Application of the Theory of Regular Solutions to Binary Phase Equilibria. II. Dependency of the Interchange Energy upon Temperature

By Kiyoharu ISHIDA

(Received January 7, 1960)

A few examples[1] have been shown for the comparison of the theories of strictly regular solutions with experiments, since there are few suitable systems for which measurements necessary to adequate comparison have been made. In cases of many systems in which mixtures of two components show so great deviations from Raoult's law that the solutions separate into two liquid phases, the solutions are generally formed from chemically dissimilar constituents which are different in molecular size, chemical structure, polarity and so on, these conditions being far from those for forming regular mixtures. It, therefore, was impossible that the comparisons of the theories with experimental results obtained for such mixtures with great deviations from ideal behavior were made in order to verify the validity of theories and to extend their application to the field of the chemical engineering design, but now the application of the theories of strictly regular solutions to most partially miscible liquid systems and the estimation of the interchange energy from the mutual solubility data have become possible as described in the previous paper[2]. It is interesting and desirable from a practical viewpoint to study what relations are obtained between the interchange energy or the co-operative energy and the temperature for such systems.

3. Theoretical Expressions for Estimating Co-operative Energy from Compositions in Two Coexisting Phases

It has been shown that the problem of the phase transition for the regular mixtures of two components is mathematically identical with that of the so-called Ising model of ferromagnetism and that there is an equivalent relation between the compositions in mutual equilibrium of two liquid phases and the intensity of spontaneous magnetization in the absence of a magnetic field[3,4]. No exact results for the three-dimensional problems are available at present that could be applied to phase equilibria, but exact closed form expressions of the free energy in the absence of a magnetic field[5], which corresponds to the theory of regular solutions with equal ratio of constituents, and of the spontaneous magnetization[6] are available for the two-dimensional model, particularly the square net, though it has been found that there is a marked difference in behavior between two- and more realistic three-dimensional model[7].

The intensity of spontaneous magnetization per spin at zero magnetic field for a two-dimensional ferromagnetic Ising square lattice is given by

$$I=\left[\frac{1+\zeta^2}{(1-\zeta^2)^2}(1-6\zeta^2+\zeta^4)^{1/2}\right]^{1/4}$$

$$\text{for } \zeta\leqq\sqrt{2}-1 \qquad (3,1)$$

$$\zeta=\exp(-\varepsilon/\boldsymbol{k}T) \qquad (3,2)$$

where ε is the interaction energy between each pair of nearest neighbor antiparallel spins assuming the interaction energy between pairs of parallel spins to be zero, and $\boldsymbol{k}$ is the Boltzmann constant.

By the correspondence of the theory of regular solutions to the Ising model, the interchange energy or one half of the energy increase of the whole system when a pair of two molecules of type I and a pair of two molecules of type II are converted into two pairs of a molecule of type I and a molecule of type II, w, will be obtained in terms of the mole fractions of component II in two coexisting phases, x, by the relation

$$\exp(w/\boldsymbol{k}T)=\left[\frac{1+[1+\{1-(1-2x)^8\}^{1/2}]^{1/2}}{\{1-(1-2x)^8\}^{1/4}}\right]^4 \qquad (3,3)$$

for the square lattice. At the critical solution temperature,

---

1) E. A. Guggenheim, "Mixtures", Oxford Press, (1952).

2) K. Ishida, *Nature*, **184**, 814 (1959). See also the preceding paper.

3) R. Peierls, *Proc. Cambridge Phil. Soc.*, **32**. 477 (1936). G. F. Newell and E. W. Montroll, *Rev. Mod. Phys.*, **25**, 353 (1953).

4) C. Domb, *Proc. Roy. Soc.*, A **199**, 199 (1949).

5) L. Onsager, *Phys. Rev.*, **65**, 117 (1944).

6) C. N. Yang, ibid., **85**, 808 (1952).

