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THE SOLUBILITY OF SOLID BENZENE IN SEVERAL NON-POLAR LIQUIDS.

By R. Negishi.

Recently, much interest has been shown in the theoretical aspects[1-4] and in the application[5-11] of regular solutions, as defined by Hildebrand[12]. Although a general expression for regular solutions which is valid to all systems, gaseous, liquid, solid, and their mixtures is derivable theoretically, when certain assumptions* are introduced, to make it applicable to actual systems, it is necessary to make several further simplifying assumptions[1].** Hildebrand[1] has shown that

$$RT \ln \frac{N_2^i}{N_2} = V_2\left(\frac{N_1 V_1}{N_1 V_1 + N_2 V_2}\right)^2 \left[\left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}} - \left(\frac{\Delta E_1}{V_1}\right)^{\frac{1}{2}}\right]^2 = V_2 \phi_1^2 D^2 \quad (1)$$

is applicable to the solubility of a solid in non-polar liquids. Here, N_2^i and N_2 are ideal and actual solubilities expressed in terms of mole fraction; V_1 and V_2 are the

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* The assumptions introduced are equivalent of saying that the molecules are non-polar, spherical, and of about the same molecular volume; the total energy of the system is given by the sum of the potential energy, taken as $-k/r^6$, of the molecule with its nearest neighbors, and the repulsive potential is considered negligibly small by comparison.

** The added assumptions are that the molal volumes are additive; the probability function, as defined by Menke[13], is independent of the temperature and it is for the different species the same function of the position of the first maximum; and the constant of the attractive potential for a pair of different molecules is the geometric mean of those of the individual molecules, so $k_{12}=(k_{11}k_{22})^{\frac{1}{2}}$.

1) a) J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, 1, 817 (1933); b) J. H. Hildebrand, "*Solubility of Non-electrolytes*", Reinhold Publish. Corp., 1936. This contains most of the relevent references to earlier papers.

2) G. Scatchard, *Trans. Faraday Soc.*, 33, 160 (1937).

3) a) E. A. Guggenheim, *Proc. Roy. Soc.*, A 148, 304 (1935); b) R. H. Fowler and E. A. Guggenheim, "*Statistical Thermodynamics*," Cambridge Univ. Press, 355 (1939).

4) J. G. Kirkwood. *J. Phys. Chem.*, 43, 97 (1939).

5) a) J. H. Hildebrand and G. R. Negishi, *J. Am. Chem. Soc.*, 59, 339 (1937); b) J. H. Hildebrand, *Trans. Faraday Soc.*, 33, 144 (1937); c) J. H. Hildebrand, *J. Am. Chem. Soc.*, 59, 2083 (1937); d) J. H. Hildebrand, *J. Phys. Chem.*, 43, 109 (1939); e) J. H. Hildebrand and J. W. Sweny, *ibid.*, 43, 297 (1939); f) J. H. Hildebrand, *Science*, 90, 1 (1939).

6) a) G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Phys. Chem.*, 43, 119 (1939); b) G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.*, 61, 3206 (1939); c) Scatchard, S. E. Wood, and J. M. Mochel, *ibid.*, 62, 712 (1940).

7) S. E. Wood, *ibid.*, 59, 1510 (1937).

8) R. D. Vold, *ibid.*, 59, 1515 (1937).

9) R. Negishi, This Journal, 14, 137 (1940).

10) V. Kirejew, *Acta Physicochim. U.R.S.S.*, 13, 531 (1940).

11) a) M. Gonikberg, *ibid.*, 12, 489 (1940); b) M. Gonikberg, *ibid.*, 12, 921 (1940). Here, the concept of regular solutions is applied to the solubility of hydrogen under pressure.

12) J. H. Hildebrand, *J. Am. Chem. Soc.*, 51, 66 (1929).

13) H. Menke, *Physik. Z.*, 33, 593 (1932).

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molal volumes of pure liquids 1 and 2 (super-cooled for the solute); ΔE_1 and ΔE_2 are the molal energies of vaporization of pure components 1 and 2, respectively; v_1 is the volume fraction of component 1, and D stands for $\left[\left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}-\left(\frac{\Delta E_1}{V_1}\right)^{\frac{1}{2}}\right]$ (or $\left[\frac{a_2^{\frac{1}{2}}}{V_2}-\frac{a_1^{\frac{1}{2}}}{V_1}\right]$), in which a_1 and a_2 are the van der Waals constants at the boiling points[9] of liquids 1 and 2).

The present determination of the solubility of solid benzene, or the freezing point lowering of benzene, has been undertaken to test further the applicability of equation (1). Although the tetrahalides of the fourth group would be most desirable for this purpose from theoretical considerations, the benzene systems are more suitable experimentally, since all such physical constants as the heat of fusion, the molal heat capacities of solid and liquid, the heat of vaporization, and the molal volume which are necessary to make a comparison of the equation with the experimental data are known fairly accurately. The accuracy in the values of the physical constants is of great importance in the investigation of a solid-liquid system owing to the fact that some unavoidable long extrapolations are necessary. This is brought about by the inherent characteristics of equation (1) which necessitates an unescapable assumption that the properties of the solute in its supper-cooled state are expressible by the same expressions for its pure liquid. Moreover, it has been shown[1), 8), 10), 14)] that the heat of mixing serves to show how closely a system obeys the conditions of regular solutions. An extension of this comparison to a solid-liquid system may be fruitful, and this is possible with benzene systems.

Experimental Details.

1) Apparatus.

A thermostat was made from a battery jar well insulated except for two windows with layers of kieselguhr about 5 cm thick. Between the window glass and the battery jar was placed some $CaCl_2$ in order to prevent the condensation of water on the surfaces of glass when the thermostat was cooled. Acetone was used in the bath and it was cooled with two copper cylinders, about 5 cm in diameter with a large number of fins soldered on each of them to increase the cooling surfaces. A mixture of alcohol-CO_2 slush was used. The bath was heated by means of dry air forced through a spiral copper tubing. The temperature was measured by means of a copper-constantan thermocouple, imbedded in paraffin, which was connected to a potentiometer whose smallest reading could be estimated to 0.004 millivolts. The temperature regulation was done by hand which required but slight attention. A schematic drawing of the thermostat is shown in Fig. 1.

