II. THE SPECIFIC HEAT OF CARBON TETRACHLORIDE AND OF ITS SATURATED VAPOR

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The Purity of the Carbon Tetrachloride Used

Some of Baker's "analyzed" C. P. carbon tetrachloride was fractionated over sodium through a Young's fractionating column and considerable trouble was experienced getting a perfectly constant boiling point. So additional commercial carbon tetrachloride was taken and purified as follows:¹ A small stick of potash was dissolved in its own weight of water and added to 200 cc of alcohol. 100 cc of this solution was added to 1000 cc of carbon tetrachloride, the mixture was heated to 50 or 60° C, and shaken for a half hour. The water was poured off and the shaking and heating repeated with 50 cc of alcoholic potash. This was repeated a third time. The carbon tetrachloride was then shaken up with 500 cc of water until the mixture rapidly cleared and separated. This was repeated. Water was removed by shaking first with potassium hydroxide and finally with metallic sodium. After standing over sodium for some days the carbon tetrachloride was fractionated until the following pure constant boiling fractions were obtained:

75.90°	under 743.7 mm pressure	=	76.69°	under 760 mm
75.70	under 739.2 mm pressure	=	76.68	under 760 mm
75.99	under 745.9 mm pressure	=	76.66	under 760 mm
75.99	under 746.3 mm pressure	=	76.64	under 760 mm

These fractions amounting in all to about 1000 cc were mixed and constituted the sample tested.

The Method Used

In a former paper² the method used was described, the determination of the calorimeter constant was given in detail,

¹ Sammlung chemischer und chemisch-technischer Vorträge, Vol. 10, 1906.

² Jour. Phys. Chem., 14, 797 (1910).

and the specific heat of benzol from its freezing point to 70°C was determined. We do not consider it necessary here to repeat any of the explanation there given. The details of the determination of the specific heat of carbon tetrachloride are given below in Table 1. If these details are not immediately understood reference to the former paper will doubtless make them sufficiently clear.

The Results Obtained

The series of experiments 1-5 inclusive, see Table 1, were made with two thermometers that were graduated only to tenths of a degree and were read to hundredths of a degree with a microscope. Experiments 5-9 were made with a Beckmann thermometer. In experiments 6 and 7 the Beckmann was set at 5.95° and no bath was used. In experiments 8 and 9 the Beckmann was set at 60.02° and the calorimeter was surrounded by a bath held at 59.5° . As related in the previous paper already cited all corrections necessary to reduce the thermometers to the correct hydrogen scale were known. The results are shown plotted in Diagram 1. From the results obtained it appears that the specific heat of carbon tetrachloride from $0-70^{\circ}\text{C}$ increases only very slightly with the temperature and can be represented by a straight line passing through the values 0.2010 at 0° and 0.2031 at 70°C . The actual values read from this line at intervals of 10° are given in Table 2. We believe that they are correct to one part in 200.

Comparison of the Results with those Obtained by Other Observers

The specific heat of carbon tetrachloride given by other observers¹ is shown in Diagram 1. Calculating the specific heat from the formulae given by Winkelmann for the total heat and the latent heat of vaporization we find the straight

¹ Sammlung chemischer und chemisch-technischer Vorträge, Vol. 10, 1906. Hirn: Ann. chim. phys., [4] 10, 63 and 91 (1867). Winkelmann: Ann. der Physik., 9, 208, 358 (1880). Sutherland: Phil. Mag., [5] 26, 298 (1888). Regnault: Mém. de l'Acad., 26, 761 (1862).

