solved in 100 cc. of glacial acetic acid and a large excess of bromine (5 cc.) was added at one time. The mixture was allowed to stand for three days and then poured into a liter of water. Sodium bisulfite was added to discharge the bromine color and after standing for several hours the product was collected on a filter. One and two-tenths grams of crude product was obtained. After two recrystallizations from a carbon tetrachloride–petroleum ether (low-boiling) mixture the material melted at 135–136°.

Anal. Calcd. for $C_{15}H_4O_2Cl_6Br_2$: C, 30.58; H, 0.685. Found: C, 30.84; H, 1.05. Mixed halogen, 0.1176 g. required 15.99 cc. of 0.1 N $AgNO_3$. Found: 16.11 cc.

The same material can be made by treating finely powdered di-(2,4,6-trichlorobenzoyl)-methane with 10% sodium hypobromite solution for a period of seven days.

Summary

2,4,6-Trichlorobenzoyl chloride reacts with methylmagnesium bromide to give di-(2,4,6-trichlorobenzoyl)-methane (III). When a large excess of the reagent is used 2,4,6-trichloroacetophenone (II) can be obtained. These compounds react with sodium hypohalites to give the expected halogenation products.

URBANA, ILLINOIS RECEIVED JUNE 3, 1937

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

Deviations of Carbon Tetrachloride and Silicon Tetrachloride Solutions from Raoult's Law[1]

BY SCOTT E. WOOD[2]

Hildebrand[3] has defined regular solutions as those solutions in which there is no change of entropy when a mole of solute is transferred from an ideal solution to a regular solution of the same concentration. Thus

$$\bar{S}^{r} - \bar{S}^{i} = 0 \qquad (1)$$

where $\bar{S}$ represents the partial molal entropy of a component and the superscripts represent regular and ideal solutions. This definition postulates that the distribution of the molecules in a regular solution would be random or the same as in an ideal solution. The study of the deviations of regular solutions from Raoult's law is thus greatly facilitated, since

$$\bar{F}^{r} - \bar{F}^{i} = \bar{H}^{r} - H^{0} = \Delta\bar{H} \qquad (2)$$

and, when the volumes of the components are additive

$$\bar{F}^{r} - \bar{F}^{i} = \bar{E}^{r} - E^{0} \qquad (3)$$

In these equations, $\bar{F}$, $\bar{H}$, and $\bar{E}$ designate the partial molal free energy, heat content, and energy, respectively, and E^0 the internal energy of one mole of the pure component.

Hildebrand and Wood[4] derived the equation

$$E = \frac{2\pi N^2}{V}\left[n_1^2 \int_{r_{11}}^{\infty} \phi_{11}(r)\ W_{11}(r)\ r^2\mathrm{d}r + n_2^2 \int_{r_{22}}^{\infty} \phi_{22}(r)\ W_{22}(r) r^2\ \mathrm{d}r + 2\ n_1n_2 \int_{r_{12}}^{\infty} \phi_{12}(r)\ W_{12}(r)\ r^2\mathrm{d}r\right] \qquad (4)$$

for the potential energy of $n_1 + n_2$ moles of solution, and also the equation

$$\bar{E}_1 - E_1^0 = 2\pi\ N^2 \left(\frac{n_2v_2}{n_1v_1 + n_2v_2}\right)^2 v_1 \left[\frac{2}{v_1v_2}\int_{r_{12}}^{\infty} \phi_{12}(r)\ W_{12}(r)\ r^2\mathrm{d}r - \frac{1}{v_1^2}\int_{r_{11}}^{\infty} \phi_{11}(r)\ W_{11}(r)\ r^2\mathrm{d}r - \frac{1}{v_2^2}\int_{r_{22}}^{\infty} \phi_{22}(r)\ W_{22}(r)\ r^2\mathrm{d}r\right] \qquad (5)$$