7) C. Domb and M. F. Sykes, *Proc. Roy. Soc.*, A**235**, 247 (1956).

$$x=1/2, \qquad \exp(w/\boldsymbol{k}T)_c=[1+\sqrt{2}]^4 \tag{3, 4}$$

The information on the behavior of the model has been provided by exact series expansion of the partition function to any desired degree of accuracy[4,7-9]. In the rigorous expansion of the partition function by Bethe-Kirkwood's method of moments[8], the molar free energy of mixing in the notation used by Guggenheim[1] is given by

$$\frac{\Delta mF}{\boldsymbol{R}T}=(1-x)\ln(1-x)+x\ln x+x(1-x)\frac{w}{\boldsymbol{k}T}$$
$$-\frac{z}{2}\left[\frac{l_2}{2!}\left(\frac{2w}{z\boldsymbol{k}T}\right)^2+\frac{l_3}{3!}\left(\frac{2w}{z\boldsymbol{k}T}\right)^3+\frac{l_4}{4!}\left(\frac{2w}{z\boldsymbol{k}T}\right)^4+\cdots\right] \tag{3, 5}$$

where z is the coordination number and

$$l_2=x^2(1-x)^2 \tag{3, 6}$$

$$l_3=x^2(1-x)^2(1-2x)^2 \tag{3, 7}$$

$$l_4=x^2(1-x)^2(1-6x+6x^2)^2+6\left(\frac{y}{z}-1\right)x^4(1-x)^4 \tag{3, 8}$$

$$l_5=x^2(1-x)^2(1-2x)^2(1-12x+12x^2)^2+60\left(\frac{y}{z}-1\right)x^4(1-x)^4(1-2x)^2 \tag{3, 9}$$

$$\begin{aligned}l_6=&x^2(1-x)^2\{1-60x(1-x)(1-2x)^2\}\\&+30\left(13\frac{y}{z}+17\right)x^4(1-x)^4\\&+120\left(\frac{\gamma_1}{z}-30\frac{y}{z}-28\right)x^5(1-x)^5\\&+120\left(\frac{\gamma_2}{z}-4\frac{\gamma_1}{z}+66\frac{y}{z}+42\right)x^6(1-x)^6\end{aligned} \tag{3, 10}$$

y, γ_1 and γ_2 are parameters depending on the lattice and defined by

$$y=\sum_{a'}z^2{}_{aa'}-z(z-1) \tag{3, 11}$$

$$\gamma_1=\sum_{a'}z^3{}_{aa'}-3\sum_{a'}z^2{}_{aa'}+2z(z-1) \tag{3, 12}$$

$$\gamma_2=\sum_{a'a''}z_{aa'}z_{a'a''}z_{a''a}-3(z-2)\sum_{a'}z^2{}_{aa'}+2z(z-1)(z-2) \tag{3, 13}$$

where $z_{aa'}$ is another coordination number denoting the number of first neighbors common to the sites a and a'.

The compositions in two coexisting phases are given by the points where the value of the first derivative of the free energy of mixing is zero, owing to the symmetry of the solubility curve. To obtain the value of $w/\boldsymbol{k}T$ it is convenient to introduce an abbreviation u defined by

$$u=\ln\frac{1-x}{x}\Big/(1-2x) \tag{3, 14}$$

Differentiating Eq. 3, 5 with respect to x and setting $\mathrm{d}(\Delta_m F/\boldsymbol{R}T)/\mathrm{d}x$ equal to zero, the expression for u/z as a power series in $2w/z\boldsymbol{k}T$ is obtained, which can be inverted into an expression for $2w/z\boldsymbol{k}T$ as a power series in u/z as follows:

$$\begin{aligned}\frac{w}{\boldsymbol{k}T}=u\Big[&1+x(1-x)\frac{2u}{z}+\frac{x(1-x)}{3}\left(\frac{2u}{z}\right)^2\\&+\frac{x(1-x)}{12}\Big\{1+2x(1-x)\\&+12x^2(1-x)^2\frac{y}{z}\Big\}\left(\frac{2u}{z}\right)^3\\&+\frac{x(1-x)}{60}\Big\{1+8x(1-x)\\&+120x^2(1-x)^2(1-2x+2x^2)\frac{y}{z}\Big\}\left(\frac{2u}{z}\right)^4\\&+\frac{x(1-x)}{360}\Big\{1+22x(1-x)\\&+4x^2(1-x)^2\left(4+195\frac{y}{z}\right)\\&+30x^3(1-x)^3\left(10\frac{\gamma_1}{z}-104\frac{y}{z}\right)\\&+360x^4(1-x)^4\Big(\frac{\gamma_2}{z}-4\frac{\gamma_1}{z}\\&+10\frac{y}{z}\Big)\Big\}\left(\frac{2u}{z}\right)^5+\cdots\cdots\Big]\end{aligned} \tag{3, 15}$$

