Substituting these and the value of ΔF^0_{298} into the free energy equation we get ΔF^0_{522} (benzoic acid) = $-36{,}491$ cal. From this it follows that the free energy of formation of benzoic acid from benzene and carbon dioxide at 522°K. is 18,172 cal. The equilibrium constant for this reaction is calculated, from the relationship $-\Delta F^0 = RT \ln K$, to be $K = 10^{-7.63}$.

It can be shown readily that this value will not be much affected by an increase of pressure of the order of 35 atmospheres. It is evident that in the reactions studied by Kinney and his students, the equilibrium amounts of carboxylic acids cannot account for the quantities actually found. The most plausible explanation, it seems to us, is that the zinc oxide of their oxide catalyst was slowly converted into the zinc salt of a carboxylic acid, and in this way appreciable amounts were built up in their apparatus. This would account also for the observation that fresh catalysts were always most effective and that the catalyst became almost inactive by the third usage.

This emphasizes the fact that catalysts may not always be purely catalysts, but that small amounts of products may result from direct chemical action with the catalyst or with one of its constituents. In such cases free energy data if available are of great value.

We acknowledge indebtedness to Professor George S. Parks for criticizing the preliminary calculations, and to Dr. Lyman G. Bonner for rechecking the final ones. The latter also has made a precise calculation of the free energy of benzoic acid at the boiling point, using complete heat capacity equations. This calculation, however, differs from ours by less than 0.5%.

SALT LAKE CITY, UTAH RECEIVED JULY 29, 1935

[CONTRIBUTION FROM THE UNIVERSITY OF AKRON]

Binary Systems of *p*-Dichlorobenzene with Diphenyl, Naphthalene and Triphenylmethane

BY ROSS E. MORRIS AND WALTER A. COOK

Schröder[1] some years ago showed that *p*-dibromobenzene forms an almost perfect solution with benzene. The purpose of this investigation was to find the nature of solutions of *p*-dichlorobenzene with various aromatic hydrocarbons. Those chosen were diphenyl, naphthalene and triphenylmethane. These solutions have not been previously investigated.

In the following report the solubilities, eutectic temperatures and eutectic compositions are compared with values calculated for perfect solutions from the equation given by Washburn[2]

$$dT_f = \frac{RT_f^2}{\Delta H_f}\,\frac{dN}{N}$$

where T_f is the freezing point of the solution, ΔH_f is the heat of fusion of the crystals separating from the solution at the freezing point, R is the gas constant and N is the mole fraction of the component which crystallizes at the freezing point. The values for ΔH_f are given in Table I.

TABLE I

HEAT OF FUSION ΔH_f

	G. cal./mole	Ref.
p-Dichlorobenzene	$-10{,}250 + 94.07T - 0.1511T^2$	3
Diphenyl	$-11{,}240 + 112.8T - 0.2835T^2 + 0.0002568T^3$	4
Naphthalene	$+4265 - 26.31T + 0.1525T^2 - 0.0002140T^3$	4
Triphenylmethane	$-9230 + 66.35T - 0.07324T^2$	4

Materials.—Commercial naphthalene and *p*-dichlorobenzene were purified by distillation until no further changes in melting points were observed. Eastman C. P. grade of diphenyl and triphenylmethane were purified by recrystallization, the former from alcohol and the latter from acetone, and dried *in vacuo*. The melting points of the purified materials are compared with the "International Critical Tables" values in Table II.

The agreement in melting points is good except in the case of triphenylmethane. The "I. C. T." value is undoubtedly too low for this compound.

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(1) Schröder, *Z. physik. Chem.*, **11**, 449 (1893).

(2) Washburn, "Principles of Physical Chemistry," McGraw-Hill Book Co., Inc., New York City, 1921 p 202.

(3) Calculated from specific heat and heat of fusion data given in "International Critical Tables," Vol. V, p. 132.

(4) Calculated from specific heat and heat of fusion data given by Spaght, Thomas and Parks [*J. Phys. Chem.*, **36**, 882 (1932)].

TABLE II

	Melting point, °C. Our material	Melting point, °C. "I. C. T."
p-Dichlorobenzene	53.2	52.9
Diphenyl	69.1	69.0
Naphthalene	80.0	80.1
Triphenylmethane	93.2	92.5

Smith and Andrews[5] in their careful work on the heat capacity and melting point of triphenylmethane found 93.1° by thermometer, which is in good agreement with our value.