Here n represents the number of moles of a component; N, Avogadro's number; $\phi(r)$, the intermolecular energy between a pair of molecules; $W(r)$, the radial distribution of molecules about a central one; v, the molal volume of a component of the solution; V, the total volume of the solution; and r, the distance of closest approach of two molecules. The subscripts (11), (22), (12) indicate the type of molecular pairs. Equation (4) is perfectly general and is applicable to gases, liquids, and solids; however, equation (5) is valid only when the volumes of the components are additive. Letting $n_2v_2/(n_1v_1 + n_2v_2) = z_2$, equation (5) may be reduced to

$$\bar{E}_1 - E_1^0 = z_2^2\ v_1 \left[\left(\frac{E_1^0}{v_1}\right)^{1/2} - \left(\frac{E_2^0}{v_2}\right)^{1/2}\right]^2 \qquad (6)$$

with the aid of the following assumptions: (1) that k_{12}, the attractive force constant between un-

---

(1) Condensed from a thesis submitted by S. E. Wood in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of California.

(2) Present address, Massachusetts Institute of Technology, Cambridge, Mass.

(3) Hildebrand, THIS JOURNAL, **51**, 66 (1929).

(4) Hildebrand and Wood, *J. Chem. Phys.*, **1**, 817 (1933). *Cf.* Scatchard, *Chem. Rev.*, **8**, 321 (1931); van Laar, *Z. physik. Chem.*, **A137**, 421 (1928); and Heitler, *Ann. Physik*, **4**, 80, 630 (1928).

like molecules, is the geometric mean of the force constant between like molecules, (2) that $\phi(r)$ is dependent only on the relative coördinates of two molecules, and (3) that $W_{11}(r) = W_{22}(r) = W_{12}(r)$, when the variable is expressed in terms of diameters. London[5] has shown that for non-polar molecules the first assumption gives a maximum value of the interaction and that the second assumption is valid. Kirkwood[6] has shown that $W(r)$ is a function of the intermolecular force, the molecular density, and the temperature. Therefore the third assumption is not true unless these variables are the same for each component.

It is the object of this paper to study the validity of these equations by means of the deviations of solutions of carbon tetrachloride and silicon tetrachloride from Raoult's law determined from measurements of the partial pressures and fugacities of the components. These solutions should be nearly regular since the molecules are non-polar and spherically symmetrical.

Experimental Part

Purification of Materials.—Stock U. S. P. carbon tetrachloride was purified by the method of Bauer and Daniels.[7] It was refluxed over alkaline permanganate solution for six hours, and distilled twice from phosphorus pentoxide, collecting the fraction boiling between 76.58 and 76.60° (761 mm.). This material was then transferred to an evacuated flask to which four special glass seals were attached (Fig. 1B). These special seals are small capillary tubes sealed in T tubes in such a way that the capillaries may be broken at will by means of a magnetic hammer enclosed in glass. In this way it was possible to distil the liquid from the flask to the apparatus without admitting air. The carbon tetrachloride was frozen, the flask evacuated, and the material melted repeatedly until no gas bubbles were visible in the frozen material. Before using the liquid, approximately 50 cc. was pumped out to remove small traces of dissolved gas.

Silicon tetrachloride was purified by a method similar to Baxter's.[8] Five distillation flasks fitted with fractionating columns were sealed in series, each being separated by one of the special seals. The entire apparatus was evacuated and flamed out three times before distilling. The silicon tetrachloride was distilled over mercury in the first two flasks. Finally it was distilled into reservoir flasks as described for carbon tetrachloride, and also frozen, evacuated, and melted repeatedly.

Apparatus.—The apparatus consisted of two small bulbs joined at the bottom and further attached by small diameter tubing to a liter flask of known volume above (see Fig. 1A). Projecting from the liter bulb was a small tube into which the vapor could be frozen and then sealed off. The pressure was measured with a mercury manometer by means of a glass click gage, as described by Smith and Taylor[9] (see Fig. 1C). On the manometer side of the click gage a liter flask was installed in order to obtain a very slow rate of change of pressure. Due to the solvent power of both carbon tetrachloride and silicon tetrachloride and the ease of hydrolysis of silicon tetrachloride it was not possible to use any stopcock in the main part of the apparatus.