And

$$\begin{aligned}(w/\boldsymbol{k}T)_c=2\Big[&1+\frac{1}{z}+\frac{4}{3}\frac{1}{z^2}+\left(2+\frac{y}{z}\right)\frac{1}{z^3}\\&+\left(\frac{16}{5}+4\frac{y}{z}\right)\frac{1}{z^4}\\&+\left(\frac{16}{3}+10\frac{y}{z}-\frac{2}{3}\frac{\gamma_1}{z}+\frac{\gamma_2}{z}\right)\frac{1}{z^5}+\cdots\cdots\Big]\end{aligned} \tag{3, 16}$$

The evaluation of the series of coefficients is increasingly tedious and complicated as the series is ascended.

Since the series converges to the exact value extremely slowly, and the presence of a magnetic field, which corresponds to regular solutions of varying concentrations, is difficult to deal with by an exact method even in

---

8) J. G. Kirkwood, *J. Chem. Phys.*, **6**, 70 (1938); *J. Phys. Chem.*, **43**, 97 (1939); H. A. Bethe and J. G. Kirkwood, *J. Chem. Phys.*, **7**, 578 (1939); T. S. Chang, ibid., **9**, 169 (1941).

9) G. S. Rushbrooke, *Nuovo cimento*, **6**, (suppl. 2), 251 (1949); A. J. Wakefield, *Proc. Cambridge Phil. Soc.*, **47**, 419, 799 (1951); C. Domb, *Proc. Roy. Soc.*, **A196**, 36 (1949); J. E. Brooks and C. Domb, ibid., **A207**, 343 (1951); T. Tanaka, H. Katsumori and S. Toshima, *Prog. Theoret. Phys.*, **6**, 17 (1951); etc.

two-dimensions, several approximate solutions have been derived in closed form[1,10,11].

In the first (pairs) approximation[1] treated according to the quasi-chemical equilibrium conditions which is equivalent to Bethe approximation, w is given by

$$\exp(w/z\boldsymbol{k}T)=(1-r)/(r^{1/z}-r^{(z-1)/z}) \qquad (3,17)$$

where r is the molecular ratio. At the critical solution temperature

$$\exp(w/z\boldsymbol{k}T)_c=\frac{z}{z-2} \qquad (3,18)$$

In the zeroth approximation[1] which corresponds to the limiting form taken by the first approximation when the coordination number is made infinite, and is equivalent to Bragg-Williams approximation,

$$\frac{w}{\boldsymbol{k}T}=\ln\frac{1-x}{x}\Big/(1-2x)=u \qquad (3,19)$$

Eq. 3, 19 is only the first term in the Eq. 3, 15 of rigorous series expansion. At the critical solution temperature

$$(w/\boldsymbol{k}T)_c=2 \qquad (3,20)$$

Several methods which are capable of yielding successively higher approximations in the quasi-chemical method have been developed[1,10,12], but the use of a large group introduces troublesome calculations in practical applications of these higher approximations. In the higher approximation for the case of the simple square lattice with the tetrahedra as basic figure[1,10], which is the simplest case treated by the method of a logical extention to larger groups of the quasi-chemical approximation for pairs, the method being equivalent to an approximation developed by Kikuchi, $w/\boldsymbol{k}T$ is obtained from

$$\exp\left(\frac{w}{\boldsymbol{k}T}\right)=\left[\frac{(\sqrt{r}+1)^2+\{(\sqrt{r}+1)^4+4r\}^{1/2}}{2\sqrt{r}}\right]^2 \qquad (3,21)$$