Experimental.—Temperatures were measured with short stem Anschütz precision thermometers. Two thermometers were used, covering the ranges -13 to 60° and 38 to 110°, respectively. Each was 155 mm. over-all length and contained an enclosed white glass scale which was divided in 0.2° unit. With the aid of a magnifying glass the thermometers could be read accurately to 0.05°. Both were compared with a thermometer standardized by the Bureau of Standards. With these thermometers there was no correction for emergent stem because the entire thermometer was enclosed with the melt.

Weighed samples in test-tubes (22 mm. in diameter) were placed in larger test-tubes which were immersed in a water-bath. The melt was allowed to cool with the bath, the difference in temperature between the melt and bath never amounting to more than three degrees. The melt was well stirred with a glass stirrer having a ring at the bottom encircling the thermometer. When supercooling occurred the highest temperature attained after crystallization started was taken as the melting point. This temperature could be checked to within 0.2°. Supercooling never amounted to more than 0.5°.

TABLE III

p-DICHLOROBENZENE–DIPHENYL

Mole per cent. *p*-Dichlorobenzene	Initial cryst. *T*, °C.	Final solidification *T*, °C.
0.0	69.1	69.1
5.0	66.3	
10.6	63.2	
17.7	58.7	
29.2	50.8	26.6
37.9	44.1	26.8
44.0	39.1	26.8
48.0	35.0	26.8
54.0	29.4	27.0
57.5E	26.9	26.9
63.0	30.8	27.1
69.0	35.2	27.0
78.8	41.2	
84.9	45.0	
93.1	49.4	
100.0	53.2	53.2

TABLE IV

p-DICHLOROBENZENE–NAPHTHALENE

Mole per cent. *p*-Dichlorobenzene	Initial cryst. *T*, °C.	Final solidification *T*, °C.
0.0	80.0	80.0
10.6	73.8	
18.2	68.9	
30.8	59.7	
37.8	53.7	30.0
44.7	47.3	
49.0	43.3	30.2
53.1	38.5	30.1
59.1	31.6	30.0
60.6E	30.2	30.2
63.2	30.9	30.2
63.9	31.1	30.1
65.2	31.8	30.0
69.9	35.6	30.2
77.1	40.0	30.0
88.1	46.4	
95.0	50.5	
100.0	53.2	53.2

TABLE V

p-DICHLOROBENZENE–TRIPHENYLMETHANE

Mole per cent. *p*-Dichlorobenzene	Initial cryst. *T*, °C.	Final solidification *T*, °C.
0.0	93.2	93.2
5.1	90.3	
12.2	86.1	
18.6	82.0	
28.1	75.9	
36.6	69.3	
43.1	64.0	
50.1	57.1	35.7
57.3	50.0	35.9
62.4	43.7	35.9
65.9	39.3	35.7
68.5E	35.9	35.9
80.2	42.2	35.8
87.0	46.1	
93.9	49.8	
100.0	53.2	53.2

The procedure of projecting back the cooling curve of the two-phase system to intersect with the liquid cooling curve and taking the point of intersection as the melting point has been used frequently in work of this type.[6] However, in this investigation we found that this procedure was inapplicable, especially at low temperatures and high concentrations of one of the constituents. The ring stirrer became caked with crystals so that uniform stirring could not be obtained and therefore the heat transfer was affected. Taylor and Rinkenbach[7] experienced the same difficulty

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(5) Smith and Andrews, THIS JOURNAL, **53**, 3644 (1931).

(6) Bell and Sawyer, *Ind. Eng. Chem.*, **11**, 1025 (1919); Lee and Warner, THIS JOURNAL, **55**, 209 (1933).

(7) Taylor and Rinkenbach, *ibid.*, **45**, 44 (1923).

TABLE VI

	p-Dichlorobenzene with		
	Diphenyl	Naphthalene	Triphenylmethane
Eutectic temperature, °C.			
Ideal	27.5	32.0	34.9
Found	26.9	30.2	35.9
Difference	−0.6	−1.8	−1.0
Eutectic composition Mole fraction p-dichlorobenzene			
Ideal	0.563	0.625	0.670
Found	.575	.606	.685
Difference	−.012	−.019	−.015

in their work on the solubility of trinitrotoluene in carbon tetrachloride.

Results and Discussion.—The data obtained are given in Tables III, IV and V, and the freezing point–composition diagrams are shown in Figs. 1, 2 and 3. The ideal solubilities calculated from the above equation are shown by the filled circles in the figures. A comparison of the ideal eutectic compositions and temperatures is presented in Table VI.