14) H. Hirobe, *J. Fac. Sci. Imp. Univ. Japan*, (1), 1, 155 (1926).

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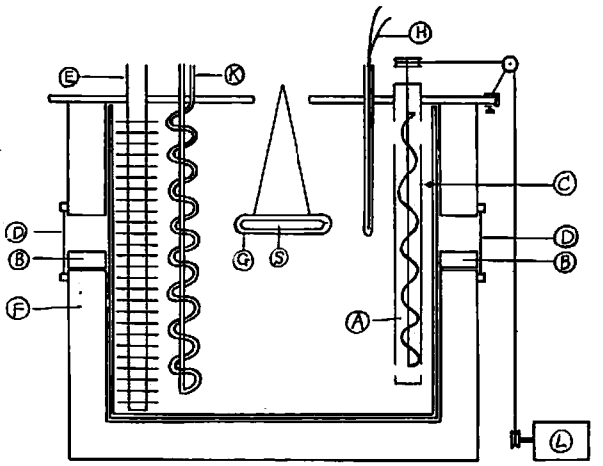

Fig. 1.

Ⓐ=Stirrer. Ⓑ=$CaCl_2$ Container. Ⓒ=Battery Jar.
Ⓓ=Window Glass. Ⓔ=Cooler. Ⓕ=Layer of Kieselguhr.
Ⓖ=Wire Basket for Supporting Sample. Ⓗ=Thermocouple.
Ⓚ=Spiral of Copper Tubing for Heating. Ⓛ=1/20 H. P. Motor.
Ⓢ=Sample.

2) Preparation of Mixtures.

Synthetic mixtures were prepared by pipetting out proper amounts of pure liquids by means of a pipet connected to a flask as shown in Fig. 2 a. The flask was evacuated, and by manipulating the cock, the liquid may be pipetted and discharged at will. A synthetic mixture was prepared and weighed in a tube, as shown in Fig. 2 b. Interchangeable ground glass joints were used. The discharging end of the pipet was drawn to a capillary so that it could be inserted beyond the constriction made in the tube. After weighing, the tube was

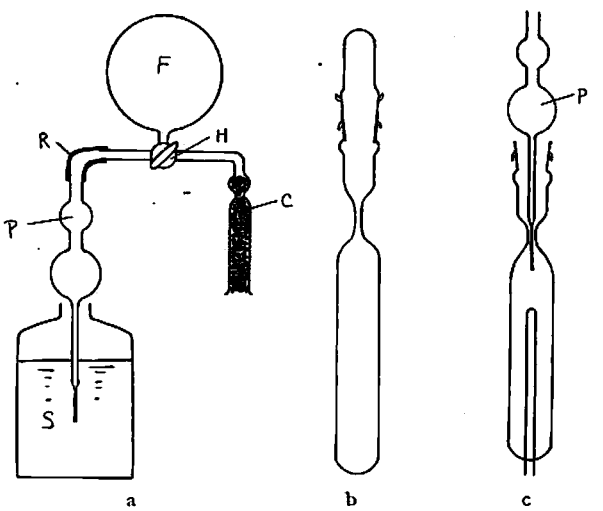

Fig. 2. F=250 cc Flask, R=Rubber Connection, C=$CaCl_2$ Tube,
P=Pipet (6.5 cc), S=Sample, H=3-Way Capillary Cock.

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connected to an evacuation system, which was capable of 10^{-6} mmHg (such a high degree of evacuation was never used owing to the fact that only CO_2-alcohol slush was available for cooling), and evacuated for two minutes* to eliminate as much air as possible. It was then sealed off with oxygen-gas flame at the constriction. Terex glass (similar to Pyrex) was used throughout.

3) Calibration of Thermocouple.

The thermocoule was calibrated against the melting points of benzene, water, and CCl_4 and against the transition point of CCl_4. The reference points used were:

Benzene	5.53	melting point[6],
CCl_4	−22.87	melting point[15],
CCl_4	−47.66	Transition point[15].

The apparatus used for the calibration is shown in Fig. 2 c. A pure liquid was charged as described for preparing a synthetic mixture. The void space was about 1 cc, as in the case of the synthetic mixutres. It was evacuated at least 10 minutes before sealing off. The thermocouple was inserted in the smaller tube partially filled with paraffin oil to improve heat conductivity. By this method sharp and constant freezing and melting curves at the same temperature were obtained. The freezing point curves remained constant until practically all had solidified which gave us assurance that the sustances were quite pure. From the points thus determined, the following equation was set-up:

$$t°C = 26.739(E) + 1.034(E)^2 + 0.593(E)^3,$$

expressing t°C in terms of millivolt.

Since the solubility of solid benzene in the various liquids investigated here showed a pronounced super-cooling effect, even when the mixture was agitated vigorously, we determined, in every case, the temperature at which the last traces of benzene had disappeared**. Near the solution temperature the rate of temperature increase was maintained at about 0.02°C/minute.

4) Purification.

Benzene. Commercial "thiophene free" benzene was frozen twice in the presence of $CaCl_2$ and was finally distilled twice over $CaCl_2$ in a column containing a Terex glass spiral about a meter long. A constant boiling fraction was collected. The distillation apparatus was all glass; ground glass joints without grease were used when necessary. Benzene was distilled into a small neck glass bottle. No special precautions were taken to prevent the air from coming in contact with the distillate; it was kept in a glass-stoppered bottle.

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* From the results of preliminary runs it was found that if evacuation was longer then three minutes, a loss in the weight of the sample was excessive (0.3%); within two minutes most of the occluded air was eliminated (although the final pressure was never better than 0.1 mm.).

15) H. L. Johnston and E. A. Long, *J. Am. Chem. Soc.*, **56**, 31 (1934).

** In several rough determinations the temperature of freezing agreed within 0.1°C of that of melting.

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Carbon Tetrachloride. It was purified by the method given by Scatchard, Wood, and Mochel[16]; distillations were, however, made in our set-up. It was kept in a glass-stoppered bottle.