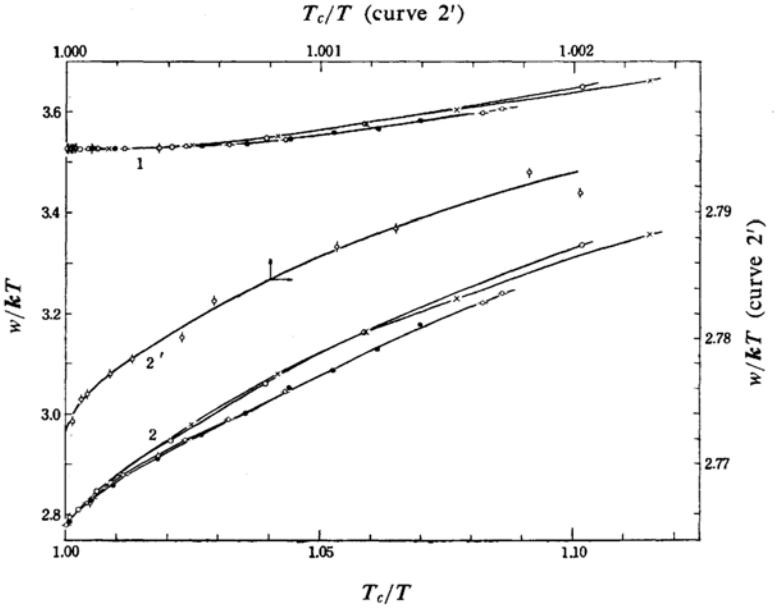

Fig. 4. Relations between $w/\boldsymbol{k}T$ and T_c/T for several systems. Values of $w/\boldsymbol{k}T$ along curve 1 are obtained from Eq. 3, 3. Corresponding values along curves 2 and 2′ are obtained from Eq. 3, 17 assuming $z=4$.

Symbol	System	Ref.
○	Ethylbenzene—Liquid ammonia	13
-○-	Carbon tetrachloride—Perfluoromethylcyclohexane	14
⦶	〃 — 〃	15
●	*n*-Butane—Perfluoro-*n*-butane	16
×	*n*-Hexane—Methanol	17

---

[10] J. A. Barker, *Proc. Roy. Soc.*, **A216**, 45 (1953).

[11] I. Prigogine, L. S. Mathot and L. van Hove. *Trans. Faraday Soc.*, **48**, 485 (1952).

[12] Y. Y. Li, *Phys. Rev.*, **76**, 972 (1949); C. N. Yang, *J. Chem. Phys.*, **13**, 66 (1945).

[13] K. Ishida, This Bulletin, **31**, 143 (1958).

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

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

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

[17] "International Critical Tables", III, McGraw-Hill Book Company, Inc., New York (1928), p. 386.

At the critical solution temperature

$$\exp (w/\boldsymbol{k}T)_c=(2+\sqrt{5})^2 \qquad (3,22)$$

When the value of $w/\boldsymbol{k}T$ is less than the value given by Eqs. 3, 4, 3, 16, 3, 18, 3, 20 or 3, 22, the separation into two liquid phases does not occur.

4. Dependency of $w/\boldsymbol{k}T$ upon Temperature

All formulae described in the above section contain the co-operative energy w in the form of the ratio $w/\boldsymbol{k}T$ or in particular $\exp (w/\boldsymbol{k}T)$. It is convenient to compare the theories with the experiment, regarding either of these quantities as a single parameter whose value determines all the thermodynamic properties at a given temperature. Using φ defined by Eq. 2,5 in the preceding paper instead of x, similar results between the functions $w/\boldsymbol{k}T$ according to each theoretical formula and T_c/T were obtained from the mutual solubility data for most binary liquid systems described in the literature as shown in Fig. 4. Accordingly, it may be sufficiently shown by the results for some representative systems how values of $w/\boldsymbol{k}T$ are affected by such various theoretical

