

of Boltzmann and Planck on a consideration of the arrangement of the elements or molecules of a system. Instead, however, of following the procedure of Boltzmann and Planck by somewhat arbitrarily defining entropy by the equation

$$S = k \log W$$

the attempt has been made in this article to discover a statistical mechanical quantity which has the same derivatives with respect to energy, volume and number of molecules as does the thermodynamic quantity entropy. In this way we have been led to an expression for entropy which differs from that of Planck by an additive term, and have shown that the addition of such a term is, as a matter of fact, necessary in order that the derivative of the entropy of the system with respect to number of molecules shall have its correct value.

2. In connection with the derivation, it has been shown that the quantity E occurring in the Maxwell-Boltzmann distribution law

$$dN = C e^{-\frac{E}{kT}} dq_1 \dots dp_n$$

must be taken, *not* as the energy of a molecule having coördinates and momenta falling in the region $dq_1 \dots dp_n$, but *rather* as the rate of increase in the total energy of the system per molecule added to the region $dq_1 \dots dp_n$, when the system is in its configuration of maximum probability. These two quantities are the same for dilute gases, but for concentrated systems may be quite different. Hence the new methods which are introduced may be of considerable importance in dealing with the properties of imperfect gases or rather concentrated systems.

3. It was pointed out that the equations obtained in this article connecting the statistical mechanical quantities occurring in the Maxwell-Boltzmann distribution law with thermodynamic quantities, do not agree with the equations of Marcelin and Adams.²

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]
THE DISTRIBUTION OF THERMAL ENERGY IN THE TETRACHLORIDES OF CARBON, SILICON, TITANIUM AND TIN.

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The determination of the specific heats and heats of fusion of several tetrachlorides of the fourth periodic group was undertaken in connection with the study of the effect of mass upon the distribution of thermal energy. When the conditions in a solid are such that the thermal energy is distributed according to the principle of the equipartition of energy, the specific heat per gram atom is independent of the mass; however, when the "equipartition conditions" are not fulfilled, whatever the exact nature of

the cause may be, the deviation of the specific heat from the value of $3R$ is larger the smaller the mass of the atoms and the greater the constraints or forces under which the atoms are vibrating.¹ In any one case, it has been impossible to state just how much the specific heat is affected by each of these two factors, especially since the actual forces between the atoms are not known quantitatively, but are estimated in terms of compressibility, atomic volume melting points, hardness, etc.

The tetrachlorides, however, seem to offer an unusual opportunity for studying the effect due to the mass, since there is considerable evidence that in these compounds the constraints are quite similar. In the first place, at room temperature they are similar non-polar liquids, and it seems quite likely that this non-polar nature is preserved in the solid state. Then if each positive atom is surrounded by 4 chlorine atoms, the solid would be held together by forces acting largely between the chlorine atoms of adjacent molecules, and the constraints in the solid would be not only small but practically the same for all these compounds. This type of solid in which the molecule preserves its identity is quite different from the polar solids such as the alkali halides. Here the molecule has lost its identity, that is, it is impossible to say that a given positive atom belongs to any one negative atom, and the solid is held together by forces which are larger the greater the difference in the positive and negative nature of the elements.

These conclusions, which might be drawn from the molecular structure, as to the similarity of the constraints in the tetrachlorides, are confirmed by consideration of the melting-point data, Table I.

TABLE I
MELTING-POINT DATA

	M. p. °C.		M. p. °C.		M. p. °C.
CCl ₄	-24	NaH	high, decomposes	CH ₄	-186
SiCl ₄	-70	NaF	980	CF ₄	- 80
TiCl ₄	-30	NaCl	804	CCl ₄	- 24
SnCl ₄	-33	NaBr	757	CBr ₄	92
PbCl ₄	-15	NaI	653	Cl ₄	decomposes

The agreement in the melting points of the tetrachlorides, which is quite close, is made more striking by comparison with the melting points of the sodium halides, which not only are much higher but vary in the order of the increasing polarity of the compounds. On the other hand, the melting points of the tetra-halogen carbon compounds vary in the same order as the melting points of the halogens themselves, again indicating that these solids are held together by forces acting between halogen atoms of adjacent molecules. Indeed many additional cases, such as the almost exact agree-

¹ Einstein, *Ann. Physik.* [4] 34, 170 (1911). Lewis and Adams, *Phys. Rev.* 4, 331 (1914).

ment of the melting points of methane and silicane, might be cited as indicating that in general the constraints in the non-polar tetra-compounds depend largely upon the nature of the four negative atoms, and are more or less independent of the positive atom.

Experimental.

