

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A Calorimetric Test of the Solubility Equation for Regular Solutions<sup>1</sup>

BY ROBERT D. VOLD

This investigation is a part of the systematic study of the properties of tetrahalide solutions which has been under way in this Laboratory for several years.<sup>2</sup> Because of the symmetrical nature of the molecular fields of these molecules it was expected that deviations of their solutions from ideality would be more amenable to quantitative formulation than is the behavior of more complicated systems where association effects, hydrogen bond formation and specific chemical interaction enter to an amount incapable of precise evaluation. That tetrahalide solutions do obey relatively simple laws has been shown by solubility data.<sup>3</sup> The deviations of such simple solutions from ideal behavior have been discussed by Hildebrand<sup>4</sup> from a thermodynamic point of view.

More recently, Hildebrand and Wood<sup>5</sup> have derived a general solubility equation from a statistical treatment of intermolecular forces and consideration of the distribution function of the molecules. At the present time knowledge of intermolecular potentials and the distribution function is insufficient to permit direct application of this equation. In order to obtain an expression directly comparable with experimental data it was necessary to make several simplifying assumptions. These have been discussed critically by Hildebrand and Wood.<sup>5,6</sup> They show that

$$\bar{E}_2 - E_2^0 = \left( \frac{N_1 V_1}{N_1 V_1 + N_2 V_2} \right)^2 v_2 \left[ \left( \frac{E}{V_1} \right)^{1/2} - \left( \frac{E_2^0}{V_2} \right)^{1/2} \right]^2 \quad (1)$$

and similarly for the other component. Here  $\bar{E}_2$  is the partial molal energy of component 2 in the solution,  $E_1^0$  and  $E_2^0$  the energies of vaporization of the two pure liquids to an infinitely dilute vapor,  $N_1$  and  $N_2$  the mole fractions of components 1 and 2 and  $v_1$  and  $v_2$  the molal volumes of the pure liquids 1 and 2.

If the further assumption is made that the solu-

tion is regular<sup>4</sup> (one in which there is no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged), then

$$\bar{F}_2^r - \bar{F}_2^i = \bar{E}_2^r - \bar{E}_2^i \equiv \bar{E}_2^r - E_2^0$$

where  $\bar{F}_2^r$  is the partial molal free energy in the regular solution,  $\bar{F}_2^i$  the partial molal free energy in the perfect solution,  $\bar{E}_2^r$  the partial molal energy in the regular solution, and  $\bar{E}_2^i$ , which is equal to  $E_2^0$ , the molal energy of the pure liquid, which is here taken as the energy of vaporization. Combining this relation with equation (1) gives

$$\bar{F}_2^r - \bar{F}_2^i = RT \ln \frac{a_2}{N_2} = v_2 \left( \frac{N_1 V_1}{N_1 V_1 + N_2 V_2} \right)^2 \left[ \left( \frac{E_1^0}{V_1} \right)^{1/2} - \left( \frac{E_2^0}{V_2} \right)^{1/2} \right]^2 \quad (2)$$

where  $a$  and  $N$  are, respectively, the activity and mole fraction of the component in the solution. This equation can be tested by comparison with experimentally determined solubilities. Hildebrand<sup>6a</sup> has done this with rather gratifying results for a number of systems.

The present determination of heats of mixing was undertaken to test further the validity of equation (1), primarily as applied to fourth group tetrahalides. These substances are well suited for a test of the equation since they probably fulfil quite closely the assumptions made in its derivation. Furthermore, the heat of mixing is directly comparable with the energy difference predicted by the equation and does not involve the assumption of regular solutions made in previous tests.<sup>6a</sup> Failure of the equation can here be confidently ascribed to failure of one or more of the assumptions made in the derivation of the simplified form (1) from the perfectly general equation of Hildebrand and Wood.<sup>5</sup> Finally, comparison of these thermal data with free energy data for the same solutions<sup>6b</sup> permits some conclusion as to the degree to which these solutions actually satisfy the requirements of a regular solution.

## Experimental

**Description of Reagents.**—Silicon tetrachloride was purified by methods previously found satisfactory in this

(1) (a) Condensed from a thesis submitted by R. D. Vold in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of California, Berkeley, Calif. (b) Present address: Chemical Division, The Procter and Gamble Co., Ivorydale, Ohio.

(2) Hildebrand and Carter, *THIS JOURNAL*, **54**, 3592 (1932).

(3) Negishi, Donnally and Hildebrand, *ibid.*, **55**, 4793 (1933).

(4) Hildebrand, *ibid.*, **51**, 66 (1929).

(5) Hildebrand and Wood, *J. Chem. Phys.*, **1**, 817 (1933).

(6) (a) Hildebrand, *THIS JOURNAL*, **57**, 866 (1935); (b) Wood, *THIS JOURNAL*, **59**, 1510 (1937).

Laboratory.<sup>6b</sup> The purification consisted essentially of a double refluxing over mercury followed by fractional distillation in a closed system. The purified product was kept in sealed flasks until shortly before use. At that time it was transferred to glass-stoppered bottles and kept in a dry box.