TABLE I
The specific heat of carbon tetrachloride

Number of experiment	1	2	3	4	5	6	7	8	9
Volts	3.8236	3.9371	4.0236	4.1328	4.2329	2.4887	2.4861	2.8265	2.8274
Amperes	2.9985	2.9985	2.9985	2.9984	2.9984	1.9952	1.9952	1.9946	1.9946
Time in minutes	10	10	10	10	10	10	10	12	13
Total calories added	1642.7	1691.5	1728.7	1775.5	1818.5	711.47	710.76	969.33	1050.44
Correction for vaporization	0.8	1.1	1.5	2.2	2.7	0.30	0.30	1.92	2.05
Temperature before	9.011	19.787	27.860	38.453	47.797	1.071	0.907	—0.105	—0.044
Temperature after	19.524	30.535	38.790	49.611	59.072	5.560	5.431	5.933	6.443
Δt	10.513	10.748	10.930	11.158	11.275	4.489	4.524	6.038	6.487
Average temperature	14.27	25.16	33.32	44.03	53.43	9.27	9.12	62.93	63.22
Calories added per degree	156.18	157.28	158.02	158.93	161.05	158.44	157.04	160.22	161.61
Calorimeter constant	12.95	13.78	14.40	15.20	16.03	14.65	14.65	17.25	17.25
Weight of CCl_4	711.12	711.12	711.12	711.12	711.12	714.11	712.75	712.24	714.35
Specific heat of CCl_4	0.2014	0.2018	0.2020	0.2021	0.2039	0.2014	0.1998	0.2007	0.2021

line shown in the diagram. Regnault determined the total heat of carbon tetrachloride to 160° , finding at 160° the value 71.00 calories, in good agreement with the value, 71.21 calories, obtained by Winkelmann. Using the value obtained by Regnault and the value of the heat of vaporization at this temperature, 37.95 calories,¹ we find that the average specific heat of carbon tetrachloride from 0 – 160° is 0.2066 calories.

Fig. 1

1. Hirn.
2. Winkelmann.
3. Sutherland.
4. From Regnault.
5. Mills and MacRae.

This average value is probably nearly correct though it is somewhat higher than the probable true value at 80° C. The values obtained by the authors for the specific heat of carbon tetrachloride are shown in the diagram and indicate that at low temperatures the specific heat of carbon tetrachloride does not increase so rapidly with the temperature as has been supposed.

The Specific Heat of the Saturated Vapor

If the heat of vaporization of the liquid at intervals of 10° and the specific heat of the liquid are known, the specific heat of the saturated vapor may be calculated. For the energy necessary to change the liquid at 0° into the saturated vapor at 10° is the same whatever may be the method pursued to effect the change. Letting the subscripts of L denote temperature, and letting σ_L denote the total heat added to the

¹ Sci. Proc. Roy. Dublin Soc., 12, 427 (1910).

liquid and σ_v that added to the vapor between the temperature limits given, we have,

$$1. \quad L_0 + \sigma_v = L_{10} + \sigma_L, \text{ or } \sigma_v = L_{10} + \sigma_L - L_0.$$

By this method we have calculated the values for the specific heat of the saturated vapor at intervals of 10° from $5-65^\circ$ from the data given in Table 2 and give the results in that table.

The heats of vaporization marked "Ther" were calculated by use of the thermodynamical equation,

$$2. \quad L = 0.043183 \frac{dP}{dT} T (V - v) \text{ calories,}$$

from the data¹ given in Table 2. In this equation L is the heat of vaporization, T is absolute temperature, P is pressure in millimeters of mercury, and v and V are the volumes of a gram of the liquid and of its saturated vapor.

The values of the heat of vaporization in the column marked "Mills" are obtained by using the equation,

$$3. \quad L = \mu'(\sqrt[3]{d} - \sqrt[3]{D}) + E_E.$$

Here μ' is a constant for any particular substance and for carbon tetrachloride has the value 44.01. E_E is the energy expended in overcoming the external pressure as the liquid expands to the volume of the saturated vapor and is given by the equation,

$$4. \quad E_E = 0.043183 P(V - v) \text{ calories.}$$

Equation 3 has been carefully and extensively studied² and seems to hold accurately for non-associated liquids at all temperatures.

¹ See Sci. Proc. Roy. Dublin Soc., 12, 427 (1910), except the density and volume of the saturated vapor from $0-60^\circ$ inclusive. At 0° the values are the theoretical values. At $10-60^\circ$ they are obtained by extrapolating an equation given by Young: Journal de Physique, Jan., 1909.

² See particularly Jour. Phys. Chem., 13, 512 (1909), and Jour. Am. Chem. Soc., 31, 1099 (1909), and references there given.