The specific heats of carbon, silicon, titanium and tin tetrachlorides were measured from the temperature of liquid air to 298° K, and, in addition, the specific heat of carbon tetrachloride was measured at still lower temperatures in order to determine the whole specific heat curve for these compounds. The heats of fusion and, in the case of carbon tetrachloride, a heat of transition, were also determined, thus giving the total thermal content at 298° K.

Method.—The method and experimental procedure employed in the measurements of specific heat between the temperatures of liquid air and 25° C were essentially the same as described in a previous paper.² In the determination of the heats of fusion the heating coil of the calorimeter was modified by decreasing the resistance in order that the rate of input of energy might be greatly increased. These values are probably accurate to within 2%.

Liquid Hydrogen Cryostat.—In order to obtain temperatures below 80° K, a small liquid hydrogen cryostat has been constructed. The details of construction will be given in a later paper. Advantage was taken of the Joule-Thomson effect of hydrogen precooled with liquid air. The success of the cryostat resulted from the use of a very efficient heat interchanger of small flattened and twisted copper tubing designed by Mr. George F. Nelson, mechanician of this laboratory. The coils of the interchanger surrounded the calorimeter and were insulated from the calorimeter and from the surrounding bath of liquid air by enclosing the coils in a brass case in which a high vacuum was maintained. Since radiation is small at these temperatures the only source of heat leaks was through the single connecting tube through which passed the coil for the incoming high-pressure hydrogen and the outgoing cold expanded hydrogen. The hydrogen was supplied by a battery of five cylinders at an initial pressure of 140 atmospheres.

Measurement of Temperature.—Between 60° and 300°K the copper-constantan couple calibrated by Eastman and Rodebush³ was available. The values for the e. m. f. of this couple may probably be extrapolated to 40° K without making a large error. The temperature of the liquid hydrogen cryostat could not be accurately determined from the boiling point of hydrogen since the back pressure of the expanded hydrogen in the

² Gibson, Latimer and Parks, *THIS JOURNAL*, **42**, 1533 (1920).

³ Eastman and Rodebush. *THIS JOURNAL*, **40**, 489 (1918).

coils was not known. The construction of the cryostat is such that a hydrogen or helium thermometer could not be used. Specific heat measurements at the lower temperatures were made in terms of a constantan resistance thermometer. It is hoped that investigations now under way will soon establish an accurate low temperature scale for this laboratory.

Purification of Materials.—Imported tetrachlorides of carbon, silicon and tin were used. The titanium tetrachloride was prepared from rutile. Each tetrachloride was distilled at a low pressure into a specially constructed U-tube which was then sealed.

The liquid was purified, first, by cooling almost to the freezing point and filtering out

TABLE II
EXPERIMENTAL RESULTS

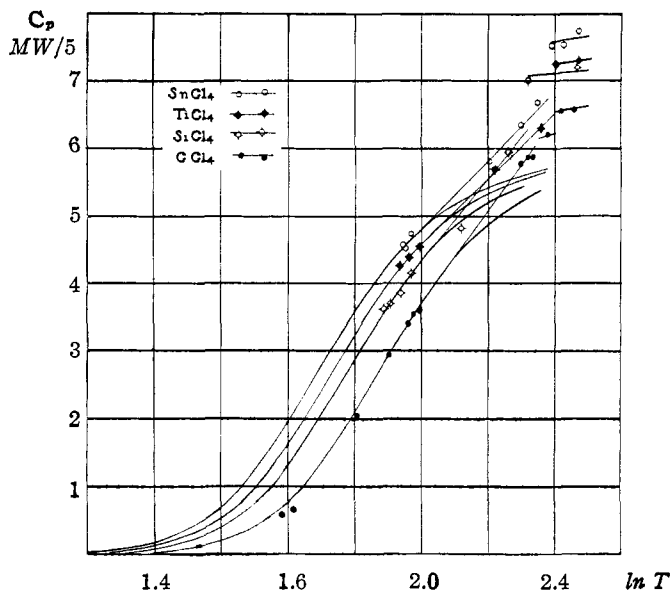
Carbon Tetrachloride			Silicon Tetrachloride			
	Temp. ° K	C_p per MW/5		Temp. ° K	C_p per MW/5	
Solid ₂	39.1	0.60	Solid.....	77.4	3.60	
	40.7	0.65		81.8	3.70	
	63.8	2.05		86.6	3.83	
	79.6	2.81		94.8	4.14	
	91.0	3.40		131.3	4.80	
	95.0	3.57		168.6	5.68	
	99.5	3.60		181.0	5.95	
	199.5	5.84		185.8	6.08	
	204.1	5.90		Liquid.....	208.8	6.74
	208.0	5.90			294.3	6.94
Solid ₁	229.4	6.20	Heat of fusion at 203.3° K, 10.85 cal. per gram.			
	232.5	6.29				
	235.6	6.22				
	238.0	6.77				
Liquid.....	253.8	6.40				
	265.1	6.30				
	290	6.34				
Heat of transition at 224.6° K, 7.10–7.19 cal. per gram.						
Heat of fusion at 249° K, 4.1–4.22 cal. per gram.						
Titanium Tetrachloride			Tin Tetrachloride			
	Temp. ° K	C_p per MW/5		Temp. ° K	C_p per MW/5	
Solid.....	86.7	4.26	Solid.....	89.0	4.59	
	92.8	4.40		89.5	4.53	
	99.3	4.54		95.0	4.73	
	194.6	6.19		95.9	4.71	
	231.8	6.31		161.2	5.89	
	247.7	6.21		200.5	6.32	
	251.6	7.26		200.7	6.33	
	294.3	7.32		205.0	6.26	
Liquid.....			227.3	6.62		
			Liquid.....	266.1	7.56	
Heat of fusion at 248.0° K, 11.77 cal. per gram.				294.0	7.86	
			Heat of fusion at 239.9° K, 8.38– 8.42 cal. per gram.			