Carbon Disulfide. It was treated according to the method given by Brown and Manov[16]. It was distilled just before use, and the distillate was collected and kept in a colored glass bottle.

Chloroform. It was purified by washing with NaOH and water[17] and refluxed over $CaCl_2$ according to the directions given by Porter, Stewart, and Branch[18], the final distillation was made over calcium chloride just before use; it was collected in a colored glass bottle and kept in dark. No further precautions were taken[19].

Toluene. It was shaken with concentrated H_2SO_4; washed with water and distilled. The distillate was dried with metallic sodium and, finally, distilled over metallic sodium[20].

Results and Discussion.

Benzene-Carbon Tetrachloride.

Since there are more data[21], [22a] available for this system, it has been investigated first. We had observed that our solution at the lowest temperature, $-29.75°$ C, where $N_2=0.5196$, seemed turbid (barely perceptible). This was probably due to a small amount of water. In this system alone, $CaCl_2$ was used instead of P_2O_5 to dry the air which was admitted to the evacuating system. Working at low temperatures, the effect of the condensation of water was the main source of uncertainty and error, and we took particular care to eliminate it in the other systems.

In our calculations the heat of vaporization, ΔH, of benzene was calculated from the equation given by Fiock, Ginnings, and Holton[23],

$$\Delta H/\text{Gram} = -0.00056185\,(290-\theta)^2+0.65028\,(290-\theta) + 74.11\,(290-\theta)^{\frac{1}{2}},$$

where ΔH was given in international joules and θ corresponded to t°C. This equation was derived from the data obtained above 10°C, but we used it at

16) O. L. I. Brown and G. G. Manov, *J. Am. Chem. Soc.*, **59**, 500 (1937).

17) W. T. Richard and J. H. Wallace, Jr., *J. Am. Chem. Soc.*, **54**, 2705 (1932). They found that by washing with H_2SO_4, NaOH, and H_2O partial oxidation to phosgene took place.

18) C. W. Porter, T. D. Stewart, and G. E. K. Branch, "*The Methods of Organic Chemistry*," Ginn and Co., 68 (1927).

19) L. Gillo, *Chem. Abst.*, **32**, 7014 (1938). According to him air and light caused rapid contamination; even prolonged treatment with Na_2CO_3 and P_2O_5 in the absence of oxygen was useless if light were admitted.

20) G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, **7**, 1087 (1939).

21) *Int. Crit. Tables* IV, 98 (1928).

22) a) W. F. Wyatt, *Trans. Faraday Soc.*, **25**, 48 (1929); b) W. F. Wyatt, *ibid.*, **24**, 429 (1928).

23) E. F. Fiock, D. C. Ginnings, and W. B. Holton, *J. Res. Bur. Std.*, **6**, 881 (1931).

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lower temperatures. 4.1836 and 78.11 were used as a conversion factor of international joules to $cal_{15°C}$ and for the molecular weight of benzene, respectively.

The molal volume was calculated from the equation[24], $d_t=0.90005-1.0636\,(t)\,10^{-3}-0.0376(t)^2 10^{-6}-2.213(t)^3 10^{-9}$. This equation was given as valid in the temperature range, 11 to 72°C, but, for want of a better one, it was used in our calculation. Since the density was practically a linear function of the temperature, the error introduced by its use at lower temperatures probably would not be appreciable.

$a_1^{1/4}$ for benzene was calculated at the boiling point, 80.10₅°C[6a], from the relation,

$$a=V\Delta E,$$

where a was the van der Waals constant, V and ΔE were the molal volume and the energy of vaporization at the boiling point of the pure liquid. $\frac{a_2^{1/4}}{V_2}$ was calculated by dividing $a_2^{1/4}$ at the boiling point by the molal volume of the pure component at the temperature of the solution in question. $a_2^{1/4}$ was 798.57 cal. cc.

The heat of vaporization of CCl_4 was calculated from the equation,

$$\Delta H=4782.02+911328.7/T,$$

derived from the vapor pressure equation given by Scatchard, Wood, and Mochel[6c],

$$\text{Log } P=6.68148-1045.022/T-99577/T^2.$$

Some of the comparative figures of ΔH found in the literature were 45.4 cal./gram[25a] (derived from vapor pressure measurements) as against 44.8 at the boiling point, 76.69[6c], from this equation; 51.8 cal./gram at 24.3°C[25b] and 48.5 cal./gram at 25°C[25b], directly measured values, as compared with 51.0 at 25°C by this equation.

The molal volumes were calculated from the equation[24],

$$d_t=1.63255-1.9110\,(10)^{-3}t-0.690\,(10)^{-6}t^2.$$

$a_1^{1/4}$ and $a_1^{1/4}/V_1$ were calculated as in the case of benzene. $a_1^{1/4}$ at the boiling point was 801.76.

The results of our measurements are plotted along with those from the Int. Crit. Tables[21] in Fig. 3. The agreement is satisfactory at lower temperatures. Wyatt's results[22a] approximated from his graph are compared with ours in the accompanying Table. Here, the agreement is good except at the lowest temperature.

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24) *Int. Crit. Tables*, III, 28, 29 (1928).

25) a) *Landolt and Boernsteins Tabellen* (1931); b) The same (1936).

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Comparison of Wyatt's Results.

N_2, Benzene	Temp. °C	
	This Run	Wyatt
0.8512	−4.65	−4.5
0.7503	−11.35	−11
0.6870	−15.93	−16
0.5793	−24.32	−24
0.5196	−29.75	−30.5

As can be seen from Fig. 3, this system obeys the conditions of regularity rather closely[5b].

Benzene-Carbon Disulfide.

The heat of vaporization, the molal volumes, and other physical constants of benzene were calculated as in the benzene-carbon tetrachloride system. The heat of vaporization of CS_2 was obtained from the equation,

$$\Delta H = 4746.21 + 566204.22/T,$$

derived from

$$\text{Log } P\text{mm} = 6.73239 - 1037.1965/T - 61866.76/T^2,$$

in which log Pmm and the constants were determined from the vapor pressure data given in the Int. Crit. Tables[26a]. ΔH at the boiling point, 45.29°C[27], from the above equation was 6525 cal./mole as compared with 6400, a directly measured value at (45.22°C)[26b].