TABLE 2
The specific heat of the saturated vapor of carbon tetrachloride

Temperature t _s	Vapor pressure p	Density of liquid $\bar{d}$	Volume of liquid $\bar{v}$	Density of vapor $\bar{D}$	Volume of vapor $\bar{V}$	External energy R_E	$\bar{v}\bar{d}$	$\bar{v}\bar{D}$	$\bar{v}\bar{d} - \bar{v}\bar{D}$
0° C	33.08	1.6327	0.6125	0.032984	3351	3.52	1.1775	0.06683	1.1107
10	35.51	1.6132	0.6199	0.034879	2050	3.62	1.1728	0.07873	1.0941
20	89.61	1.5939	0.6274	0.037614	1313	3.74	1.1681	0.09132	1.0768
30	139.64	1.5748	0.6350	0.001150	869.6	3.86	1.1634	0.10476	1.0586
40	210.71	1.5557	0.6428	0.001686	593.3	3.98	1.1587	0.11901	1.0397
50	308.09	1.5361	0.6510	0.002399	416.7	4.08	1.1538	0.13389	1.0199
60	440.67	1.5165	0.6594	0.003347	298.8	4.18	1.1489	0.14958	0.9993
70	613.8	1.4963	0.6683	0.004570	218.8	4.26	1.1438	0.16595	0.9779

TABLE 2—(Continued)

Temperature t _s	Specific heat of liquid	Heat of vaporization		Specific heat smoothed		Specific heat unsmoothed		
		Ther.	Mills	Ther.	Mills	Temp.	Ther.	Mills
0° C	0.2010	51.83	52.40	0.170	0.140	5	0.1172	0.138
10	0.2013	50.99	51.77	0.160	0.138	15	0.1535	0.137
20	0.2016	50.51	51.13	0.150	0.135	25	0.1478	0.134
30	0.2019	49.97	50.45	0.140	0.132	35	0.1371	0.131
40	0.2022	49.32	49.74	0.130	0.128	45	0.1254	0.125
50	0.2025	48.55	48.97	0.120	0.124	55	0.1247	0.122
60	0.2028	47.77	48.16	0.110	0.119	65	0.1040	0.117
70	0.2031	46.78	47.30	0.100	0.115	—	—	—

While equation 2 is correct if the data is absolutely accurate we have shown in the paper cited that slight inaccuracies in the data are often greatly multiplied in their proportionate effect upon the values of the heat of vaporization. For this reason we consider the smoothed values of the specific heat of the saturated vapor as given under the heading "Mills" in Table 2 to be the most accurate.

Analysis of the Specific Heat of Benzol and of Carbon Tetrachloride

The object of this research was to throw light upon the nature and cause of the energy changes involved during the rise in temperature of a liquid. So far as the writers are aware the specific heat of any substance is supposed to be due to the following energy changes:

1. *The energy necessary to overcome the external pressure as the substance expands.*—This energy can be easily calculated if the external pressure and the volumes before (v) and after (v') expansion are known. If the pressure is given in millimeters of mercury and the volumes of a gram in cubic centimeters, the equation takes the form,

$$5. \quad E_{\text{External}} = E_E = 0.043183 P(v' - v) \text{ calories.}$$

2. *The energy necessary to overcome the molecular attraction as the substance expands.*—The investigation upon molecular attraction by one of the authors¹ has led to the belief that this amount of energy can be calculated from the equation,

$$6 \quad E_{\text{attraction}} = E_a = \mu' (\sqrt{d} - \sqrt{d'}),$$

where μ' is a constant characteristic of the substance, and d is the density of the substance before, and d' the density of the substance after, expansion. This equation is certainly applicable to the expansion of a liquid at constant temperature and under constant pressure from its volume as a liquid to its volume as a saturated vapor. That it is likewise ap-

¹ Jour. Phys. Chem., 6, 209 (1902); 8, 383 (1904); 8, 593 (1904); 9, 402 (1905); 10, 1 (1906); 11, 132 (1907); 11, 594 (1907); 13, 512 (1909); Jour. Am. Chem. Soc., 31, 1099 (1909).

plicable to the expansion of a substance when both temperature and pressure are variable has not been proved, but it seems to the authors likely to constitute at least one *term* of the energy necessary for such expansion. We expect the investigation when completed to throw light upon this point.

3. *The energy necessary to increase the translational motion of the molecules as the temperature of the substance is raised.*—If the substance is a perfect gas and the kinetic theory of gases is true, the total amount of this translational energy for 1 gram of substance is, at the absolute temperature T , simply $\frac{2.982 T}{m}$ calories. Therefore,

$$7. \quad E_{\text{kinetic}} = E_k = \frac{2.982}{m} \text{ calories,}$$

where m is the molecular weight of the substance. It is possible that equation 7 does not apply to substances whose molecules are under the action of attractive forces, more particularly solids and liquids. To obtain further evidence upon this point was one of the objects in view in the present investigation.