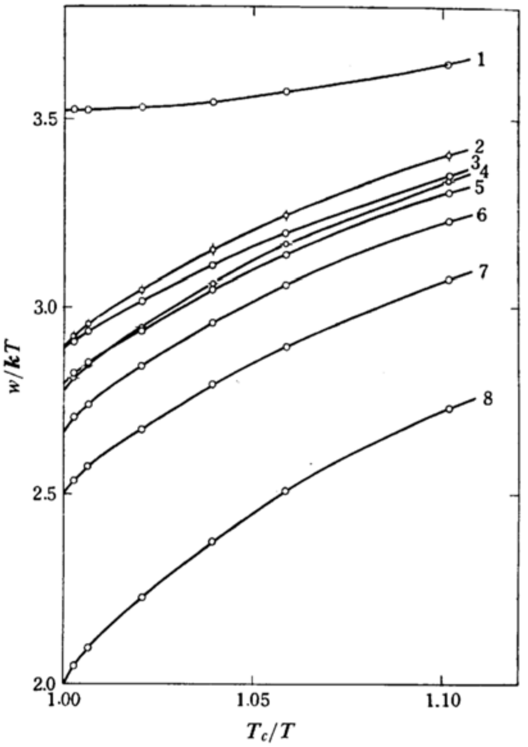

Fig. 5. Plot of values of $w/\boldsymbol{k}T$ obtained from several theoretical expressions against T_c/T for the system ethylbenzene —liquid ammonia.

Curve 1 is obtained from Eq. 3,3; curve 2 is obtained from Eq. 3,21; curve 3 is the expansion to terms of order $(2u/z)^4$ as given by Eq. 3,15 assuming $z=4$; curve 4 corresponds to Eq. 3,17 assuming $z=4$; curves 5, 6 and 7 are the expansions to terms of order $(2u/z)^3$, $(2u/z)^2$ and $(2u/z)$ as given by Eq. 3,15 assuming $z=4$, respectively; curve 8 is obtained from Eq. 3,19.

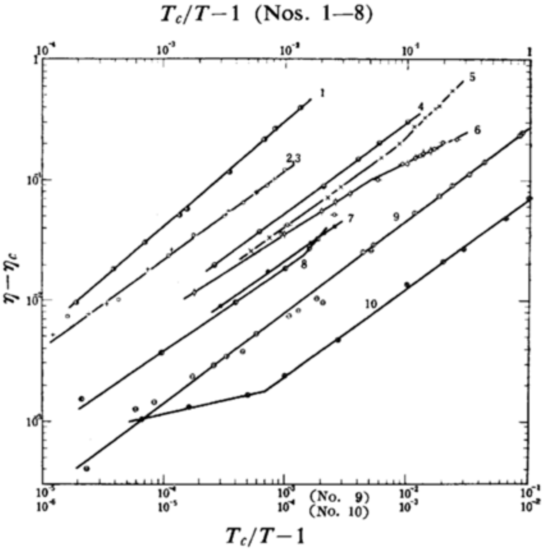

Fig. 6. Plot on logarithmic coordinates $\eta-\eta_c$ against $|T_c/T-1|$ for several systems.

No.	Symbol	System	Ref.
1	◑	Octene—Liquid sulfur dioxide	18
2	+	Methyldiethylamine—Water	19
3	○	Palmitic acid—Liquid propane	20
4	◒	Ethylbenzene—Liquid ammonia	13
5	×	*n*-Heptane—Furfural	21
6	⦶	Phenol—Water	22
	-○-	Phenol—Water	17
7	●	Isooctane—Stannic iodide	23
8	◐	Silicon tetrachloride—Stannic iodide	24
9	⏀	Carbon tetrachloride—Perfluoromethylcyclohexane	14
	⊖	Carbon tetrachloride—Perfluoromethylcyclohexane	15
10	⊕	Cyclohexane—Aniline	25

---

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

19) J. L. Copp, *Trans. Faraday Soc.*, **51**, 1056 (1955).

20) D. A. Drew and A. N. Hixson, *Trans. Am. Inst. Chem. Engrs.*, **40**, 675 (1944).

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

22) A. E. Hill and W. M. Malisoff, *J. Am. Chem. Soc.*, **48**, 918 (1926).