Carbon tetrachloride was purified by the method of Bauer and Daniels<sup>7</sup> and freshly distilled off phosphorus pentoxide shortly before the mixing experiments.

Eastman Kodak best quality normal heptane was used without additional purification. That any impurity present in this sample did not affect the results seems likely since values of the specific heats determined with it in this research are in satisfactory agreement with literature values for the specific heat of pure heptane.

Baker and Adamson reagent quality stannic chloride, colorless and free from sediment, was used in heat capacity determinations without additional purification.

Eastman Kodak best quality thiophene-free benzene was used directly in most instances. Results with a specially pure dry sample prepared by W. D. Kumler of this Laboratory were the same as those with the untreated Eastman product.

**Apparatus.**<sup>8</sup>—A cross section diagram is given in Fig. 1 of the calorimeter finally devised after many unsuccessful attempts with other designs. A is a silvered Dewar flask of Pyrex glass, with a ground glass joint of 5-cm. diameter at its top. The over-all interior height is 25.5 cm. It was placed in a wooden box and firmly packed in place with excelsior.

B is a glass propeller of 3.1-cm. total diameter mounted on a glass rod of 0.5-cm. diameter. The propeller revolved about 7.5 cm. above the bottom of the Dewar.

C is a mica sheet 7 × 4 cm. which serves as a base for the heating coil and as a baffle plate to ensure good circulation of liquid in the calorimeter. Five feet of No. 30 Chromel

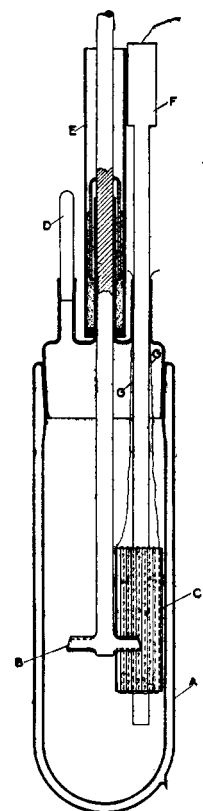


Fig. 1.—Cross section diagram of calorimeter.

A wire was mounted on it with Insa-lute.<sup>9</sup> The coil resistance was unchanged by a six-degree increase in temperature and was unaffected by dry silicon tetrachloride. The coil and mica plate were held in place by a small glass spacer fastened to the metal sheath of the resistance thermometer F with Insa-lute.

(7) Bauer and Daniels, *THIS JOURNAL*, **56**, 378 (1934).

(8) Full details of the construction of the calorimeter, calibration of the electrical instruments, corrections of the observed measurements and details of the method of operation are given in the dissertation of Robert D. Vold, "A Calorimetric Test of the Solubility Equation," on file in the University of California Library at Berkeley.

(9) A porcelain cement obtained from the Technical Products Co., Pittsburgh, Pa.

The leads, GG, to the heating coil were successively No. 26, No. 22 and No. 18 copper wire. They were inclosed in thin glass capillaries to prevent short circuits and were led out of the calorimeter through the entrance tube for the thermometer. There was no corrosion so long as the liquids in the calorimeter were kept dry.

F is a Leeds and Northrup calorimetric platinum resistance thermometer. Using it in conjunction with a sensitive galvanometer and wall scale, temperatures could be read directly to 0.0002°. The metal sheath of the thermometer was heavily gold-plated to prevent corrosion.

The top of the calorimeter was made from the male portion of a No. 50 ground glass joint. D is a No. 7 ground glass joint through which the calorimeter was filled. E is a mercury seal for the stirrer such that the vapors from inside come in contact only with glass and mercury. The thermometer was inserted in the calorimeter through a flattened glass tube and sealed in place with Insa-lute.

Due to density differences, satisfactory mixing was not obtained by breaking a glass bulb containing the second liquid inside the calorimeter. Therefore the liquids were mixed by pouring the second liquid into the calorimeter from another vessel. A silvered Dewar flask equipped with another calorimetric resistance thermometer was used for this purpose. A delivery tube, provided with a stopcock with a 6-mm. bore was led out through the bottom of the Dewar and offset and narrowed down to facilitate its insertion through the opening D in the calorimeter.

The ground glass joints were lubricated with a special grease developed by Meloche and Frederick.<sup>10</sup> Despite the possibility of dehydration, no appreciable reaction took place between the calorimetric liquids and the lubricant during the time of an experiment.

The calorimeter and auxiliary flask were located inside a large double-walled combination air thermostat and dry box. The metal walls were grounded, thus providing an equipotential shield. Manipulations inside the thermostat were made by means of a rubber glove fastened in the wall by a metal ring. A stream of dried nitrogen was passed through the thermostat to prevent entrance of moisture. Thermostat temperatures were determined by a mercury thermometer reading directly to tenths of a degree. Good equalization of temperature inside the thermostat was obtained by use of a small fan.

The calorimeter stirrer was driven by a 0.05 horse power motor operated at 277 r. p. m. Over a period of a few hours the speed was found to be constant.