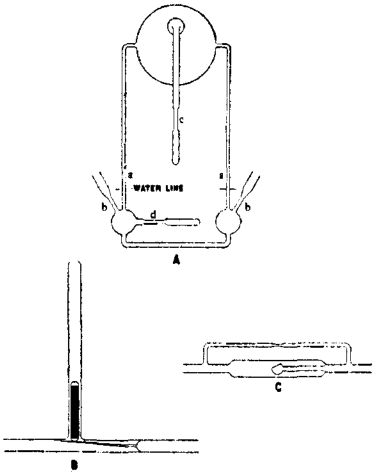

Fig. 1.

The glass apparatus was supported in an iron frame equipped with an eccentric in order to stir the liquid and also to produce surges in the vapor to speed up the attainment of equilibrium. The entire apparatus was placed in a water and air thermostat so that the small bulbs were entirely in the water and the liter bulb in the air. The water thermostat was regulated to 25.00 ± 0.01°. The air thermostat was kept at approximately 29° (varying slightly with room conditions) in order to prevent condensation of the vapor on the walls of the apparatus.

Procedure. **1. Calibration of Click Gage.**—The apparatus was evacuated, the by-pass around the click gage sealed, and the apparatus placed in the thermostat. Twelve to twenty-four hours were allowed to attain equilibrium. The click gage was then calibrated by admitting air to the manometer side until the glass diaphragm just clicked in. The click was sufficiently audible to be heard outside of the thermostat. The pressure was read on the manometer by means of a cathetometer reading to 0.1 mm. The pressure on the manometer side was then reduced until the gage clicked out. The procedure was repeated until a constant reading was obtained. It was found that the click-in gave readings accurate to 0.1 mm. but that the click-out was not sufficiently accurate.

2. Determination of the Vapor Pressure of the Pure Liquids and Solutions.—The reservoir flasks were sealed to either side of the small bulbs at b (Fig. 1A) and the apparatus was evacuated. It was then flamed three times under a vacuum to remove adsorbed air and water. After the by-pass around the click gage was sealed, the desired amount of each liquid was distilled into the apparatus, and the reservoir sealed off. A preliminary pressure read-

---

[5] London, *Z. Physik*, **11**, 222 (1930).

[6] Kirkwood, *J. Chem. Phys.*, **3**, 300 (1935).

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

[8] Baxter, Weatherill and Scripture, *Proc. Am. Acad. Soc.*, **58**, 245 (1923); Baxter and Fertig, THIS JOURNAL, **45**, 1228 (1923).

[9] Smith and Taylor, *ibid.*, **46**, 1393 (1924).

ing was obtained after twenty-four hours by the same method used to calibrate the gage, the final reading being taken after about forty-eight hours. The largest difference between these two readings was 0.2 mm., most of the readings checking within 0.1 mm. The final pressure was used in all cases. The vapor pressure was calculated by subtracting the calibration of the gage from the measured pressure after all readings were reduced to 0°. The liquid phase was then sealed from the vapor phase at a (Fig. 1A). In sealing off the tubes the temperature of the air thermostat rose 0.8° or less. Approximately one minute was used in the sealing-off process. The vapor was frozen out in tube c and then sealed off. The liquid was sampled in tube d.

3. **Analysis.**—Two methods of analysis were used. In the first method, the vapor sample was frozen with liquid air after its weight was determined. The tube was then broken and the sample placed in a small test-tube fitted with a glass ground joint. This was connected to a partially evacuated flask containing excess sodium hydroxide solution. The sample was slowly distilled into the sodium hydroxide and allowed to stand for several hours to insure complete hydrolysis. The carbon tetrachloride was then evaporated on a steam-bath. The solution was neutralized and finally the chloride ion was titrated with standardized silver nitrate solution, using chromate ion as an indicator. The glass tube was washed with hot dilute sodium hydroxide solution, dried and weighed. The liquid was analyzed similarly, hydrolyzing the entire liquid and taking aliquot parts instead of using a small sample of the liquid. Run 4 was analyzed by this method.