4. *An amount of energy which we propose to call "internal energy", the office of the energy being unknown.*—This energy is roughly proportional to the number of atoms within the molecule, being zero for a monatomic molecule, such as mercury or argon. If from the specific heat of the substance as a perfect gas at constant volume, the kinetic energy necessary to raise the temperature of the substance 1° (see 3 above) be subtracted, the remainder is the internal energy as we have defined it. This "internal energy" change is probably not a change of the chemical energy of the atoms within the molecule, but seems to be required for even the most stable polyatomic molecule. It may have to do with the rotation of the molecule as a whole. Numerous attempts, of which particularly the efforts of Boltzmann may be mentioned, to give a satisfactory explanation of this internal energy have failed. For a perfect gas, while the gas is chemically stable, the

internal energy appears to be proportional to the translational energy and may be obtained from the equation,

$$8. \quad E_{\text{Internal}} = E_{\text{I}} = \frac{5/3 - \gamma}{\gamma - 1} E_k,$$

where γ is the ratio of the specific heat of the gas at constant pressure to its specific heat at constant volume.

5. *The energy which binds the atoms together.*—This energy might be called chemical energy. We are inclined to believe that for a stable chemical compound, far removed from its point of decomposition, the chemical energy of the body is not affected by changes in temperature.¹

Hence except for a substance nearing the point of, or undergoing, decomposition, we think that,

$$9. \quad E_{\text{chemical}} = E_c = 0.$$

6. *Other possible energy changes.*—It is well to bear in mind that there may be other energy changes of which we know nothing. Thus the total heat added to a solid, probably monatomic, metal to raise its temperature from -273°C to its melting point and bring it into the liquid condition is about $9T/m$ calories. This amount of energy is far greater than has yet been accounted for. Therefore for the present we have called,

$$10. \quad E_{\text{unknown}} = E_u = \sigma - (E_e + E_a + E_k).$$

Whether E_u will prove identical with E_{I} is a very interesting point.

We have in the manner indicated analyzed the specific heat of benzol and of carbon tetrachloride and give the results in Tables 3 and 4. The data for benzol is given in the former paper already cited. The measurements have not yet been carried over a sufficient range of temperature, nor extended to enough substances, to enable conclusions to be drawn with certainty. We would, however, call attention to the following points:

¹ Trans. Am. Electrochem. Soc., 14, 35 (1908).

TABLE 3
Analysis of the specific heat of benzol

Tempera- ture	Specific heat of liquid					Specific heat of saturated vapor				
	σ_{liquid}	E_e	E_a	E_k	E_u	σ_{vapor}	E_e	E_a	E_k	E_u
0° C	0.3970	Not appreciable				0.284	0.025	0.0975	0.0382	0.318
10	0.4027					0.282	0.025	0.1040	0.0382	0.323
20	0.4084					0.279	0.024	0.1108	0.0382	0.328
30	0.4141					0.277	0.024	0.1174	0.0382	0.332
40	0.4198					0.275	0.023	0.1240	0.0382	0.338
50	0.4255					0.273	0.022	0.1308	0.0382	0.344
60	0.4312					0.270	0.020	0.1373	0.0382	0.349
70	0.4369					0.268	0.018	0.1438	0.0382	0.356

$m = 78.05$ $\mu' = 109.26$. The results under E_a and E_e were smoothed

TABLE 4
Analysis of the specific heat of carbon tetrachloride

Temperature	Specific heat of liquid					Specific heat of saturated vapor				
	σ liquid	E_e	E_a	E_k	E_u	σ vapor	E_e	E_a	E_k	E_u
0° C	0.2010	Not appreciable	0.0207	0.0194	0.1609	0.140	0.0115	—0.0506	0.0194	0.160
10	0.2013		0.0207	0.0194	0.1612	0.138	0.0115	—0.0538	0.0194	0.161
20	0.2016		0.0207	0.0194	0.1615	0.135	0.0115	—0.0573	0.0194	0.161
30	0.2019		0.0209	0.0194	0.1616	0.132	0.0115	—0.0607	0.0194	0.162
40	0.2022		0.0211	0.0194	0.1617	0.128	0.0110	—0.0641	0.0194	0.162
50	0.2025		0.0216	0.0194	0.1615	0.124	0.0100	—0.0674	0.0194	0.162
60	0.2028		0.0220	0.0194	0.1614	0.119	0.0090	—0.0706	0.0194	0.161
70	0.2031		0.0224	0.0194	0.1613	0.115	0.0080	—0.0735	0.0194	0.161

$m = 153.8 \mu' = 44.01$. The results under E_a and E_e were smoothed

(a) The energy changes in the saturated vapor due to the molecular attraction are far greater than has usually been supposed.