The auxiliary flask was held by two rings in a double lazy tong joint fastened on the thermostat wall. By means of this device it could be pulled back and forth or up and down as necessary during insertion of its delivery tube into the calorimeter.

The heat supplied the calorimeter was calculated by the relation  $cal. = t \times e^2 / 4.1833 R$ , where  $t$  is the time in seconds,  $e$  the potential across the heating coil in international volts and  $R$  the coil resistance in international ohms.

The energy current for the heating coil was supplied by two six-volt storage batteries in series. During the heating the e. m. f. never changed more than 0.2%.

The potential across the heating coil was measured with a standard potentiometric set up, using a Leeds and Nor-

(10) Meloche and Frederick, *THIS JOURNAL*, **54**, 3264 (1932).

thrup type K potentiometer and a volt box. The resistance of the heating coil,  $33.21 \pm 0.02$  ohms, was measured with a Leeds and Northrup type S Test Set reading directly to 0.01 ohm. A correction of 0.1% was applied to the observed resistance to correct for lead resistance and loss of heat generated in the leads between the point of attachment of the potential leads and the calorimeter.

Time signals were obtained from a small electric clock which operated a buzzer every minute. Its reliability was checked by comparison with several stop watches. This comparison also showed that current through the heater coil could be started and stopped with an error of not more than 0.05 second.

The resistance of the calorimetric thermometers was determined with a Mueller Thermometer Bridge and a Leeds and Northrup galvanometer H S 2285b. The bridge was packed in a box of excelsior to minimize temperature fluctuations. The galvanometer was mounted on a Julius suspension to reduce vibrations. The sensitivity of 0.000031 ohm per scale division remained essentially constant but was redetermined before each experiment.

**Calibrations and Technique of Measurements.**—The Bureau of Standards calibration of the resistance thermometers was checked by determination of the ice-point, steam-point and transition temperature of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . Temperatures on the centigrade scale were obtained from the observed resistances by means of the conversion table of Callendar and Hoare.<sup>11</sup> It was determined experimentally that changes in depth of immersion of the resistance thermometers or in the temperature gradient along their sheaths did not cause abrupt changes in resistance. Solutions of the required concentrations were made by measuring the liquids out of calibrated volumetric flasks at thermostat temperature. Weights were obtained from the measured volumes by use of the "I. C. T." density equations.<sup>12</sup> These equations were also used to calculate the molal volumes of the pure liquids at 25°.

In specific heat determinations the heating current was passed through the coil two minutes in all cases and produced a temperature rise of 0.86 to 0.99° depending on the liquid. The same total volume of liquid, 330 cc., was used in all specific heat determinations and also as the final volume in all heat of mixing experiments. This volume minimized the vapor space and also was such that contact of the liquid with the top of the calorimeter was prevented.

The heat capacity of the empty calorimeter was obtained by calibration with benzene, using the "I. C. T." value,<sup>13</sup> 0.4104 cal./deg./gram at 25° for its specific heat. It was only 4 cal. per degree compared to heat effects of about 100 cal. in the actual experiments. The accuracy of the values obtained for heat capacities is consequently linearly dependent on the accuracy of the value adopted for the heat capacity of benzene, as well as on the accuracy with which the electrical energy required to produce a given temperature rise, and the temperature rise itself, are measured. The accuracy of the values obtained for the heats of mixing is, however, almost independent of the value of the heat capacity adopted for benzene, because the tempera-

ture change on forming the solution in the calorimeter is compared directly with the temperature change produced by passing a measured amount of electrical energy into the solution in the calorimeter. The heat capacity of the empty calorimeter enters into this calculation only in correcting for the initial temperature difference of the two liquids just before mixing.

In heat of mixing experiments time-temperature curves were determined before mixing for both the liquid in the calorimeter and that in the auxiliary flask, from which the initial temperatures of the two liquids just before mixing were calculated. In the average experiment the temperature difference between the liquids before mixing had to be known to 0.0005° to reduce error arising from temperature uncertainty to 0.1%. Ten to twenty seconds were required to pour one liquid into the other. During this operation care was taken to ensure that the second liquid fell directly into the calorimeter without running down the sides where it might have remained unmixed. No containers of silicon tetrachloride or stannic chloride were opened until the thermostat had been dried at least twelve hours with phosphorus pentoxide.

In most experiments a straight line relation between time and temperature was reached not later than four minutes after electrical heating or seven minutes after mixing two liquids. From these rates of temperature change, the temperatures before and after mixing were determined by analytic extrapolation to the mid-point of the reaction time according to a method in Ostwald-Luther.<sup>14a</sup> Although this procedure, in general, is not so accurate as extrapolation to the time at which 67% of the temperature change has occurred,<sup>14b</sup> it is simpler experimentally, and in the present work gave identical results within 0.2% with the more exact method.