any solid impurities which separated, and second, by repeated crystallization pouring off each time that portion of the liquid which remained after most of the sample had crystallized. Both of these operations could be carried out in the same sealed U-tube. The rise in the values of the specific heat just below the melting point was very marked when the unpurified compounds were used, but was decreased enormously by the purification carried out. The melting point of the purified silicon tetrachloride was approximately 20° higher than the value given in the literature.

The experimental results are summarized in Table II. Measurements on carbon tetrachloride at lower temperature have not been included because of the uncertainty in regard to the accuracy of the temperature scale.

Discussion of Results.

In Fig. 1 the so-called "Class I" or Debye⁴ curves have been drawn for C_p per average gram atom against T . These curves are all the same



function of T/θ , where θ is a constant which shifts their position along the $\log T$ axis. Although the specific heat of most metals follows this regular curve, the specific heats of compounds in general do not, and a great many explanations have been offered for the deviations.⁵ It seems to the writer that this curve probably represents the manner in which a single atom gains thermal energy, and only when all the atoms of a substance are of similar mass and held by similar constraints will the C_p curve for the substance be of the same form. Hence for a compound such as mercurous

⁴ Lewis and Gibson, *THIS JOURNAL*, 39, 2534 (1917).

⁵ Lewis, "A System of Physical Chemistry," Longmans, Green and Co., 1919, Vol. 3.

chloride, even though both the mercury and chlorine atoms gain thermal energy according to this typical curve, the C_p curve for the mercury will lie above that for the chlorine, and the C_p curve for the compound, which must be the average of the two, will deviate from this typical curve. On the other hand, the C_p curve for potassium chloride agrees very closely with the regular curve due to the close agreement of the masses of the potassium and chlorine atoms. Examples of the quantitative agreement of the average specific heat curves with the mean of two Class I curves could be given for many substances. In the case of the tetrachlorides the curves for silicon and titanium should follow the shape of the regular curve very closely. The greatest deviation is to be expected with tin tetrachloride, but since there are 4 chlorine atoms to 1 atom of tin, even in this case, the error introduced in assuming the regular curve for extrapolating over the low temperature should not be very great. The deviation of the C_p values at higher temperatures is due of course, to the increasing difference between C_p and C_p . From these curves the entropies of the 4 compounds have been calculated. These calculations are summarized in Table III.

TABLE III
ENTROPIES OF FOUR TETRACHLORIDES

	CCl ₄	SiCl ₄	TiCl ₄	SnCl ₄
S_{TP} Solid II.....	31.80			
ΔH of transition..1100				
T of transition. 224.6				
ΔS of transition.....	4.90			
S_{mp} Solid I.....	3.14	33.85	43.80	44.50
ΔH of fusion....644		18.45	22.33	21.88
T of fusion....249° K		203.3	248°	23.99
ΔS of fusion.....	2.59	9.08	9.01	9.11
S liquid.....	6.63	13.50	6.70	8.23
S_{298}	49.06	56.43	59.51	61.84
ΔS_{298} of formation....	-50.84	-48.27	-47.09	-49.66
ΔH_{298} of formation....	-75.700	-128.100		-128.010
ΔF_{298} of formation....	-60.550	-113.710		-113.210

The value S_{TP} , Solid II, for carbon tetrachloride, 31.80, is the entropy, $\int_T \frac{C_p dT}{T}$, of the crystalline form stable at low temperatures, at its transition point. Since C_p has been plotted against $\log T$, the entropy is given by the area under the curve. The increase of entropy by the transition $\Delta H/T$ is 4.90; the increase of entropy of Solid I from the transition point to the melting point, obtained again from the area under the curve, is 2.14; the entropy of fusion, 2.59; and the gain of entropy of the liquid from the melting point to 298° K, 6.63. The sum of these values gives S_{298} for

liquid carbon tetrachloride, 49.06. In the row designated as ΔS_{298} of formation, the figures given are the calculated values for the entropy of formation of the compounds from their elements. In calculating these values S_{298} of the elements chlorine, carbon, silicon, titanium and tin were taken as 25, 1.3, 2.7, 6.6, and 11.5, respectively. The heats of formation⁶ of these compounds are also given in the table. Although these values are probably not of great accuracy, they have been used in calculating the free energy of formation of the compounds from their elements by the relation $\Delta F = \Delta H - T \Delta S$.

