[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE CARNEGIE INSTITUTE OF TECHNOLOGY AND THE CARNEGIE HIGH SCHOOL]

The System Biphenyl–Bibenzyl–Naphthalene. Nearly Ideal Binary and Ternary Systems

BY H. HOWARD LEE AND J. C. WARNER

In this investigation, the freezing point–composition diagrams have been determined for the binary systems (I) biphenyl–bibenzyl, (II) biphenyl–naphthalene and (III) bibenzyl–naphthalene, and for the ternary system biphenyl–bibenzyl–naphthalene. In each of the binary systems, and in the ternary system, solubilities, eutectic temperatures and eutectic compositions are compared with values calculated for ideal solution behavior. Washburn and Read[1] reported the eutectic temperature and composition in the biphenyl–naphthalene system but did not give complete freezing point–composition data.

Materials.—Eastman's "Highest Purity" biphenyl, 1,2-bibenzyl and naphthalene were purified by recrystallization until no further changes in melting points were observed. The melting points of these substances, as used, are given in Table I.

Experimental.—The method used for calibrating thermometers, determining initial crystallization temperatures, temperatures for disappearance of solid and final solidification temperatures has been described in previous papers.[2] All temperatures for disappearance of solid were obtained with samples sealed in glass tubes.

TABLE I

	M. p., °C.	Calories per mole at m. p.		
		ΔH_f	C_p(l)	C_p(s)
Biphenyl	69.0	4235[3]	63.5[4]	54.8[4]
Bibenzyl (1,2)	51.25	5390[5]	74.75[5]	67.0[5,6,7]
Naphthalene	80.05	4495[8]	$\Delta H_f = -2375 + 38.10\ T - 0.0528\ T^2$	

The Binary Systems

The freezing point–composition diagrams for the three binary systems are given in Figs. 1, 2 and 3. These diagrams are based upon the data given in Tables II, III and IV. The ideal solubilities, shown by the filled circles in the figures, were calculated from the following solubility

TABLE II

(I) BIPHENYL–BIBENZYL

N Biphenyl	Initial cryst. temp., °C.	Disapp. of solid, °C.	Final solidification temp., °C.
0.000	51.25		51.25
.100	46.9		
.200	42.8	42.8	
.250	40.1	40.5	
.300	37.5	37.8	29.55
.350	34.9	35.4	29.65
.400	32.4	32.6	29.65
.423		30.9	
.433		30.3	
.440		29.9	
.442		29.8	
.443E		29.65	29.65
.445		29.8	
.447		29.95	
.450	29.9	30.2	29.55
.500	34.8	35.1	29.65
.600	43.8		
.700	50.8		
.800	57.5		
.900	63.6		
1.000	69.0		69.0

TABLE III

(II) BIPHENYL–NAPHTHALENE

N Biphenyl	Initial cryst. temp., °C.	Disapp. of solid, °C.	Final solidification temp., °C.
0.000	80.05		80.05
.230		66.1	
.300	60.8		
.303		61.1	
.393		54.3	
.400	53.6		39.53
.449		49.6	
.500	45.4		39.54
.526		42.5	
.541		41.0	
.550	39.8	40.1	39.5
.552		40.0	
.553		39.7	
.555E	39.6	39.7	39.5
.556		39.8	
.573		42.5	
.600	42.9		39.53
.657		47.8	
.700	50.3		39.57
.806		57.8	
.898		63.5	
1.000	69.0		69.0

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(1) Washburn and Read, *Proc. Nat. Acad. Sci.*, **1**, 191 (1915).

(2) Lee and Warner, THIS JOURNAL, **55**, 209, 4474 (1933).

(3) Warner, Scheib and Svirbely, *J. Chem. Phys.*, **2**, 590 (1934).

(4) Spaght, Thomas and Parks, *J. Phys. Chem.*, **36**, 882 (1932).

(5) Ferry and Thomas, *ibid.*, **37**, 253 (1933).

(6) Smith and Andrews, THIS JOURNAL, **53**, 3653 (1931).

(7) Huffman, Parks and Daniels, *ibid.*, **52**, 1547 (1930).

(8) Ward, *J. Phys. Chem.*, **38**, 761 (1934).