(b) The total energy change unaccounted for, which we have called the unknown energy, and designated E_u , is a constant for carbon tetrachloride to within the limit of error of the measurements. It is not a constant for benzol.

(c) If we compare the energy changes at 0°C of molecules of benzol and carbon tetrachloride we find them similar to a remarkable degree as shown below.

LIQUID.

	$\sigma \times m$	$E_k \times m$	$E_a \times m$	$E_u \times m$
Benzol	30.98	2.98	3.22	24.78
Carbon tetrachloride	30.91	2.98	3.18	24.74

SATURATED VAPOR.

	$\sigma \times m$	$E_k \times m$	$E_a \times m$	$E_u \times m$
Benzol	22.17	1.95	-7.61	24.84
Carbon tetrachloride	21.53	1.77	-7.78	24.55

(d) γ has been measured for benzol by Stevens¹ who obtained the value 1.105 at 99.7° , and by Wiedemann² who obtained the value 1.129. For carbon tetrachloride Capstick³ obtained the value 1.130. For benzol using the value of Stevens we obtain 0.2044 for E_i from equation 8. For carbon tetrachloride similarly we obtain 0.0800. When γ is nearly equal to one slight errors in the measurement of γ cause greatly increased errors in E_i and it is unfortunate that for this reason no very great reliance can be placed upon these values.

(e) The total heat necessary to raise 6.05 grams of hydrogen from -273° to 20°C is 6740 calories.⁴ The total heat

¹ Stevens: Ann. der Physik., [4] 7, 285 (1902).

² Wiedemann: Wied. Ann., 2, 195 (1877).

³ Capstick: Proc. Roy. Soc., 57, 322 (1895).

⁴ Trans. Am. Electrochem. Soc., 14, 35 (1908).

necessary to raise 72 grams of carbon as graphite from -273° to 20° is approximately 1480 calories, and similarly as diamond 800 calories.¹ Nordmeyer and Bernouilli² have determined the average specific heat of benzol from 20° to -185°C to be 0.176, allowing 30 calories for the heat of fusion. Estimating the average specific heat of benzol from -185° to -273° to be 0.08 we find that 5707 calories of energy would be required to raise the temperature of 78.05 grams of benzol from -273° to 20°C . If the carbon and hydrogen existed as elements the necessary energy for a similar rise in temperature would be 7540 calories if the carbon were in the form of diamond, and 8220 calories if the carbon were in the form of graphite. Since about 1745 calories of this energy is due to external work this amount might be subtracted, leaving 5795 and 6475 calories respectively. Nearly as much energy is therefore required to raise the temperature of the carbon and hydrogen from -273° to 20°C when they are combined to form benzol as when they exist separately.

Summary

1. The specific heat of liquid carbon tetrachloride is found to vary linearly with the temperature between 0° and 70°C . The line passes through the values 0.2010 at 0° and 0.2031 at 70°C .

2. The specific heat of the saturated vapor of carbon tetrachloride has been determined and the following values obtained, $0^{\circ} = 0.140$, $10^{\circ} = 0.138$, $20^{\circ} = 0.135$, $30^{\circ} = 0.132$, $40^{\circ} = 0.128$, $50^{\circ} = 0.124$, $60^{\circ} = 0.119$, $70^{\circ} = 0.115$.

3. The results obtained both for carbon tetrachloride and for benzol have been discussed and certain facts concerning the energy changes involved have been pointed out.

The above work was done in the chemical laboratory of the University of North Carolina.

*University of North Carolina,
August 11, 1910*

¹ Dewar: Proc. Roy. Soc., 76a, 325 (1905).

² Verh. der deutsch. Phys. Ges., 9, 175 (1907).