It will be observed that the entropies of the compounds increase, as is to be expected, in the order of increasing molecular weight. The most striking fact, however, is the close agreement of the entropies of formation; for although the entropies of the compounds differ by more than 13 entropy units, the entropies of formation differ by less than 4 units. In other words, the entropy of the compound is the sum of the entropies of the elements minus a constant. This indicates that the difference in the entropies of the tetrachlorides is due entirely to the difference in the mass of the positive atoms. Quantitatively this difference is approximately

$$3/2 R \ln \frac{\text{at. wt.}_1}{\text{at. wt.}_2}$$

This relation accounts very closely for the difference in entropy of all the solid compounds whose elements have a value for their Kopp's-law constant of approximately $-3R$. Since the constraints in these compounds obviously vary within rather wide limits, it would seem the conclusion must be drawn that there is a limiting value for the constraints below which the effect upon the entropy is negligible. The data for a large number of compounds, including the tetrachlorides, have been discussed in a previous paper.⁷

Although a survey of the data on the entropy of fusion of a large number of substances shows certain marked relationships, it is impossible to make any generalization such as Trouton's rule for the entropy of vaporization. However, the agreement of the entropies of fusion of silicon, titanium and tin tetrachlorides indicates that such a relationship, although masked by other factors in many cases, does exist. The entropy of a substance is a measure of the complexity of thermal motion. Now while the complexity of thermal motion in many liquids is doubtless much the same, the complexity of motion of the atoms in a solid with low constraints must be quite different from that in a solid with high constraints. Hence, it is not surprising that the entropy of fusion varies far more than the entropy of vaporization, and yet is constant for many classes of solids. The

⁶ Landolt-Börnstein, "Tabellen."

⁷ Latimer, *THIS JOURNAL*, **43**, 818 (1921).

entropy of fusion of chlorine, 9.5 entropy units, agrees well with the value found for the three tetrachlorides.

Summary.

The specific heats of carbon, silicon, titanium and tin tetrachlorides have been measured from the temperature of liquid air to 298° K and, in addition, the specific heat of carbon tetrachloride was measured at still lower temperatures in order to determine the whole specific-heat curve for these compounds. The heats of fusion and, in the case of carbon tetrachloride, a heat of transition, were also determined, thus giving the total thermal content at 298° K.

The entropy of each of the compounds at 290° K and the entropy change in the formation of the compound from its elements have been calculated, and the results considered in reference to the mass of the atoms involved.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

INDUCTION PERIODS IN REACTIONS BETWEEN THIOSULFATE AND ARSENITE OR ARSENATE:¹ A USEFUL CLOCK REACTION.

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Vortmann² in 1889 obtained arsenious sulfide from arsenite or arsenate and thiosulfate in acid solution. Neither he nor any later worker in this field³ mentions the reaction's sharp and highly reproducible induction period, though von Szilágyi says that the compound $K_3As(S_2O_3)_3$ which he obtained from arsenious chloride, potassium chloride and sodium thiosulfate "decomposes in water solution, in a shorter or longer time, according to concentration and temperature, and deposits As_2S_3 ."

Molal arsenite solution was prepared from sodium hydroxide and purest commercial arsenious oxide. Each portion used was converted to arsenious acid by the calculated volume of standard hydrochloric acid. Molal thiosulfate solution was standardized against iodine, purified, re-sublimed and dried. Standard solutions of hydrochloric and acetic acids were referred ultimately to properly dehydrated sodium carbonate.

Into one beaker we discharged from burets arsenite, water, neutralizing acid, and acetic or hydrochloric acid in excess; into a larger beaker,

¹ The work on arsenates was performed mainly by O. J. Walker.

² Vortmann, *Ber.*, **22**, 2308 (1889).

³ Weinland and Gutmann, *Z. anorg. Chem.*, **17**, 409 (1898).

Mackenzie and Marshall, *J. Chem. Soc.*, **93**, 1726 (1908).

Gutmann, *Ber.*, **38**, 1728, 3277 (1905); J. von Szilágyi, *Z. anorg. allgem. Chem.*, **40**, 2818 (1907); **41**, 1650 (1908). **113**, 75 (1920).