Several factors which might affect the accuracy of the final results were investigated experimentally. A stirring speed of 277 r. p. m. proved to be sufficiently fast to provide thorough mixing and slow enough so that small variations did not affect the heat of stirring. Calculation on the basis of Raoult's law and the perfect gas laws showed any correction to the measured heat quantities for volatilization into the vapor space was negligible. Distillation of liquid onto the under side of the cover did not occur. The effect of cooling by evaporation or other thermal disturbances during the mixing process was investigated by running carbon tetrachloride from the auxiliary flask into carbon tetrachloride in the calorimeter and measuring the heat effect. Although there was no erratic temperature change there was a small systematic deviation linearly dependent on the temperature difference between the two samples. The directly measured heats of mixing were corrected for this effect. This correction never exceeded 5% of the total value.

The heat capacity of the empty calorimeter was 4.29 cal. per deg. Although it remained essentially constant, the value was redetermined at frequent intervals throughout the course of the experiments.

As a test of the reproducibility of the calorimetric results eight determinations were made of the specific heat of car-

(11) Callendar and Hoare, "Correction Tables for Use with Platinum Resistance Thermometers," Edward Arnold and Co., London, 1938.

(12) "International Critical Tables," Vol. III, 1928, pp. 23, 28, 29.

(13) *Ibid.*, Vol. V, 1929, p. 115.

(14) (a) Ostwald-Luther, "Physiko-chemische Messungen," Akademische Verlagsgesellschaft, Leipzig, 1931, p. 422; (b) Dickinson, *Bull. Natl. Bur. Standards*, 11, 230 (1914).

bon tetrachloride. The mean value at 25° was 0.2066 cal. per degree with an average deviation of  $\pm 0.00045$  cal. per degree.

**Experimental Results.**—The heat of mixing and specific heat determinations were not all made at exactly 25° but were always within a few degrees of this temperature. To facilitate comparison the directly measured quantities have all been recalculated to values for the systems at 25°.

In the case of specific heats this was done by obtaining values of  $dC_P/dT$  for the pure liquids from the literature and using the additive value for the solutions. Values of  $dC_P/dT$  for the range from 20 to 30° were calculated from a table of specific heats at various temperatures compiled by Richards and Wallace.<sup>15</sup>

In Table I are given values of the specific heat at 25° as determined in this work and by previous investigators. The agreement is quite satisfactory between the present direct calorimetric results and the indirect results of Richards and Wallace determined from the adiabatic temperature pressure coefficient.

TABLE I

COMPARATIVE VALUES OF SPECIFIC HEATS AT 25°

|                          | Benzene | Carbon tetrachloride | Toluene | Normal heptane |
|--------------------------|---------|----------------------|---------|----------------|
| V. <sup>a</sup>          | ....    | 0.2066               | 0.4059  | 0.5312         |
| R. & W. <sup>b</sup>     | 0.4133  | .2030                | .4055   | .5343          |
| W. & D. <sup>c</sup>     | .4096   | .1972                | .3942   | .5110          |
| "I. C. T." <sup>d</sup>  | .4104   | ....                 | .4027   | ....           |
| T. <sup>e</sup>          | .4141   | ....                 | .4185   | ....           |
| H., P. & D. <sup>f</sup> | .4127   | ....                 | ....    | ....           |
| M. & Mc. <sup>g</sup>    | ....    | .2018                | ....    | ....           |
| P., H. & T. <sup>h</sup> | ....    | ....                 | ....    | .5294          |

<sup>a</sup> Vold, this paper. <sup>b</sup> Richards and Wallace, ref. 15.

<sup>c</sup> Williams and Daniels, THIS JOURNAL, 46, 1569 (1924).

<sup>d</sup> "International Critical Tables." <sup>e</sup> Trehin, *Ann. phys.*, [9]

15, 246 (1921). <sup>f</sup> Huffman, Parks and Daniels, THIS JOURNAL,

52, 1547 (1930). <sup>g</sup> Mills and McRae, *J. Phys. Chem.*,

15, 54 (1911). <sup>h</sup> Parks, Huffman and Thomas, THIS

JOURNAL, 52, 1032 (1930).

Since  $\partial \Delta H / \partial T = \Delta C_P$  where  $\Delta H$  is the molal heat of mixing and  $\Delta C_P$  the difference between the molal heat capacities of the solutions and the pure liquids, it follows that over a small temperature range  $\Delta H_2 = \Delta H_1 + (C_{P_{sol.}} - \Sigma C_{P_{liq.}})(T_2 - T_1)$ . Here  $\Delta H_2$  is the heat of mixing at  $T_2$ ,  $\Delta H_1$  at  $T_1$ ,  $C_{P_{sol.}}$  the molal heat capacity of the solution and  $\Sigma C_{P_{liq.}}$  the sum of the products of the molal heat capacities of the pure liquids by their mole fraction in the solution. The experimental results presented in Table II were recalculated to 25° by this equation.

(15) Richards and Wallace, THIS JOURNAL, 54, 2705 (1932).