The molal volumes[28] were calculated from the equation,

$$d_4^t = 1.2931 - 0.001508\, t^{[26c]},$$

and from the molecular weight, 76.13. $a_1^{\frac{1}{2}}$ at the boiling point, 45.29°C, was 567.92.

The results of our measurements are plotted in Fig. 3. Measurements on the same system by other investigators[26d] are also plotted, there. The agreement between ours and the Int. Crit. Table data is good only to N_2 is about 0.7 and below this concentration it is rather bad. In our measurements we have been careful to prevent the condensation of moisture, and we have eliminated as much air as possible from the system, and the fact that our system has been com-

26) a) *Int. Crit. Tables*, III, 213 (1928); b) *ibid.*, V, 138 (1929); c) *ibid.*, III, 23 (1928); d) *ibid.*, IV (1929).

27) Mathews, *J. Am. Chem. Soc.*, **48**, 562 (1926).

28) J. Mazur, *Nature*, **144**, 328 (1939). According to him CS_2 has anomalous thermal expansion at lower temperatures.

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pletely sealed, we believe that our data are more reliable. Since CS_2 decomposes on standing, we have used freshly distilled sample for our investigation. The solubility of this system deviates from that of an ideal a great deal, and also from being regular*,[29], as indicated by the solubility curve and by D^2 given in Table I.

When $(\Delta E_2/V_2)^{1/2}$ and $a_2^{1/2}/V_2$ calculated from the vapor pressure of the pure liquid are compared with those obtained from solubility, a difference much too large is found. This is a consequence of the form of equation (1) as written, and there is nothing fundamentally incompatible with the theory. Since

$$\left(\frac{\Delta E_2}{V_2}\right)^{1/2}=\left(\frac{\Delta E_1}{V_1}\right)^{1/2}+\frac{RT\ln\dfrac{N_2'}{N_2}}{V_2^{1/2}v_1},$$

if $(\Delta E_1/V_1)^{1/2}$ is larger than $(\Delta E_2/V_2)^{1/2}$, the difference becomes larger by the above calculation. In equation (1) it is D^2 that measures the degree of deviation from ideality and regularity, and it is the absolute value of the difference of the energy densities of the pure species that is important.

Benzene-Chloroform.

The heat of vaporization of chloroform was calculated from the data given in Landolt-Boernsteins Tabellen[30]. The molecular weight was taken as 119.39. The molal volume was calculated from the equation[24],

$$d_4=1.52643-1.8563\,(10^{-3})\,t-0.5309\,(10^{-6})\,t^2-8.81\,(10^{-9})\,t^3.$$

The results of our measurements are plotted in Fig. 3 and are compared with those of Wyatt[22a] in the Table below. Since his values have been approximated from a graph, this comparison must be rough. The agreement is satisfactory except for the lowest temperature.

Comparison of Wyatt's Data.

N_2, Benzene	Temp. °C	
	This Run	Wyatt
0.8629	−3.91	−4
0.7602	−12.27	−12
0.6609	−20.90	−22
0.5391	−32.56	−33
0.4167	−48.09	−51

* The solubility of iodine in CS_2 at lower temperatures seems also irregular (G. R. Negishi, L. H. Donnally, and J. H. Hildebrand, *J. Am. Chem. Soc.*, 55, 4793 (1933)).

29) C. E. Waring, H. Hyman, and S. Steingiser, *J. Am. Chem. Soc.*, 62, 2028 (1940). They have found that magnetic-optic rotation in benzene-CS_2 system is irregular.

30) *Landolt-Boernsteins Tabellen*, 2730 (1936).

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From Fig. 3 it is apparent that the solubility curve lies above that of an ideal. This means that benzene-chloroform systems give negative deviations. This is also the case with the heat of mixing of the two liquids, as shown in Table IV. Negative deviations ordinarily indicate a strong attraction between unlike species, and a greater solubility than that of an ideal. Chloroform is much more reactive* chemically than CCl_4, although its structure is also tetrahedral[31], and this may be one of the factors causing negative deviations. Since equation (1) is applicable only to those systems giving positive deviations, this system has not been further considered.

Benzene-Toluene.

The heat of vaporization of toluene was calculated from the equation[30],

$$-108.7+0.26\,t-0.0005\,t^2,\ \text{cal./gram.}$$

This equation was for the range, 26.87 to 42.85°C, but at 109.6°C it gave a value, −86.50, as compared with −86.21 given in the literature[25b]. We, therefore, used the same equation in our temperature range. $a_1^{\frac{1}{2}}$ at the boiling point, 110.8[32], was 922.04. The molal volumes were calculated from the equation[24],

$$d_t=0.88412-0.92248\,(10^{-3})\,t+0.0152\,(10^{-6})\,t^2-4.223\,(10^{-9})\,t^3,$$

and from the molecular weight of 92.135.

From the considerations of its molecular structure and of the nearness of its energy density to that of benzene, this system would be regular. This, indeed, is the case is well indicated by Fig. 3 and by the results in Tables I and II. The same conclusion could have been drawn from the heat of mixing measurements (Table IV). Unfortunately, not sufficient data are available to calculate its excess entropy of mixing, but we believe it would be rather small, as in the benzene-CCl_4 system.

Benzene-Cyclohexane.

The results of the measurements by Mascarelli and Pestalozza have been used,[33]

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* According to Wyatt's experimental results[22a], there exist in the benzene-chloroform system relatively strong forces of attraction between the two species of molecules (negative deviation throughout the whole range of concentration), but no compounds are formed, while in the benzene-CCl_4 system unstable compounds of the formula,  $\cdot CCl_4$ and  $\cdot 2CCl_4$ are formed.

31) C. Degard, *Compt. rend.*, **201**, 95 (1935). He states that the molecular structure of $CHCl_3$ has been reexamined by the method of electron diffraction, and the results deduced therefrom are shown to be consistent with both the ordinary tetrahedral formula and Urban's coordinate formula, $CCl_3\cdot HCl$, within the limits of error.