A more accurate method was used in the other runs, the liquid and vapor being treated exactly the same. The samples after weighing were frozen as before and placed in a large excess of carbon tetrachloride in a platinum dish. The carbon tetrachloride was cooled to within a few degrees of its freezing point. After the sample was melted, the glass tube was removed and washed with carbon tetrachloride. Cold water was floated over the carbon tetrachloride, the mixture being evaporated to dryness on a hot plate. The silica was ignited to constant weight. The glass tube was cleaned and weighed as before. A small error entered due to the loss of silicon tetrachloride during the melting. However, this method proved to be the best of several that were tried. On a series of three samples of pure silicon tetrachloride, the average error was 0.3% low, the maximum being 0.6%.

Results

1. **Pure Liquids.**—The pressures and fugacities at 25° of the pure liquids are given in Table I.

TABLE I

	p, mm.	f, mm.
CCl_4	114.9	114.5
$SiCl_4$	238.3	234.5

The volume of the vapor flask was determined to 1 cc.; the temperature of the air thermostat was determined at the time of sealing the connecting tubes to the liquids; and the total number of moles of vapor were determined from the weight of the vapor. The ideal pressure could then be calculated and the fugacities obtained by use of the approximate equation[10]

$$f/p = p/p^i \qquad (7)$$

Although the temperature of the air thermostat is approximately 29°, the calculated ideal pressure is that at 25° if the ideal gas laws are assumed. This is certainly a very close approximation since the molecules are non-polar and spherically symmetrical and further since the pressures are low.

The values given for carbon tetrachloride are averages of four determinations. The average deviation for both pressure and fugacity is 0.2% with a total variation of 0.6 mm. for the pressure and 0.7 mm. for the fugacity. Two comparative values of the vapor pressure of carbon tetrachloride may be obtained from the "International Critical Tables;"[11] these are 112.5 and 114.5 mm. The experimental values given for silicon tetrachloride are averages of twelve determinations of the pressure and eleven determinations of the fugacity. The average deviation of the pressure is 0.4% with a maximum variation of 3.4 mm. The average deviation of the fugacity is 0.56% with a maximum variation of 6.8 mm. Comparative values of the pressure are 238.5 mm.[12] and 238.2 mm.[13]

The question may well arise as to the reason for the rather large fluctuations, particularly with silicon tetrachloride. The variation of the pressure with the temperature is 5 mm./degree for carbon tetrachloride and 10 mm./degree for silicon tetrachloride. The click gage is accurate to 0.1 mm. The only uncontrolled factor that may cause the fluctuations is the surface condition of the glass apparatus. This may well account for these variations, especially in the case of silicon tetrachloride due to its great ease of hydrolysis. This would tend to give too high a value.

2. **Solutions.**—Table II gives the mole fraction N_2 of the liquid and the vapor; the total pressure p; the partial pressures p_1 and p_2; the sum of the fugacities of the components f; and the fugacities of the components themselves, f_1 and f_2. The subscripts 1 and 2 refer to carbon tetrachloride and silicon tetrachloride, respectively.

---

[10] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, Inc., New York, N. Y., 1923, p. 198.

[11] "International Critical Tables," McGraw-Hill Book Company, Inc., New York, N. Y., Vol. III, 1928, pp. 213, 215.

[12] Gmelin-Kraut, "Handbuch der anorganischen Chemie," Carl Winter's Universitätsbuchhandlung, Heidelberg, Vol. III, 1912, p. 194.

[13] Wintgen, *Ber.*, **52**, 724 (1919).

The total fugacity, or the sum of the fugacities of the components, was determined as for the pure liquids, the total number of moles occupying the vapor space being determined by analysis. It is necessary to assume Dalton's law in the vapor phase. This is justified, since the deviations are expected to be negligible due to the type of substances used.