TABLE II

HEAT CAPACITIES AND HEATS OF FORMATION OF VARIOUS SOLUTIONS AT 25°

| Mole fraction $N_1$  | $C_P$ cal./deg./gram | $\Delta H$ cal./mole |                     |  |            |
|--|----------------------|----------------------|---------------------|--|------------|
|  |                      | Exptl.               | Calcd. from av. $D$ | Calcd. from $\Delta(\epsilon^0/v)^{1/2}$ | $D$ Exptl. |
| The System: $\text{SiCl}_4\text{-CCl}_4$ ( $N_1$ refers to $\text{SiCl}_4$ )                                 |                      |                      |                     |  |            |
| 0.0000   | 0.2066               | ...                  | ...                 | ...                                      | ....       |
| .1840  | .2052                | 19.1                 | 21.0                | 18.3                                     | 1.0690     |
| .2680  | ....                 | 24.9                 | 27.1                | 23.5                                     | 1.0743     |
| .5647  | .2023                | 32.3                 | 32.2                | 28.0                                     | 1.1219     |
| .5647  | .2011                | ...                  | ...                 | ...                                      | ....       |
| .6594  | .2010                | 32.2                 | 29.0                | 25.2                                     | 1.1825     |
| .8613  | .2004                | 15.8                 | 14.9                | 13.0                                     | 1.1532     |
| .8613  | .2009                | ...                  | ...                 | ...                                      | ....       |
| 1.0000   | .2008                | ...                  | ...                 | ...                                      | ....       |
| The System: $\text{C}_6\text{H}_6\text{-CCl}_4$ ( $N_1$ refers to $\text{C}_6\text{H}_6$ )                   |                      |                      |                     |  |            |
| 0.0000   | 0.2066               | ...                  | ...                 | ...                                      | ....       |
| .1408  | .2203                | 9.65                 | 9.85                | 4.01                                     | 0.9394     |
| .2102  | .2304                | 12.9                 | 13.6                | 5.54                                     | .9257      |
| .4135  | ....                 | 18.6                 | 20.2                | 8.22                                     | .9123      |
| .4135  | ....                 | 18.8                 | 20.2                | 8.22                                     | .9172      |
| .5207  | .2800                | 20.8                 | 21.0                | 8.54                                     | .9460      |
| .6261  | .3010                | 20.6                 | 19.8                | 8.08                                     | .9661      |
| .7141  | .3207                | 17.6                 | 17.4                | 7.10                                     | .9549      |
| .7141  | ....                 | 18.8                 | 17.4                | 7.10                                     | .9761      |
| .7141  | ....                 | 18.4                 | 17.4                | 7.10                                     | .9653      |
| .8160  | .3487                | 13.4                 | 12.9                | 5.26                                     | .9660      |
| 1.0000   | (.4104)              | ...                  | ...                 | ...                                      | ....       |
| The System: $\text{CCl}_4\text{-SnCl}_4$ ( $N_1$ refers to $\text{CCl}_4$ )                                  |                      |                      |                     |  |            |
| 0.0000   | 0.1451               | ...                  | ...                 | ...                                      | ....       |
| .4413  | .1621                | ...                  | ...                 | ...                                      | ....       |
| 1.0000   | .2066                | ...                  | ...                 | ...                                      | ....       |
| The System: $n\text{-C}_7\text{H}_{16}\text{-CCl}_4$ ( $N_1$ refers to $n\text{-C}_7\text{H}_{16}$ )         |                      |                      |                     |  |            |
| 0.0000   | 0.2066               | ...                  | ...                 | ...                                      | ....       |
| .2995  | .2738                | 63.8                 | ...                 | 35.3                                     | 1.5435     |
| .2995  | ....                 | 63.7                 | ...                 | ...                                      | ....       |
| 1.0000   | .5312                | ...                  | ...                 | ...                                      | ....       |
| The System: $n\text{-C}_7\text{H}_{16}\text{-C}_6\text{H}_6$ ( $N_1$ refers to $n\text{-C}_7\text{H}_{16}$ ) |                      |                      |                     |  |            |
| 0.0000   | (0.4104)             | ...                  | ...                 | ...                                      | ....       |
| .2824  | .4394                | 157.7                | ...                 | 77.6                                     | 2.4932     |
| .2823  | ....                 | 157.3                | ...                 | ...                                      | ....       |
| 1.0000   | .5312                | ...                  | ...                 | ...                                      | ....       |

The accuracy of the heat of mixing values is not nearly so great as that of the specific heats. Consideration of the results shown in Figs. 2 and 3 indicates that the probable uncertainty in the values is about  $\pm 0.5$  cal. Values toward the 50 mole % composition are in general somewhat more accurate than this while values toward the composition extremes, obtained by heat of dilution measurements, tend to show somewhat larger deviations. The absolute magnitude of the probable error does not change much from system to system.