32) H. Hoag and R. A. Henkes, *J. Am. Chem. Soc.*, **69**, 17 (1938).

33) Mascarelli and Pestalozza, *Gazz. chimica italiana*, 38-1, 38 (1908); *Int. Crit. Tables*, IV, 133 (1928).

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since we do not have our own data. This investigation is under-way in our laboratory. These results are unfortunately, probably not quite reliable, since the melting points of benzene and cyclohexane have been given, respectively, as 5.0 and 6.2. More recent values are for benzene 5.5[31] and 5.53[6a], the latter value of which we have used in our calculation; for cyclohexane, 6.50[34], 6.63[35], and 6.49[6a]. We have used 6.50°C.

The heat of vaporization was calculated from the equation,

$$\Delta H = 4761.973 + 959724.48/T,$$

derived from the vapor pressure equation,

$$\text{Log } P = 6.65859 - 1040.641/T - 104865/T^2,$$

given by Scatchard, Wood, and Mochel[6c]. ΔH calculated at 29.22°C from the above equation was 7830 cal./mole as compared with a directly measured value of 7820 at the same temperature, given in Landolt-Boernsteins[30]. $a_1^{\frac{1}{4}}$ at the boiling point, 80.74[6c], was 887.20.

The molal volumes were calculated from the equation[24],

$$d_t = 0.79707 - 0.8879\,(10^{-3})\,t - 0.972\,(10^{-6})\,t^2 + 1.55\,(10^{-9})\,t^3,$$

and from the molecular weight, 84.16.

From the fact that the heat of mixing for this system is largest in the present series of investigations, its deviation from an ideal solubility may also be largest. This is actually the case. A similar conclusion may be drawn from the value of the excessive entropy of mixing shown in Table IV.

Some quite interesting facts come to light when this system is compared with that of the benzene-toluene. We shall reserve this for a later discussion and here we shall summarize the equations used to express the results of our solubility measurements as a function of the temperature. These expressions have been used to calculate the solubilities at zero and at −20°C to supply the necessary data for Table II.

System	Equation
Benzene-CCl_4	$\text{Log } N_2 = 3.52050 - 614.60380/T - 0.53668 \text{ log } T$
Benzene-CS_2	$\text{Log } N_2 = 84.37257 - 3909.37235/T - 28.772 \text{ log } T$
Benzene-Toluene	$\text{Log } N_2 = 20.63104 - 1234.72565/T - 6.5529 \text{ log } T$
Benzene-Cyclohexane	$\text{Log } N_2 = 23.15897 - 1547.22620/T - 7.1932 \text{ log } T$

34) J. Timmermans and F. Martins, *J. chim. phys.*, **23**, 750 (1926).
35) L. Rotinjanz and N. Nagornow, *Z. physik. Chem.*, **A 169**, 20 (1934).

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The probable accuracy of our calculations and measurements will be mentioned in passing. It is difficult to estimate the order of the magnitude of the error involved in our calculations. The main source of error is in the determination, which requires fairly large extrapolations, of the molal volumes and the heats of vaporization of the liquids in our temperature range. The former should be fairly accurate (except for a substance like CS_2[28]), but in the latter there may be room for a large source of error. The vapor pressure measurements of Scatchard, Wood, and Mochel are accurate, and we have used their results to derive appropriate expressions for the heats of vaporization of benzene, cyclohexane, and carbon tetrachloride. However, how accurately their measurements give the proper values of ΔH at our temperatures is difficult to say. Judging from a number of the heats of vaporization data found in Landolt-Boernsteins Tabellen and International Critical Tables where the values of the same substance may differ not infrequently from 2 to 3%, we shall assume that the accuracy of our heat of vaporization calculations cannot be greater than 2.

Our solubility measurements are more accurate. The total loss in the weight of our sample was, in every case, less that 0.2%. The temperatures of the solutions could be estimated to 0.2°C with ease, and the relative temperatures were close to 0.1°C, although the absolute temperatures might have been off much more. The liquids employed appeared quite pure, as indicated by their sharp and constant freezing curves. We have assumed, therefore, that the accuracy of our measurements is about 0.4% and relative temperatures are within 0.2°C.

General Discussion.

The results of the measurements of the five systems are summarized in Tables I, II, III, and IV and represented graphically in Fig. 3. Comparisons with the published data and with ideal solubilities have been made. The latter have been calculated by two methods. First, by employing the equation,

$$\text{Log } N_2^i = -\frac{\Delta L}{4.576}\left(\frac{1}{T}-\frac{1}{T_m}\right), \qquad (3)$$

where N_2^i is the ideal solubility at the temperature, T, of the solid solute expressed in terms of mole fraction; ΔL is the heat of fusion at the melting point, and here, it has been assumed to be independent of the temperature; T_m is the melting point in the absolute temperature. Second, by taking into account of the change, which depends on the difference between the molal heat capacities of the liquid and solid forms, in the heat of fusion, ΔL.

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Table I.

Solubilities of Benzene.