TABLE II

Run	N_2, liq.	N_2, vap.	p, mm.	p_1, mm.	p_2, mm.	f, mm.	f_1 mm.	f_2, mm.
4	0.266	0.436	153.0	86.3	66.7	150.4	84.8	65.6
8	.287	.463	157.0	84.3	72.7	154.5	83.0	71.5
10	.472	.648	179.1	63.0	116.1	175.7	61.9	113.8
7	.502	.669	184.2	61.0	123.2	182.6	60.5	122.1
9	.632	.773	198.5	45.1	153.4	195.7	44.5	151.2

Figure 2 is a graph of the fugacity plotted against the mole fraction of silicon tetrachloride. The solid lines show the values calculated from equation (6) as will be discussed later. The dotted lines give the ideal values of the fugacities assuming Raoult's law, $f^i = f^0N$, where f^0 is the fugacity of the pure substance. It is seen that the deviations are small and positive, the actual fugacity at $N_2 = 0.5$ being about 6% larger than the ideal fugacity. It is further evident that the values of the fugacities are lower than those calculated from the equation. The errors in the experiment tend to give too high a result.

Discussion

From a thermodynamic standpoint, one measure of the deviations from Raoult's law is the ratio of the actual fugacity of a component to its ideal fugacity. The thermodynamic relations are

$$\overline{F} - \overline{F}^i = RT \ln f/f^i \qquad (8)$$

and

$$F - F^i = N_1(\overline{F}_1 - \overline{F}_1^i) + N_2(\overline{F}_2 - \overline{F}_2^i) \qquad (9)$$

where $\overline{F}$ and $\overline{F}^i$ are the partial molal free energies in the actual and ideal solutions, respectively, and F and F^i are the total free energies of the solutions. Equation (8) is identical for both components. The theoretical values may be calculated by means of equations (3) and (6). Then

$$RT \ln f_1/f_1^i = z_2^2 v_1 D^2 \qquad (10)$$

where

$$D = (E_1^0/v_1)^{1/2} - (E_2^0/v_2)^{1/2} \qquad (11)$$

The molal volumes at 25° for carbon tetrachloride and silicon tetrachloride are 97.09 and 115.36 cc., respectively, calculated from their densities as given in the "International Critical Tables"[11] (pp. 22, 128). The values of E_1^0 and E_2^0 may be obtained by subtracting RT (592.34 cal.) from the heats of vaporization of the liquids at 25°. I am indebted to Dr. R. D. Vold[14] and to Dr. M. J. Young of this Laboratory for calculating these values. They made use of vapor pressure data accounting for the volume of the liquid and reducing this value to zero pressure, making use of Berthelot's equation of state. Their values for E_1^0 and E_2^0 are 7148.3 and 6550.4 cal., respectively. D is then calculated to be 1.0451.

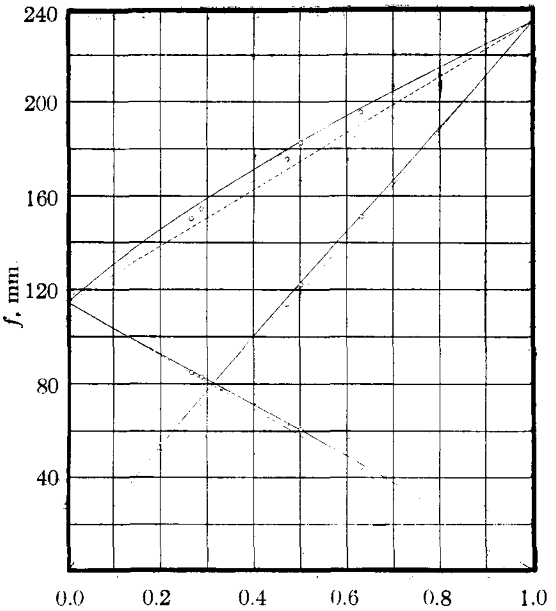

Fig. 2.

Table III gives the mole fraction of silicon tetrachloride N_2, its volume fraction z_2, the ratios f_1/f_1^i and f_2/f_2^i, and the excess partial molal free energy, $\overline{F} - \overline{F}^i$, of both components together with the corresponding values calculated by means of equation (10), assuming N_2 to be correct. It is

TABLE III

Run	N_2	z_2	f_1/f_1^i Obsd.	f_1/f_1^i Calcd.	f_2/f_2^i Obsd.	f_2/f_2^i Calcd.
4	0.266	0.301	1.01	1.02	1.05	1.11
8	.287	.324	1.02	1.02	1.06	1.10
10	.472	.515	1.02	1.05	1.03	1.05
7	.502	.545	1.06	1.05	1.04	1.04
9	.632	.671	1.05	1.08	1.02	1.02