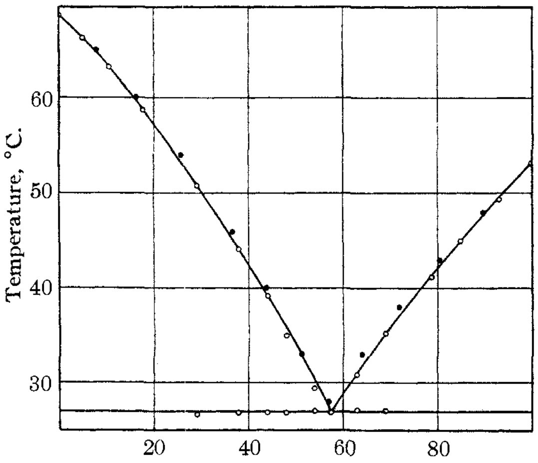

Fig. 1.—p-Dichlorobenzene–diphenyl.

One may conclude that these three binary systems show a fairly close approach to ideal properties.

Although p-dichlorobenzene is non-polar, the presence of the chlorine atoms in the molecule evidently influences the properties of the latter sufficiently to make its solution with hydrocarbons somewhat less perfect than mixtures of hydrocarbons. For example, Lee and Warner[8] have shown that diphenyl, dibenzyl and naphthalene form practically perfect solutions among themselves.

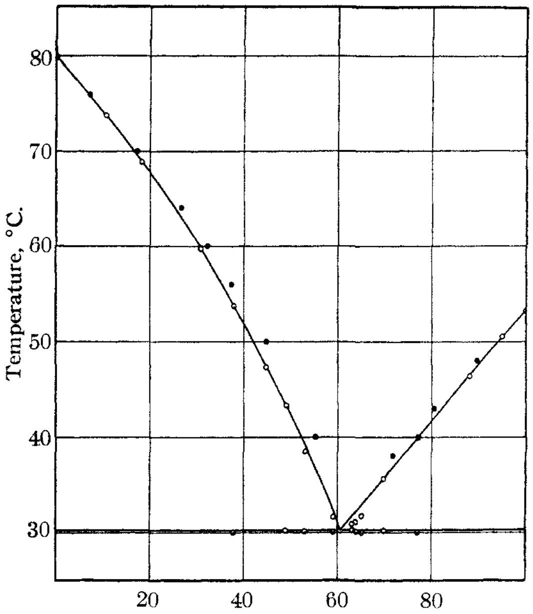

Fig. 2.—p-Dichlorobenzene–naphthalene.

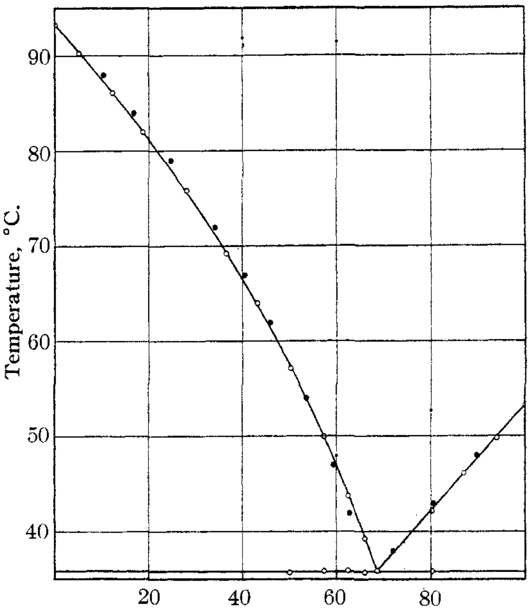

Fig. 3.—p-Dichlorobenzene–triphenylmethane.

We wish to thank Professor D. E. Anderson for the use of his laboratory and the Goodyear Tire and Rubber Co. for standardizing the thermometers in their laboratories.

Summary

1. The system p-dichlorobenzene with diphenyl shows a simple eutectic at 26.9° and 57.5 mole per cent. p-dichlorobenzene, with naphthalene a simple eutectic at 30.2° and 60.6

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[8] Lee and Warner, THIS JOURNAL, **57**, 318 (1935).

mole per cent. *p*-dichlorobenzene, and with triphenylmethane a simple eutectic at 35.9° and 68.5 mole per cent. *p*-dichlorobenzene.