Temp. °C	$-\log N_2$	$-\log N_2^i$	Mol. Volume (cc) V_1	Mol. Volume (cc) V_2	v_1	D^2 Found	D^2 Calc'd from $(\Delta F/V)^{1/2}$	D^2 Calc'd from $(a^{1/4}/V)$
Solvent, CCl_4								
−4.65	0.0700	0.0692	93.72	86.31	0.1695	0.3861	0.6660	0.4871
−11.35	0.1284	0.1172	92.99	85.64	0.2654	1.5092	0.6550	0.4939
−15.93	0.1630	0.1509	92.51	85.18	0.3310	1.5318	0.6461	0.5015
−24.32	0.2371	0.2151	91.62	84.36	0.4410	1.5282	0.6216	0.5125
−29.75	0.2844	0.2583	91.06	83.83	0.5010	1.3791	0.6006	0.5200
Solvent, CS_2								
−5.71	0.0858	0.07664	58.48	86.20	0.1291	7.8052	0.7039	0.1995
−13.58	0.1508	0.1334	57.96	85.41	0.2818	3.0611	0.7208	0.2022
−20.51	0.2261	0.1855	57.50	84.73	0.4636	2.5771	0.7475	0.2044
−24.45	0.2751	0.2160	57.25	84.35	0.6000	2 2132	0.7613	0.2058
−28.42	0.3291	0.2475	56.99	83.96	0.7693	1.8373	0.7783	0.2069
Solvent, Chloroform*								
−3.91	0.0641	0.0639	77.85	86.38	0.1253			
−12.27	0.1191	0.1237	77.07	85.54	0.2213			
−20.90	0.1798	0.1884	76.28	84.69	0.3161			
−32.56	0.2683	0.2812	75.25	83.57	0.4350			
−48.09	0.3802	0.4149	73.91	82.10	0.5575			
Solvent, Toluene								
−1.13	0.0492	0.0461	104.03	86.65	0.1259	2.8238	0.0034	0.1236
−7.42	0.0919	0.0887	103.38	86.03	0.2206	0.9178	0.0075	0.1394
−15.80	0.1569	0.1498	102.49	85.19	0.3435	0.8222	0.0536	0.1424
−22.21	0.2150	0.1986	102.03	84.56	0.4360	1.1714	0.0247	0.1371
−28.02	0.2663	0.2443	101.55	84.00	0.5057	1.1445	0.0345	0.1328
Solvent, Cyclohexane[33]								
−6.9	0.0969	0.0850	104.79	86.08	0.2333	3.0904	0.8604	0.6564
−12.4	0.1549	0.1247	104.17	85.53	0.3430	3.5827	0.8601	0.6717
−18.4	0.2219	0.1694	103.51	84.94	0.4483	3.5833	0.8553	0.6901
−25.0	0.3010	0.2204	102.81	84.29	0.5495	3.5991	0.8420	0.7120
−32.2	0.3980	0.2782	102.06	83.60	0.6468	3.7735	0.8234	0.7387

* The last three columns have not been calculated, since this system gives negative deviations which make the value of D^2 imaginary.

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Table II.

Comparison of $\left(\frac{\Delta E_2}{V_2}\right)^{1/2}$ and $\left(\frac{a_2^{1/2}}{V_2}\right)$ from Solubility. with Those from Vapor Pressure.**

Solvent	at −20°C				% Deviation from Vap. Pressure Value	
	$\left(\frac{\Delta E_1}{V_1}\right)^{1/2}$	$\left(\frac{\Delta E_2}{V_2}\right)^{1/2}$*	$\left(\frac{a_1^{1/2}}{V_1}\right)$	$\left(\frac{a_2^{1/2}}{V_2}\right)$*	$(\Delta E_2/V_2)^{1/2}$	$a_2^{1/2}/V_2$
CS_2	10.61	12.97	9.87	12.23	33.0	29.8
CCl_4	9.25	10.46	8.70	9.92	7.3	5.3
Toluene	9.90	10.94	9.04	10.06	12.2	6.8
Cyclohexane	8.82	10.72	8.59	10.47	10.0	10.6
	From vapor pressure 9.75			9.42		

* From Solubility.

at 0°C

CS_2	10.33	13.50	9.65	12.82	42.2	39.4
CCl_4	8.97	9.97	8.51	9.52	5.2	3.5
Toluene	9.54	11.01	8.85	10.32	16.1	12.2
	From vapor pressure 9.48			9.20		

** In this Table chloroform and cyclohexane at 0°C have been left out, because in these systems there result negative deviations which make the value of D imaginary.

Table III.

Comparison of N_2 Calculated with N_2 from Solubility.

Solvent, CCl_4

Temp. °C	N_2 Calc'd from		N_2 Found	% Deviation from N_2 Found		
	$\left(\frac{\Delta E}{V}\right)^{1/2}$	$\left(\frac{a^{1/2}}{V}\right)$		$\left(\frac{\Delta E}{V}\right)^{1/2}$*	$\left(\frac{a^{1/2}}{V}\right)$*	$\left(\frac{\Delta E}{V}\right)^{1/2}$** and ΔL=Const.
−4.65	0.8501	0.8508	0.8512	−0.12	−0.05	−0.04
−11.35	0.7578	0.7592	0.7503	0.99	1.18	0.58
−15.93	0.6982	0.7001	0.6870	1.63	2.05	0.82
−24.32	0.5971	0.5997	0.5793	3.07	3.52	1.62
−29.75	0.5375	0.5394	0.5196	3.45	3.82	1.31

* N_2 calculated from Eqs. (1) and (6).
** N_2 calculated from Eqs. (1) and (3).

Solvent, CS_2

−5.71	0.8366	0.8378	0.8207	1.92	2.08	
−13.58	0.7287	0.7337	0.7066	3.12	3.83	
−20.51	0.6349	0.6475	0.5941	6.86	8.99	
−24.45	0.5803	0.6005	0.5307	9.34	13.14	
−28.42	0.5223	0.5547	0.4687	11.43	18.34	

Solvent, Toluene					
−1.33	0.8993	0.8990	0.8929	0.72	0.69
−7.42	0.8144	0.8144	0.8094	0.85	0.62
−15.80	0.7075	0.7063	0 6969	1.52	1.35
−22.21	0.6323	0.6302	0.6095	3.72	3.31
−28.02	0.5686	0.5663	0.5417	5.00	4.35
Solvent, Cyclohexane					
−6.9	0.8160	0.8175	0.80	2.0	2.2
−12.4	0.7380	0.7407	0.70	5.4	5.8
−18.4	0.6579	0.6604	0.60	9.6	10.7
−25.0	0.5765	0.5804	0.50	15.2	16.1
−32.2	0.4962	0.4993	0.40	24.1	24.8

Table IV.

Heat of Mixing of Benzene Systems at 18°C for 50 Mole % Mixtures.