23) M. E. Dice and J. H. Hildebrand, ibid., **50**, 3023 (1928).

24) J. H. Hildebrand and G. R. Negishi, ibid., **59**, 339 (1937).

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

TABLE I. COMPARISON OF ESTIMATED VALUES FOR CRITICAL SOLUTION POINT WITH OBSERVED VALUES

System		T_1	T_2	Observed value		Eq. 2,7	Eq. 5,1	Eq. 1,10	Ref.
Component I	Component II	°C	°C	T_c °C	x_c Mole fraction	x_c Mole fraction	ΔT_c °C	ΔT_c °C	
Cyclohexane	Methanol	31.30	39.05	45.14	0.507	0.537	0.46	1.18	26
Cyclohexane	Aniline	27.459	29.339	29.422	0.447	0.445	0.007	0.023	25
n-Heptane	Furfural	37.4	48.8	93.7	0.56	0.596	11.7	17.2	21
n-Butane	Perfluoro-*n*-butane	−53.2	−45.2	−41.0	0.37	0.365	0.5	1.0	16
Methyldiethylamine	Water*	51.28	50.52	49.42	0.902	0.922	0.10	−0.01	19
Carbon tetrachloride	Perfluoromethylcyclohexane	4.0	14.4	26.8	0.30	0.301	2.3	3.7	14
〃	〃	27.92	28.232	28.310	0.290	0.289	−0.010	0.000	15
Benzene	Perfluoromethylcyclohexane	61.1	81.6	85.3	0.27	0.255	1.3	1.8	14
Phenol	Water	25.0	35.0	65.85	0.910	0.924	−2.75	3.39	22
Octene	Liquid sulfur dioxide	−47.1	−32.8	−16.4	0.801	0.749	4.0	6.0	18
Butanol	Water	80.0	90.0	125.15	0.895	0.915	−4.23	4.64	17
Isooctane	Stannic iodide	185.4	191.6	195.4	0.501	0.506	0.2	0.6	23
Silicon tetrachloride	Stannic iodide	133.4	138.2	139.8	0.432	0.389	0.1	0.3	24
Cetylstearate	Liquid propane*	99.5	97.0	95.2	0.979	0.972	−0.4	−1.2	20
Palmitic acid	Liquid propane*	100.5	98.5	96.9	0.966	0.936	−0.2	−0.4	20
n-Hexane	Methanol	25.0	30.0	42.6	0.548	0.573	0.2	1.6	17
Ethylbenzene	Liquid ammonia	0.0	10.0	10.7	0.827	0.823	0.1	0.2	13
Isopropylbenzene	Liquid ammonia	0.0	10.0	20.0	0.835	0.839	1.9	3.0	13
Mesitylene	Liquid ammonia	0.0	20.0	33.9	0.841	0.826	3.6	5.4	13
1-Methylnaphthalene	Liquid ammonia	0.0	20.0	28.8	0.861	0.846	1.8	3.1	13
Aniline	Water	80.0	100.0	167.5	0.844	0.862	0.8	15.9	17

ΔT_c indicates the difference between observed and calculated values.

* These are systems which show a lower critical solution temperature.

expressions. Fig. 4. shows the relations between $w/\boldsymbol{k}T$ by Eqs. 3, 3 and 3, 17 in which z is assumed to be 4 and T_c/T for systems of ethylbenzene—liquid ammonia[13], carbon tetrachloride—perfluoromethylcyclohexane[14,15], *n*-butane—perfluoro-*n*-butane[16] and *n*-hexane—methanol[17]. Plots are made of values of $w/\boldsymbol{k}T$ obtained from formulae according to several approximations for square lattice against T_c/T for the system ethylbenzene—liquid ammonia in Fig. 5, compared with results obtained from Eq. 3, 3. As will be clear from these figures, simple uninflected curves convex downward are obtained by exact solution for the two dimensional model, while similar curves convex upward by several approximate solutions, and it is observed that w can be represented by neither a linear function of T nor a constant since no linear relationships are observed in these figures.