Comparison with data in the literature is very

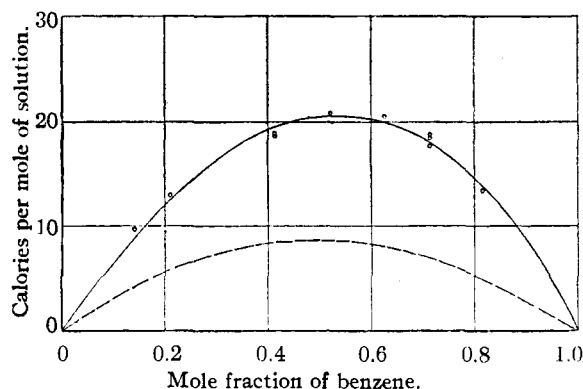


Fig. 2.—Heat of mixing of benzene and carbon tetrachloride: dotted line, theoretical values; circles, experimental points.

unsatisfactory in the case of heat of mixing. Madgin, Peel and Briscoe<sup>16</sup> determined the temperature changes on mixing equal volumes of many pairs of different liquids. Their experimental method was so inexact, however, that their results can be given only qualitative significance. Hirobe<sup>17</sup> and Baud<sup>18</sup> give values for the heat of mixing of benzene with carbon tetrachloride which are some 20% higher than the values found in the present work.

In order to obtain an independent check on the magnitude of the heat of mixing of carbon tetrachloride with benzene, the adiabatic volume change on mixing was determined roughly in a dilatometer similar to that used by Hildebrand and Carter.<sup>2</sup> A rough value of 20.8 cal. was calculated for the molal heat of mixing when the mole fraction of benzene is 0.44 from this coefficient, the specific heat of the solution, and the volume change on isothermal mixing. This compares with a value of 20.0 cal. from the present work and 25.6 cal. for Hirobe's data.

**Calculation of Energy of Vaporization.**—In order to calculate theoretical heats of mixing for comparison with experimental values the energy of vaporization must be known for the pure liquids. These values were calculated from vapor pressure data assuming that the vapors obey Berthelot's equation of state.  $\Delta H$ , the heat of vaporization, is given by

$$\Delta H = T(V_g - V_l) \frac{dP}{dT} \text{ where } V_g = \frac{RT}{P} \left[ 1 + \frac{9PT_0}{128P_0T} - \frac{54PT_0^3}{128P_0T^3} \right]$$

(16) (a) Madgin and Briscoe, *J. Soc. Chem. Ind.*, **46**, 107T (1927); (b) Madgin, Peel and Briscoe, *J. Chem. Soc.*, 2873 (1927); (c) Peel, Madgin and Briscoe, *J. Phys. Chem.*, **32**, 285 (1928).

(17) Hirobe, *J. Faculty Sci. Tokyo Imp. Univ.*, **1**, 155 (1926).

(18) Baud, *Bull. soc. chim.*, [4] **17**, 329 (1915).

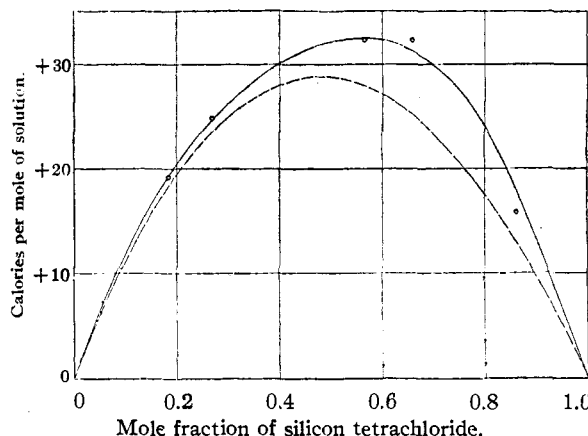


Fig. 3.—Heat of mixing of silicon tetrachloride and carbon tetrachloride: dotted line, theoretical values; circles, experimental points.

and  $dP/dT$  is obtained by differentiation of the vapor pressure equation. This value is then corrected to zero gas pressure by the relation

$$\Delta(\Delta H) = -\frac{RT_0}{128P_0} \left( 1 - \frac{18T_0^2}{T^2} \right) P$$

which is obtained by substituting Berthelot's equation of state in the thermodynamic equation

$$\left( \frac{\partial H}{\partial P} \right)_T = v - T \left( \frac{\partial v}{\partial T} \right)_P$$

$E^0$ , the molal energy of the liquid with respect to the infinitely dilute gas, is obtained from the ideal heat of vaporization by subtracting  $RT$ . Values determined as described above agreed within 300 cal. with other determinations of the heats of vaporization.

The vapor pressure equations used in the calculations were obtained by fitting the "I. C. T." data as closely as possible with empirical equations, using values around 25° for some of the points determining the curves. In these equations pressures are in mm. of mercury and temperatures in degrees absolute.

$$\text{Carbon tetrachloride } \log p = 6.84591 - \frac{1152.6}{T} - \frac{82463}{T^2}$$

$$\text{Silicon tetrachloride } \log p = -\frac{1740.55}{T} + 1.75 \log T - 0.0043857T + 5.19623$$

$$\text{Benzene } \log p = 5.61623 - \frac{388.20}{T} - \frac{207691}{T^2}$$

$$\text{Normal heptane } \log p = 4.46317 - \frac{796.86}{T} - \frac{166847}{T^2}$$

These equations represent the vapor pressure data within the experimental error of its determination for the following temperature ranges:  $\text{CCl}_4$ , 253–383°K.;  $\text{SiCl}_4$ , 252–330°K.;  $\text{C}_6\text{H}_6$ , 281–314°K.;  $n\text{-C}_7\text{H}_{16}$ , 293–313°K.