Solvent	ΔH Cal/Mole of Solution	S_X^E Cal/Mole °C	Note
CCl_4	26.3	0.017[10]	
CS_2	146.5	0.268[10]	ΔH Cal/Mole=133.5 at 25°C[10]
Chloroform	−77	—	* at 16°C
Toluene	20*	—	
Cyclohexane**	175.8[6c]	0.341[6c]	** at 25°C

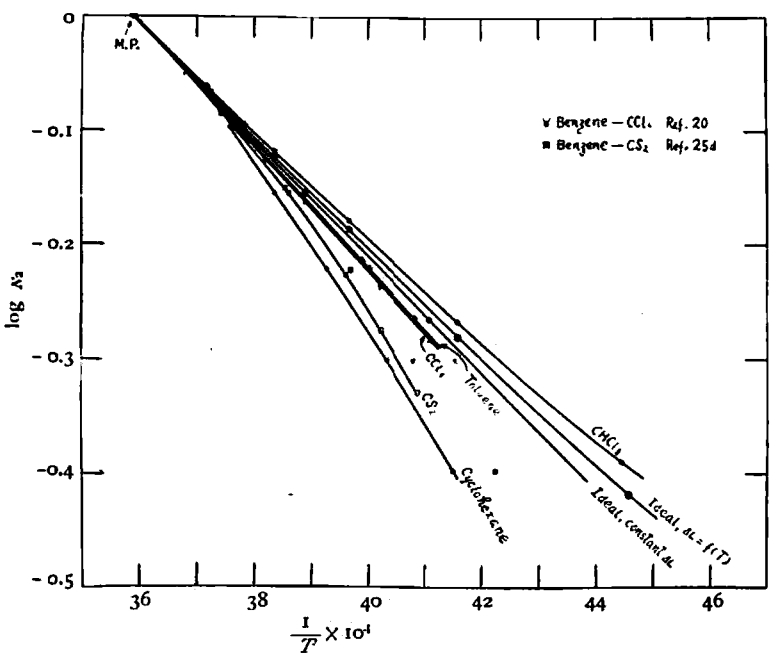

Fig. 3. Solubility of Benzene in Non-polar Liquids.

The molal heat capacity of liquid benzene has been calculated from the equation given by Fiock, Ginnings, and Holton[35],

$$c_\pi \cong c_p = 1.7184 + 0.02016\,(\theta/10) + 0.007386\,(\theta/10)^2.$$

Here, c_p is the specific heat in terms of the international joules and θ corresponds to °C. Since for a small range of temperatures in which we are interested, the molal heat capacity expressed in a linear form would be more convenient, so we have calculated several points from the above equation and fitted them into a linear form. We have, thus, derived the equation,

$$C_{pl} = 19.9245 + 0.04452\ T, \qquad (4)$$

in which C_{pl} is the molal heat capacity of liquid benzene in calories. A linear expression for the molal heat capacity of the solid has been obtained by drawing a straight line through the points which have been determined by Aoyama and Kanda[36]. The equation obtained is

$$C_{ps} = 3.3741 + 0.09063\ T \qquad (5)$$

By combining the equations (4), (5) with ΔL, 2351 cal./mole, at the melting point, 5.53°C, we have derived an expression for the ideal solubility, N_2^i,

$$\text{Log}\ N_2^i = 102.8104/T + 8.3293\ \log\ T - 0.005038\ T - 19.3304. \qquad (6)$$

$-\log N_2^i$ calculated by the second method (equation 6) lies above that by the first method (equation 3) and it is not a linear function of $\frac{1}{T}$.

In the benzene-CCl_4 system alone a further comparison of N_2 has been made by employing equation (3) instead of (6). The apparent agreement is better when equation (3) is used. For the same range of concentration, the maximum error is 1.6%, entirely within the error of calculation. In spite of a better agreement when equation (3) is used, we shall compare our solubility data in the other systems with N_2 calculated using equation (6), since the latter is based on a more sound theoretical foundation.

From Tables I and II we can say that either $(\Delta E/V)^{1/2}$ or $(a^{1/2}/V)$, where a is the van der Waals constant at the boiling point[9], can be employed to calculate satisfactorily the actual solubility of a non-electrolytic solid in non-polar liquids, or slightly polar, as indicated by their dipole moments. There is but a little to choose between the two.

Theoretically and experimentally it is generally accepted that a liquid is more like a solid than a gas, and many of the properties of a liquid can be correlated

36) Aoyama and Kanda, *Sci. Rep. Tohoku Univ.* (1), 24, 119 (1935).

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to those of a solid without abrupt changes. Similarly, many properties of a liquid-liquid system can be extended to those of a solid-liquid system. In this connection the heat of mixing is useful in furnishing some information as to the degree of regularity and of deviations from ideality of a solid-liquid system composed of the same components as in the liquid-liquid system. In Table IV are listed the heats of mixing for the benzene systems of 50 mole percent at 18°C (unless otherwise stated) taken from Schmidt's paper[37], and the excess entropy of mixing, S_x^E, for CCl_4 and CS_2 by Kirejew[10] and that of cyclohexane by Scatchard[6a]. Unfortunately, no data have been found for the others. The measured values of the heat of mixing for the same systems by different authors vary within a wide range of limits, so for the purpose of comparison, we have taken them from the same source (not necessarily the most accurate), namely, Schmidt's paper[37]. S_x^E has been included for the sole purpose of giving some information concerning the order of the magnitude of the excess entropy of mixing, and no more significance should be attached to it at present, since part of the excess entropy of mixing is due to the volume change on mixing[6], but this correction has not been applied for in this paper. Nevertheless, the relative order of both the heats of mixing and the excess entropy of mixing is in agreement with what has been found experimentally in our solutions.

The calculated values of D^2 from $(\Delta E/V)^{1/2}$ and $(a^{1/2}/V)$ of the pure components are compared with those obtained from solubility in Table I. The agreement between them is not good except for the benzene-CCl_4 system, for which it is tolerable. This comparison is, as has been mentioned elsewhere[7),8)], too severe, since, here, a small difference between large numbers is involved, and the magnitude of a small error is magnified to the extent entirely out of proportion to it. A more suitable method of comparison is to compare directly N_2 calculated from equations (1) and (6). The results of this comparison are shown in Table III. Now, the agreement is much better, and it is, indeed, gratifying for the benzene-CCl_4 and benzene-toluene systems which should be regular from theoretical considerations and from the heats of mixing data of their liquid systems. For these two systems a difference is less than 5% for N_1 as high as 45 mole percent. The agreement is excellent in view of the fact that our calculation of the energy of vaporization per cc cannot probably be better than 2% and that equation (1) contains a number of assumptions, whose information as to what extent they are

37) G. G. Schmidt, *Z. physik. Chem.*, 121, 221 (1925).

valid* is lacking for some of them.