Inspection of literature data on partially miscible binary liquid systems reveals that $w/\boldsymbol{k}T$ is satisfactorily expressed by the following exponential functions

$$w/\boldsymbol{k}T-(w/\boldsymbol{k}T)_c=K(|T_c/T-1|)^n \qquad (4,1)$$

where K and n are constants. When values of $|T_c/T-1|$ are small, using the abbreviation η for the quantity $\exp(w/z\boldsymbol{k}T)$, this formula may be transformed into

$$\eta-\eta_c=K\eta_c(|T_c/T-1|)^n/z \qquad (4,2)$$

by expanding η/η_c in terms of $K(T_c/T-1)^n/z$ and neglecting higher than square.

Plots of $\log(\eta-\eta_c)$ against $\log(|T_c/T-1|)$ for several binary liquid systems are shown in Fig. 6 where values of η are evaluated from the mutual solubility data described in the literature according to Eqs. 3, 17 and 3, 18 assuming $z=4$. It will be seen from Fig. 6 that fair straight lines are obtained from these plots over a wide range of temperatures.

---

26) E. L. Eckfeldt and W. W. Lucasse, *J. Phys. Chem.*, 47, 164 (1943).

5. Prediction of the Critical Solution Temperature

It has been observed that the quasi-chemical approximation is considerably more accurate than the zeroth approximation and the results given by the first approximation differ little from those given by the higher approximations. Considering the possibility of the application of the theory of regular solutions to the vapor-liquid equilibria, it will be convenient at present to estimate $w/\boldsymbol{k}T$ by the Eqs. 3, 17 and 3, 18 according to the first approximation.

Since two empirical constants K and n, besides the critical solution temperature T_c, are involved in Eqs. 4, 1 or 4, 2, three pairs of data are required for the estimation of the critical solution temperature. However, it is observed in Fig. 6 that the average value of n for many systems is about 5/7 in the first approximation when z is assumed to be 4. When the approximate value of five seventh is used for n in Eq. 4, 2, it is possible to estimate the critical solution temperature and the solubility relationships at any other temperature from two pairs of the mutual solubility data.

In Table I are given critical compositions estimated by Eq. 2, 7 from the solubility data at temperatures T_1 and T_2 and critical solution temperatures calculated according to the expression

$$T_c=\frac{T_1T_2\{(\eta_1-\eta_c)^{7/5}-(\eta_2-\eta_c)^{7/5}\}}{T_1(\eta_1-\eta_c)^{7/5}-T_2(\eta_2-\eta_c)^{7/5}} \qquad (5,1)$$

which is derived from Eq. 4, 2 by the use of approximate value of five seventh for n and the notation of η_1 and η_2 for the respective values of exp $(w/z\boldsymbol{k}T)$ at temperatures T_1 and T_2, compared with experimental values and the calculated values of critical solution temperature according to Eq. 1, 10.

It will be seen that with few exceptions in which m in Eq. 1, 9 is not a constant over a wide range of temperatures, showing two straight lines having different slopes on plots of $\log\{(1-x')/x'\}$ against $\log\{(1-x'')/x''\}$ such as shown in Figs. 1—3 in the preceding paper, the agreement between the experimental and calculated values of T_c by Eq. 5, 1 is about as good as the experimental accuracy even though the approximation of $n=5/7$ is used, better than the results given by Eq. 1, 10 which has been proposed by Cox and Herington[27].

Summary

Theoretical expressions for estimating the interchange energy w were given in such form as to be obtained from the mutual solubility data. It has been found that the dependency of the interchange energy estimated from mutual solubility data in terms of φ-fractions upon temperature is satisfactorily expressed by the form of equations $w/\boldsymbol{k}T-(w/\boldsymbol{k}T)_c=K(|T_c/T-1|)^n$. The method of predicting the critical solution point was described as an example of the application of the theory of regular solutions.

The Chemical Research Institute of
Non-Aqueous Solutions
Tohoku University
Katahira-cho, Sendai

---

[27] J. D. Cox and E. F. G. Herington, *Trans. Faraday Soc.*, 52, 926 (1956).