In this case, by the definition of Eq. 2, 2 the molecular

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[12] J. L. Copp, *Trans. Faraday Soc.*, **51**, 1056 (1955).

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[16] W. F. Seyer and L. Hodnett, *J. Am. Chem. Soc.*, **58**, 996 (1936).

[17] H. L. Cox, W. L. Nelson and L. H. Cretcher, ibid., **49**, 1080 (1927).

[18] H. L. Cox and L. H. Cretcher, ibid., **48**, 451 (1926).

ratio, r', becomes

$$r'=\frac{1-\varphi'}{\varphi'}=\frac{1-x'}{x'}\cdot\frac{x_c}{1-x_c} \tag{2, 3}$$

Sometimes values of the interchange energy estimated from the compositions in one phase, x', differ a little from those estimated by the use of the compositions in the other phase, x'', since a constant m is not always exactly equal to unity as shown in Figs. 1—3. Of course, both values should coincide with each other when they are calculated by φ' and φ'' using the value of m estimated from the mutual solubility data determined at two temperatures by Eq. 1, 9, but calculations are considerably tedious.

It is convenient to introduce a variable x_k defined by

$$\frac{x_k}{1-x_k}=\left(\frac{x'}{1-x'}\cdot\frac{x''}{1-x''}\right)^{1/2} \tag{2, 4}$$

and to use the variable x_k instead of critical composition x_c setting the value of m equal to unity. Then,

$$\varphi'=\frac{\{x'/(1-x')\}^{1/2}}{\{x'/(1-x')\}^{1/2}+\{x''/(1-x'')\}^{1/2}}$$

$$=\frac{\{(1-x'')/x''\}^{1/2}}{\{(1-x')/x'\}^{1/2}+\{(1-x'')/x''\}^{1/2}}\equiv\varphi$$

and Eq. 2, 3 is replaced by Eq. 2, 6

$$r=\frac{1-\varphi}{\varphi}=\left(\frac{x''}{1-x''}\cdot\frac{1-x'}{x'}\right)^{1/2} \tag{2, 6}$$

Thus, by using x_k instead of x_c and putting $m=1$, the solubility curve can always be represented symmetrically with respect to φ and the molecular ratio and the interchange energy at a given temperature can be evaluated by simpler calculation.

The value of x_k may be dependent of the temperature and different from x_c to a certain extent when m is not unity, but x_k corresponds to x_c at the critical solution temperature. It may be easily proved by further algebraic arguments that there are straight line relationships between the functions $\log\{x_k/(1-x_k)\}$ and $\log\{x'/(1-x')\}$ and between the functions $\log\{x_k/(1-x_k)\}$ and $\log\{x''/(1-x'')\}$, and that x_c is given by the following equation

$$\log\frac{x_c}{1-x_c}=\left[\log\frac{1-x_2'}{x_2'}\log\frac{x_1''}{1-x_1''}-\log\frac{1-x_1'}{x_1'}\log\frac{x_2''}{1-x_2''}\right]\Bigg/\left[\log\left(\frac{x_1'}{1-x_1'}\cdot\frac{1-x_2'}{x_2'}\right)-\log\left(\frac{x_1''}{1-x_1''}\cdot\frac{1-x_2''}{x_2''}\right)\right] \tag{2, 7}$$

where subscripts 1 and 2 denote the values at temperatures T_1 and T_2, respectively.

Thus it should be possible to predict the solubility relationships of the system from mutual solubility data, determined at more than one temperature, when the dependence of the interchange energy estimated from mutual solubility data in terms of φ-fractions upon temperature is known.

Summary

The same expression for the correlation of compositions in mutual equilibrium of two liquid phases as that which is immediately obtained from the empirical relations used by Cox and Herington was derived thermodynamically. The method has been given in such a manner as to represent the solubility curve for a binary liquid system symmetrically and to estimate the interchange energy from the mutual solubility data by applying the theory of regular solutions.

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