## Discussion

Since  $H = N_1\bar{H}_1 + N_2\bar{H}_2$ , the molal change in heat content on mixing two liquids to give a solution in which the mole fractions are  $N_1$  and  $N_2$ , respectively, can be written on the basis of equation (1) as

$$\Delta H = \frac{N_1V_1N_2V_2}{N_1V_1 + N_2V_2} \left[ \left( \frac{E_1^0}{V_1} \right)^{1/2} - \left( \frac{E_2^0}{V_2} \right)^{1/2} \right]^2 = \frac{N_1V_1N_2V_2}{N_1V_1 + N_2V_2} D_{12}^2 \quad (3)$$

The significant features of this equation are (1) the dependence of the heat of mixing on a quantity related to the volume of the solution, and (2) the form of the constant of proportionality,  $D_{12}^2$ , as the square of the difference between the square roots of the internal pressures of the two pure liquids.

The validity of the dependence of the heat of mixing on the concentration as expressed by equation (3) may be tested by examining the constancy of  $D$  calculated for each composition from the measured heat of mixing. The results of this calculation for the carbon tetrachloride-silicon tetrachloride and carbon tetrachloride-benzene systems appear in column 6, Table II.

Inasmuch as the probable error in the experimental values of  $\Delta H$  is about 3%, it appears that the equation fits the data rather well. Apparently the equation is adequate for the calculation of  $\Delta H$  as a function of concentration when one value is available from which to obtain an empirical  $D$ . As an example of the accuracy attainable by such a process, values of  $\Delta H$  for the carbon tetrachloride-silicon tetrachloride and carbon tetrachloride-benzene systems calculated from average empirical  $D$  values are given in Table II, column 4. Equation (2), which permits calculation of solubilities, is equally valid provided the solutions are regular.

If equation (3) holds for three binary systems involving the same three liquids, A, B and C, it can be shown that  $D_{AC} = D_{AB} + D_{BC}$ . The degree to which this relation holds, when experimental values of the heat of mixing are used to calculate  $D$  values, is a good criterion of the applicability of equation (3) to the systems. The results of a test of this relation appear in Table III. However fortuitous so precise an agreement is, in view of the variations in  $D$  with concentration, it speaks well for both the validity of equation (3) and the accuracy of the experimental results.

TABLE III

| TEST OF THE RELATION: $D_{AC} = D_{AB} + D_{BC}$ |   |   |   |
|--|---|---|---|
| $D_{AB}(\text{exptl.})$                          | $D_{BC}(\text{exptl.})$                         | $D_{AC}(\text{calcd.})$                                 | $D_{AC}(\text{exptl.})$                                 |
| $\text{CCl}_4\text{-C}_6\text{H}_6$              | $\text{CCl}_4\text{-}n\text{-C}_7\text{H}_{16}$ | $\text{C}_6\text{H}_6\text{-}n\text{-C}_7\text{H}_{16}$ | $\text{C}_6\text{H}_6\text{-}n\text{-C}_7\text{H}_{16}$ |
| 0.9492   | 1.5435  | 2.4927  | 2.4932  |

It remains to determine how well that property of the two pure liquids determining  $D$  is represented by the square root of the internal pressure. Since the difference between values of  $(E^0/V)^{1/2}$  for two liquids is small compared to the magnitude of the quantities themselves, direct comparison of  $D_{\text{exptl.}}$  and  $D_{\text{theoretical}}$  exaggerates the deviations to an unwarranted degree. A fairer test is to calculate  $E^0$  for one component from the heat of mixing and the  $E^0$  of the second component, and compare this quantity with the known value of  $E^0$  obtained from vapor pressure data. The results of this comparison are given in Table IV. The agreement between theoretical and experimental results, although not complete, is quite encouraging.

TABLE IV

CALCULATION OF  $E^0$  FOR ONE COMPONENT FROM HEAT OF MIXING

| System  | $E^0$ assumed correct for | $E^0$ for other comp. from exptl. $\Delta H$ , cal./mole | $E^0$ for other comp. from vap. data |
|---|---------------------------|--|--------------------------------------|
| $\text{CCl}_4\text{-C}_6\text{H}_6$                     | $\text{CCl}_4$            | 8115   | 7541                                 |
| $\text{CCl}_4\text{-SiCl}_4$                            | $\text{CCl}_4$            | 6419   | 6550                                 |
| $\text{CCl}_4\text{-}n\text{-C}_7\text{H}_{16}$         | $\text{CCl}_4$            | 7299   | 8144                                 |
| $\text{C}_6\text{H}_6\text{-}n\text{-C}_7\text{H}_{16}$ | $\text{C}_6\text{H}_6$    | 6593   | 8144                                 |