Run	$\overline{F}_1 - \overline{F}_1^i$, cal. Obsd.	$\overline{F}_1 - \overline{F}_1^i$, cal. Calcd.	$\overline{F}_2 - \overline{F}_2^i$, cal. Obsd.	$\overline{F}_2 - \overline{F}_2^i$, cal. Calcd.
4	5.4	9.6	29.5	61.6
8	9.8	11.1	35.3	57.6
10	13.4	28.1	16.7	29.6
7	35.2	31.5	21.4	26.1
9	31.6	47.7	12.0	13.6

---

(14) Vold, THIS JOURNAL, **59**, 1515 (1937).

evident that there are somewhat large fluctuations in the experimental values. This is due in a large part to the rapid increase of percentage of error in taking the logarithms of the ratios of the fugacities, which are very close to unity. Equation (10) may also be used to calculate the values of D, the average of these values being 0.84 compared with the calculated value of 1.05. Further, the total free energy of mixing, and hence the fugacity, may be compared with the calculated quantity by means of the equation derived from equations (2), (8), and (9)

$$RT\,\Sigma_j N_j \ln f_j = \Delta H + RT\,\Sigma_j N_j \ln f_j^{i} \qquad (12)$$

where

$$\Delta H = \frac{N_1 v_1 N_2 v_2}{N_1 v_1 + N_2 v_2} D^2 \qquad (13)$$

Table IV gives N_2, $RT\ \Sigma_j N_j \ln f_j$, $RT\ \Sigma_j N_j \ln f_j^{i}$, ΔH, and the sum of the third and fourth columns. It will be noted in both Tables III and IV the experimental values are lower than the calculated values.

TABLE IV

Run	N_2	RT $\Sigma_j N_j \ln f_j$	RT $\Sigma_j N_j \ln f_j^{i}$	ΔH	Sum
4	0.266	2590	2578	23.4	2601
8	.287	2592	2575	24.5	2600
10	.472	2614	2599	28.8	2628
7	.502	2639	2611	28.8	2640
9	.632	2706	2687	26.2	2713

A rough determination of the excess entropy of mixing and test of equation (1) may be obtained by comparison of the total excess free energy of the solutions and the heats of mixing of these solutions as determined by Vold.[14] Table V gives N_2; the total excess free energy, $F - F^{i}$; the heats of mixing as interpolated from Vold's graph, ΔH; the excess entropy of mixing, S^{E}; and the ideal entropy of mixing, $S^{M} = -R(\Sigma_j N_j \ln N_j)$. While the results vary considerably, there appears to be an excess of the entropy above that of the ideal. Attention should be called to runs 7 and 10 where the difference in the values of $F - F^{i}$ varies by more than the indicated difference between $F - F^{i}$ and ΔH. Consequently no definite conclusions on this point can be drawn until more accurate data are available. The program of research, which was interrupted, calls for an extension of such measurements to other tetrahalides where the deviation from ideal behavior is expected to be great enough that experimental errors will be small in comparison.

TABLE V

Run	N_2	$F - F^{i}$	ΔH	S^{E}	S^{M}
4	0.266	11.8	24.6	0.04	1.15
8	.287	17.1	25.7	.03	1.19
10	.472	14.9	31.7	.06	1.37
7	.502	28.3	32.2	.01	1.37
9	.632	19.2	31.9	.04	1.30

The author wishes to express his sincere thanks to Professor Joel H. Hildebrand for his kind help and encouragement in this work. He also wishes to acknowledge the Shell Research Fellowship granted to him for the year 1934–1935, and to thank Mr. John Lyman for his help in part of this work.

Summary

The vapor pressures and fugacities at 25° of the system carbon tetrachloride and silicon tetrachloride have been measured and the deviations from Raoult's law have been calculated. It is found that the deviations are all positive but are smaller than those calculated from the equation derived by Hildebrand and Wood. The excess entropy of mixing has been calculated making use of heat of mixing data.

RECEIVED MAY 11, 1937