TABLE IV

(III) BIBENZYL–NAPHTHALENE

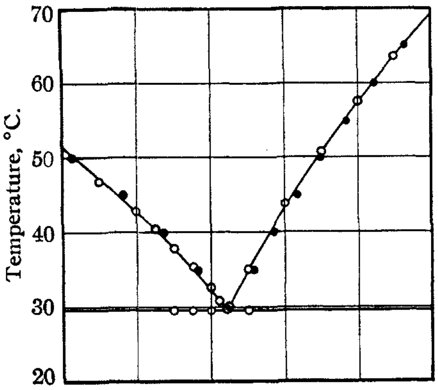
N Bibenzyl	Initial cryst. temp., °C.	Disapp. of solid, °C.	Final solidification temp., °C.
0.000	80.05		80.05
.199		68.1	
.228		66.4	
.390		53.9	
.490		45.4	
.580		36.5	
.610	33.0		32.5
.614E	32.5	32.6	32.5
.620	32.9		32.5
.649	34.7		32.5
.701		37.5	
.799		42.3	
.900		47.0	
1.000	51.25		51.25

equations which are based upon the melting points, heats of fusion (ΔH_f) and heat capacities (C_p) given in Table I.

$$\text{Log } N \text{ (biphenyl)} = -(274.0/T) + 4.380 \log T - 10.299$$

$$\text{Log } N \text{ (bibenzyl)} = -(610.2/T) + 4.021 \log T - 8.221$$

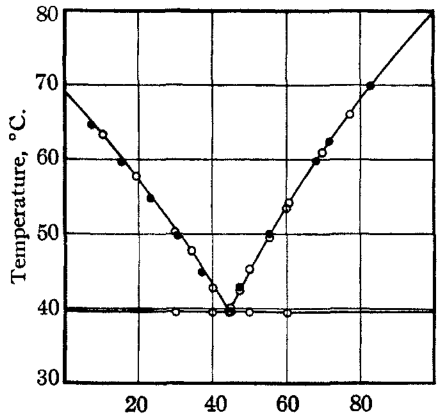
$$\text{Log } N \text{ (naphthalene)} = (518.9/T) + 19.170 \log T - 0.0115\,T - 46.253$$



Mole per cent. of biphenyl.

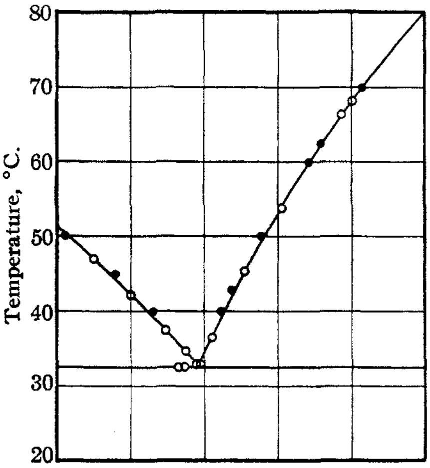
Fig. 1.—Bibenzyl-biphenyl.

In calculating the ideal solubility of biphenyl and bibenzyl, sufficient accuracy is obtained by assuming that ΔC_p is constant. With naphthalene, however, the variation in ΔC_p is so great between the melting point and room temperature that the additional term in T should be kept in the solubility equation. In Table V, the ideal eutectic temperatures and compositions are compared with those determined by experiment for the three binary systems. Our values for the eutectic temperature and composition in the biphenyl–naphthalene system are in good agreement with the values reported by Washburn and Read (39.4° and 0.560 mole fraction biphenyl).



Mole per cent. of naphthalene.

Fig. 2.—Biphenyl-naphthalene.



Mole per cent. of naphthalene.

Fig. 3.—Bibenzyl-naphthalene.

One may conclude that these three binary systems are practically ideal. The differences between the ideal and experimental values of the eutectic temperatures and compositions (Table V)

TABLE V

System	Eutectic temperature, °C. Ideal	Eutectic temperature, °C. Intersect. of liquidus curves	Eutectic temperature, °C. Final solidification	Eutectic composition Mole fraction Ideal	Eutectic composition Mole fraction Expt.
Biphenyl-bibenzyl	29.3	29.5	29.6	0.457	0.443 biphenyl
Biphenyl-naphthalene	39.2	39.4	39.5	.560	.555 biphenyl
Bibenzyl-naphthalene	33.6	32.7	32.5	.386	.386 naphthalene

are no greater than might be expected from a consideration of the possible errors in method, heats of fusion and heat capacities.

The Ternary System

The freezing point–composition data for the ternary system biphenyl–bibenzyl–naphthalene are given in Table VI. Figure 4 shows the distribution of samples and the contours for the liquidus surfaces.