Two important simplifying assumptions made by Hildebrand and Wood<sup>5</sup> in the derivation of equation (1) from the completely general relation are: (1) that the different molecular species are randomly mixed in the solution; and (2) that the attraction constant for a pair of unlike molecules,  $a_{12}$ , is the geometric mean of the attraction constants for pairs of like molecules,  $(a_{11}a_{22})^{1/2}$ . It is significant that the agreement of equation (3) with experimental data is best for carbon tetrachloride-silicon tetrachloride solutions. These molecules are symmetrical and similarly shaped and hence their distribution in solution should be more nearly random than that of unlike molecules. Another reason for the good agreement in this case is found in Hildebrand and Carter's<sup>2</sup> experimental proof that for these solutions,  $a_{12} = (a_{11}a_{22})^{1/2}$ . Evidence on this point is lacking for the other systems studied.

As has been pointed out, the mathematical form of the equation involves the small difference be-

tween two fairly large quantities. Consequently, values of the heat of mixing calculated from constants of the pure liquids are not in very good agreement with the experimental values. The extent of the deviation is evident from Figs. 1 and 2 and from the values in col. 5 of Table II. However, in a free energy calculation (vapor pressure or solubility) the heat of mixing appears only as a correction term to a value calculated by Raoult's law. For this reason relatively rough values for the heat of mixing determined by equation (3) are sufficiently accurate to permit calculation, in conjunction with Raoult's law, of fairly accurate values for the free energy of regular solutions.

**Acknowledgment.**—The author wishes to express his gratitude to Professor Joel H. Hildebrand for suggesting this research and for his kind advice and help during the course of the work. He also wishes to thank Dr. M. J. Young and Mr. Melvin Arighi who assisted with some of the calculations and experimental measurements.

### Summary

A calorimeter has been devised which is suitable for the measurement of heat capacities and of heats of mixing of corrosive liquids which must be

kept in a closed system to avoid decomposition. The experimental data obtained include heat capacities and heats of formation of solutions of carbon tetrachloride and silicon tetrachloride, carbon tetrachloride and benzene, carbon tetrachloride and *n*-heptane, benzene and *n*-heptane, and heat capacities of solutions of stannic chloride and carbon tetrachloride and of all the pure liquids, all at 25°.

The heats of mixing have been used to test the validity of the equation:

$$\Delta H = \frac{N_1 V_1 N_2 V_2}{N_1 V_1 + N_2 V_2} \left[ \left( \frac{E_1^0}{V_1} \right)^{1/2} - \left( \frac{E_2^0}{V_2} \right)^{1/2} \right]^2 = \frac{N_1 V_1 N_2 V_2}{N_1 V_1 + N_2 V_2} D_{12}^2$$

It is concluded that (1) the equation can be used to calculate satisfactory values of the heat of mixing over the whole concentration range if one experimental value is available from which to determine the parameter  $D_{12}^2$  empirically, and (2) the equation gives encouraging results for the heat of formation of carbon tetrachloride-silicon tetrachloride solutions when the parameter  $D_{12}^2$  is determined from  $E^0/v$  values. These substances satisfy most closely the assumptions made in deriving the equation.

BERKELEY, CALIF.

RECEIVED MAY 24, 1937

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

## The Compressions of Solutions of Certain Salts in Water, Glycol and Methanol

BY R. E. GIBSON

During the last few years papers from this Laboratory have reported the results of measurements of the compressions up to 1000 bars of a number of aqueous solutions mostly of salts.<sup>1</sup> It was found that the volume changes of aqueous solutions may be well represented as functions of the pressure by equations of the type

$$-\Delta P v / x_1 + x_2 / x_1 \Delta P v_e = C \log \frac{B + P_e + P}{B + P_e}$$

and, as  $B$  and  $C$  are obtained from measurements on pure water ( $x_1 = 1$  and  $P_e = 0$ ), one compression measurement is sufficient to determine  $P_e$ , the effective pressure of the solution. Thus from measurements of compressions between 1 and 1000 bars it was possible to obtain close estimates

of the compressibilities of the solutions at any pressure.

In the course of these investigations several questions concerning the specific effects of different salts on the thermodynamic properties of water arose. A comparison of the effects of equivalent amounts of salts on the compressibility of water showed that in general a lyotropic series of anions and of cations was discernible, that is to say, the larger the ion or the smaller its charge the less was its effect in lowering the compressibility of water and consequently the less was the effective pressure of the solution. Ions with high values of the charge to radius ratio such as  $\text{Li}^+$ ,  $\text{Be}^{++}$  or  $\text{Mg}^{++}$ , however, lowered the compressibility of water much less than a simple picture of the forces between the ions and the

(1) (a) R. E. Gibson, *THIS JOURNAL*, **56**, 4 (1934); (b) *ibid.*, **56**, 865 (1934); (c) *ibid.*, **57**, 284 (1935); (d) *ibid.*, **57**, 1551 (1935).