If equation (1) were strictly applicable, D^2 should be independent of temperature. The constancy of D^2 in turn indicates the regularity of the system. The results of our calculations given in Table I give some information on this point. D^2 of the systems, benzene-CCl_4 and benzene-toluene, which are regular, is independent of the temperature within the accuracy of our calculations. The values of D^2 at the highest temperatures should not be seriously taken into consideration, since at these temperatures the values of N_1 are very small, and the results of our calculation are unreliable. D^2 for the benzene-cyclohexane system is nearly constant, but there seems to be a definite trend with temperature. The trend is, however, in accord with the theory. The trend indicates that this system is also regular, but less so than the above systems. In the benzene-CS_2 system D^2 is not at all independent of the temperature, and even the trend is not as it should be if the system were regular.

It is also D^2 that expresses the deviation of the system from ideal behavior. From this consideration alone, regardless of the structure and of the chemical properties of the individual species, they will form a nearly ideal solution when their energies of vaporization per cc, or the energy densities, are nearly equal. This actually is the case is shown in Fig. 3 and in the accompanying Table. In these systems the energy density of toluene is nearest to that of benzene, followed by CCl_4 and CS_2, while that of cyclohexane differs most widely. Our solubility

D^2 and Deviations from Ideality. At −20°C.

Component	$(\Delta E/V)^{1/2}$*	D	D^2
Toluene	9.90	0.15	0.0225
CCl_4	9.25	0.50	0.2500
Benzene	9.75	0.00	0.0000
CS_2	10.61	0.86	0.7396
Cyclohexane	8.82	0.93	0.8469

* Calculated from vapor pressure measurements.

* No quantitative information can be gained but from the experimental data as to how much less is the constant of the attractive potential between two different molecules from the geometric mean of the constant of the individual molecules in the relation, $k_{12} \leqq (k_{11}k_{22})^{1/2}$. It is equal to the mean as a limit. In the liquid-liquid system[6], benzene-CCl_4 and cyclohexane-CCl_4, $k \cong (k_{11}k_{22})^{1/2}$, while in the benzene-cyclohexane it is appreciably smaller.

The effect of the neglect of the contribution to the field of a given molecule beyond the further side of the next molecule, and the effect of over-lapping and repulsive force[38] that the molecules exert on one another as they condense to from a close packed liquids are neither so readily calculable, actually.

38) J. F. Kincaid and H. Eyring, *J. Phys. Chem.*, **43**, 37 (1937).

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measurements show the deviations from an ideal solubility in the corresponding manner. The magnitude of the heats of mixing for the systems follows the same order, as has already been referred to in the preceding section.

The deviation from ideality and regularity is connected with randomness of the molecules. Some information on this point can be drawn from the benzene-toluene and benzene-cyclohexane systems. In the former the deviation from ideality and regularity is least, as can be seen from Fig. 3 and from the values of D^2 in Table I which are independent of the temperature, while in the latter system the deviation from ideality is largest, and while the system is regular, it is less so than the former, as indicated by the slight trend with temperature of D^2. Since the molecular structure of toluene is not so different from that of benzene, changing one benzene molecule with that of toluene would not cause much disturbance in the relative orientation and also in the intermolecular forces of the pair. This will not be so simple in the case of cyclohexane and benzene, because of a large difference in their structures. While in the benzene molecule the carbon atoms are all in the same plane, in the cyclohexane molecule they are not[39),40)], and the latter molecule forms a "chair." Scatchard, Wood, and Mochel have observed that benzene-cyclohexane systems show a positive excess entropy of mixing when a solution is formed and they have explained the fact by assuming that benzene molecules are less randomly oriented[41)] in the pure liquid than in the solution where structually different cyclohexane molecules prevent the preferred orientations of the benzene molecules.

From the study of the five systems here considered, it may be concluded that equation (1) is applicable to these systems with the exception of the benzene-chloroform system, and in the systems as benzene-CCl_4 and benzene-toluene, in which the assumptions involved in the derivation of equation (1) are fairly well satisfied, the agreement is nearly complete. In these two systems the actual solubilities of benzene can be approximated to better than 5% from the physical constants of the pure components alone.

It is our intention to investigate next the solubilities of solid cyclohexane in these solvents.

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39) a) Kohlrausch and Stockmair, *Z. physik. Chem.*, B 31, 382 (1936); b) V. Schomaker and D. P. Stevenson, *J. Chem. Phys.*, 8, 637 (1940).

40) A. Langseth and B. Bak, *J. Chem. Phys.*, 8, 403 (1940). They have found that according to their Raman studies, the structure of cyclohexane is also a plane. Their argument is disputed by Schomaker and Stevenson[39 b)].

41) E. Steuer and K. L. Wolf, *Z. physik. Chem.*, B 39, 101 (1938). They have defined so-called "Assoziationsgrad" and showed that benzene, cyclohexane, and hexane are somewhat "associated".

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Summary.

The solubilities of solid benzene, or the freezing point lowering, in carbon tetrachloride, carbon disulfide, chloroform, and toluene have been determined.

Deviations from ideality and regularity of these and of the benzene-cyclohexane system, and the applicability of the equation,

$$RT \ln N_2^l/N_2 = V_2 \mathcal{V}_1^2 D^2$$

to these systems have been tested.

It has been found that benzene-chloroform gives negative deviations, and benzene-carbon disulfide and benzene-cyclohexane systems deviate quite appreciably from an ideal solubility. Benzene-carbon tetrachloride and benzene-toluene systems are regular, and for these systems the actual solubility can be predicted better than 5 percent from the physical constants of the pure components alone.

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