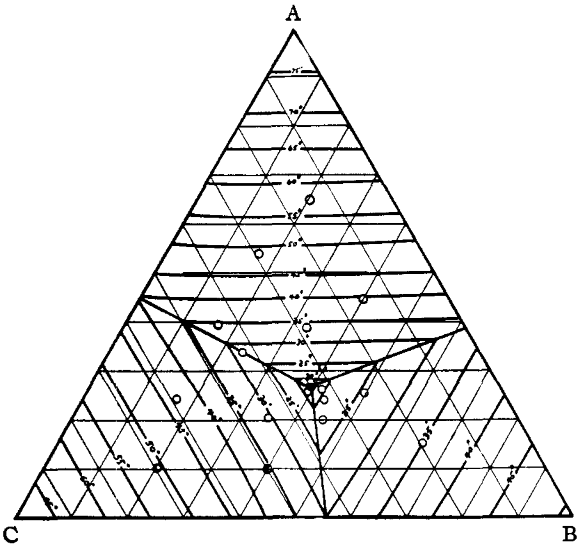


Fig. 4.—Ternary systems: A, naphthalene; B, bibenzyl; C, biphenyl.

Since the ternary eutectic temperature must be the only temperature at which the sum of the mole fraction solubilities is equal to unity, the ideal ternary eutectic temperature and composition may be obtained[9] by plotting $(N_1 + N_2 + N_3)$ against temperature, or better by plotting log $(N_1 + N_2 + N_3)$ against $1/T$. The temperature at which $\Sigma N_i = 1$ is the ideal eutectic temperature and the ideal solubilities of the components at this temperature represent the ideal eutectic composition.

The ideal ternary eutectic temperature and composition may also be calculated by applying Newton's method of approximation.[10] If one lets $\log N_i = x_i$ where $x_i = x_i(T)$, then at the eutectic temperature $\Sigma N_i = \Sigma e^{x_i} = 1$. This is an equation of the form $f(T) = 1$ and if T_0 is an approximate solution, it may be written approximately; $f(T_0) + f'(T_0)(T - T_0) = 1$, or

$$T = T_0 + \left[\frac{1 - \Sigma e^{x_i}}{\Sigma x_i' e^{x_i}}\right]_{T = T_0}$$

The value of T resulting from the first approximation is used as T_0 in the next approximation. If, as a first approximation, one takes $T_0 = 300$, the value of T converges to 290.8 after repeating the process four or five times. In Table VII the ternary eutectic temperature and composition are compared with values calculated for ideal solution behavior by the two methods outlined above.

TABLE VI

BIPHENYL–BIBENZYL–NAPHTHALENE

Region Fig. 4	Mole fraction Biphenyl	Bibenzyl	Naphthalene	Freezing point, °C.	Final solidification, °C.
	0.150	0.200	0.650	57.3	
	.296	.164	.540	48.3	
	.152	.398	.450	39.7	
	.441	.164	.395	33.9	
A	.287	.325	.388	33.4	
	.297	.398	.305	21.9	
	.325	.390	.285	19.4	
	.347	.377	.276	19.0	17.4
	.335	.388	.277	18.5	
Eut.	.338	.392	.270	17.4	17.4
	.333	.398	.269	18.1	17.4
	.330	.400	.270	18.3	
	.333	.402	.265	18.5	
	.327	.413	.260	19.5	17.4
	.330	.430	.240	20.9	
B	.351	.449	.200	22.3	
	.250	.496	.254	25.5	
	.197	.650	.153	34.8	
	.100	.650	.250	34.8	
	.336	.392	.272	17.7	
	.337	.393	.270	17.65	17.4
	.340	.390	.270	18.15	
	.347	.393	.260	19.0	17.4
C	.425	.237	.338	27.8	
	.449	.349	.202	30.3	
	.500	.399	.101	35.2	
	.590	.165	.245	42.8	
	.697	.200	.103	50.8	

TABLE VII

TERNARY EUTECTIC

		Temp., °C.	Composition, mole fractions Biphenyl	Bibenzyl	Naphthalene
Experimental		17.4	0.338	0.392	0.270
Ideal	Newton	17.7	.350	.390	.260
	Johnston	17.5	.352	.384	.264

The difference between the results obtained by the two methods for calculating the ideal eutectic temperature may be attributed to the fact that in applying Newton's method, ΔC_p for naphthalene was assumed constant. The differences between the experimental and ideal ternary eutectic temperature and compositions in this system are, we

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[9] Johnston, Andrews and Kohman, *J. Phys. Chem.*, **29**, 882, 914, 1041, 1317 (1925).