2. Solubilities, eutectic temperatures and eutectic compositions in each of the three binary systems are a close approach to those calculated for ideal solutions.

AKRON, OHIO RECEIVED AUGUST 30, 1935

[CONTRIBUTION FROM THE JARVIS CHEMICAL LABORATORY OF TRINITY COLLEGE]

Equilibrium in the System, Lithium Phthalate–Phthalic Acid–Water

BY STERLING B. SMITH, WILLIAM A. STURM AND EDWARD C. ELY

Introduction

The use of acid phthalates as standards in volumetric analysis has become widespread during the past twenty years. Both the potassium and the sodium acid salts are used. Their use was first suggested by Dodge[1] and by Hendrixson.[2] A phase rule study of the system potassium phthalate, phthalic acid and water has been made by Smith,[3] and the system sodium phthalate, phthalic acid and water by Smith and Sturm.[4] It is possible that the acid phthalates of other alkali metals could be used for similar purposes and it is with this point in mind that an investigation of the solubility relations in the system lithium phthalate, phthalic acid and water has been undertaken.

Experimental Part

Materials and Methods.—Phthalic acid was prepared by crystallizing from aqueous solution sublimed phthalic anhydride obtained from the Eastman Kodak Co.

Lithium phthalate was prepared by neutralizing in aqueous solution an equivalent weight of phthalic acid with C. P. lithium carbonate. The resulting solution was boiled to drive off carbon dioxide, evaporated to a small volume and allowed to crystallize. The resultant crystals of lithium phthalate were filtered on a Büchner funnel and dried in the air. The composition of this salt was found by analysis to be $2Li_2C_8H_4O_4 \cdot 3H_2O$.

Lithium acid phthalate, while not a component of this system, appears as one of the important solid phases and is used in the preparation of mixtures for analysis. This salt as will be apparent later cannot be crystallized from aqueous solution at room temperature and was prepared by adding less than the equivalent weight of phthalic acid to each equivalent of lithium phthalate prepared as above, and allowing the acid salt to crystallize from a solution of lithium phthalate.

Solubilities were determined by analyzing solutions obtained by rotating for a minimum of twenty-four hours mixtures of the three components in an electrically controlled thermostat. At zero degrees the temperature was maintained constant by the use of ice and a small amount of salt. Temperature variations were within ±0.1°. When equilibrium was attained, the mixtures were allowed to settle and samples for analysis removed from the clear supernatant liquid by means of a pipet. At elevated temperatures the pipet was previously warmed to prevent crystallization during the sampling. When necessary, to prevent entrance of solid phase into the pipet, a small plug of cotton was placed in a short length of rubber tubing slipped over the end of the pipet.

Phthalic acid was determined by titration with alkali using phenolphthalein as the indicator. Lithium phthalate was determined by conversion into lithium sulfate with sulfuric acid and evaporating to dryness. The excess sulfuric acid was removed by ignition in a stream of ammonia. Water was determined by difference.

In making up the original mixtures, wherever possible the salts were used which exist as solid phases after equilibrium has been reached. The composition of the solid phases was determined by the analysis of wet residues according to Schreinemakers.[5] Because of the viscosity of many of the solutions, no attempt was made to determine their density.

Experimental Results.—Isotherms at 0, 25 and 50° have been completed. Compound formation takes place at all these temperatures. The solubility isotherms at these temperatures consist of three intersecting curves, representing isothermally univariant equilibrium between the solutions and one solid phase, and two isothermally invariant points where two solid phases are in equilibrium with the solutions. Inasmuch as no new solid phases appeared and the same solid phases remained at these three temperatures, no further isotherms were completed.

Experimental results are given in Table I. The symbol "P" is used here as in previous work to designate the phthalate radical, $C_8H_4O_4$. The figures representing the composition of the solutions at the isothermally invariant points are the average of several closely agreeing results.

The Acid Salt.—The composition of the acid salt, $LiHP \cdot 2H_2O$, is most important as it is this material that has possibilities as a standard in volumetric analysis. The composition of this salt has been determined both graphically and by analysis. The extrapolated tie lines at each

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[1] F. D. Dodge, *J. Ind. Eng. Chem.*, **7**, 29 (1915).

[2] W. S. Hendrixson, THIS JOURNAL, **37**, 2352 (1915).

[3] S. B. Smith, *ibid.*, **53**, 3711 (1931).

[4] S. B. Smith and W. A. Sturm, *ibid.*, **55**, 2414 (1933).

[5] Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893).