[10] The application of Newton's method to this problem was suggested by Dr. T. L. Smith, Department of Mathematics.

believe, within the limit of error in method, heats of fusion and heat capacities.

Summary

1. The freezing point–composition diagram for the system biphenyl–bibenzyl shows a simple eutectic at 44.3 mole per cent. biphenyl and at 29.5°; biphenyl–naphthalene a simple eutectic at 55.6 mole per cent. biphenyl and at 39.4°; bibenzyl–naphthalene a simple eutectic at 38.6 mole per cent. naphthalene and at 32.7°.

2. Solubilities, eutectic temperatures and eutectic compositions in each of the three binary systems are within the limits of error equal to those calculated for ideal solutions.

3. The freezing point–composition diagram for the ternary system biphenyl–bibenzyl–naphthalene shows a simple ternary eutectic at 33.8 mole per cent. biphenyl, 39.2 mole per cent. bibenzyl, and at 17.4°.

4. The ternary eutectic temperature and composition are in good agreement with the values calculated for ideal solution behavior by two methods.

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Isotopic Exchange Equilibria

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Equilibrium constants involving hydrogen and deuterium have been calculated from statistical theory in recent years and these constants have been beautifully confirmed by experiment. Two such instances are the equilibrium constants of the reactions

$$H_2 + 2DI \rightleftharpoons 2HI + D_2, \text{ and} \quad (1)$$
$$H_2 + D_2 \rightleftharpoons 2HD \quad (2)$$

which have been calculated and experimentally confirmed by Urey and Rittenberg,[1] and in the case of the second reaction particularly nicely observed by Gould, Bleakney and Taylor.[2] The values of the constants obtained in these cases by calculation are exact, since the energy levels of the molecules involved are well known. In addition, the equilibrium constants of the reactions

$$D_2O + H_2 \rightleftharpoons H_2O + D_2 \quad (3)$$
$$H_2 + HDO \rightleftharpoons HD + H_2O \quad (4)$$

have been calculated and experimentally confirmed by others,[3] who used approximate formulas valid at ordinary temperatures and higher. These have been found to agree very satisfactorily with experimental values.

Equilibria in exchange reactions involving isotopes of other elements therefore become of interest and can be made with confidence. In this paper we shall present calculations of the equilibrium constants for exchange reactions involving isotopes of some of the lighter elements. These equilibrium constants differ by small factors from the values expected if the isotopes were distributed by chance between the molecules. It is predicted from an evaluation of the effect of such exchange that appreciable variations in the determinations of the atomic weights of elements are to be expected. Moreover, it seems possible that some concentration of the less abundant isotopes may be accomplished through the use of such exchange reactions.

Theoretical

The equilibrium constant, K, of a reaction

$$a\text{A} + b\text{B} + \ldots \rightleftharpoons m\text{M} + n\text{N} + \ldots$$

is given by the relation

$$-RT \ln K = \Delta F^\circ = -RT \ln \frac{f_{\text{N}}^{n}\, f_{\text{N}}^{n}}{f_{\text{A}}^{a}\, f_{\text{B}}^{b}} \quad (5)$$

where $K = p_{\text{A}}^{a}\, p_{\text{B}}^{b} / p_{\text{M}}^{m}\, p_{\text{N}}^{n}$, and f_{M} is the distribution function of molecule M. This distribution function, f, of a diatomic or polyatomic molecule is given by the relation

$$f = M^{3/2}\, T^{5/2}\, Q\, \frac{(2\pi)^{3/2}\, k^{5/2}}{h^3\, N^{3/2}} \quad (6)$$

Here Q is the summation of state and the remaining symbols have their usual meaning. For diatomic molecules the summation of state is

$$Q = \sum_{v,j} p_j \exp - \frac{E(J, v)}{kT} \quad (7)$$

and the energy of a diatomic molecule is given by the formula

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[1] Urey and Rittenberg, *J. Chem. Phys.*, **1**, 137 (1933); THIS JOURNAL, **56**, 1885 (1934); Rittenberg, Bleakney and Urey, *J. Chem. Phys.*, **2**, 48 (1934).

[2] Gould, Bleakney and Taylor, *ibid.*, **2**, 362 (1934).

[3] Crist and Dalin, *ibid.*, **2**, 735 (1934); Farkas and Farkas, *Nature*, **132**, 894 (1933); *Proc. Roy. Soc.* (London), **A144**, 467 (1934).