DETERMINATION OF THE HEATS OF PHASE TRANSITION OF ELEMENTS AND COMPOUNDS AT A PRESSURE OF 760 MM Hg. I.

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Theoretically derived expressions relating the temperature and heat of phase transition in elements and compounds are presented. The principles of their behavior and relationship to other properties are discussed.

The absolute temperature of a system is one of the fundamental qualities used in physics. It is a measure of fundamental system properties and characterizes the state of a body independent of its mass and chemical composition. For this reason it is termed a parameter of state, and methods and means for its measurement have been developed in great detail.

Many physical properties — the volume of a body, transition from one aggregate state to another, electrical resistivity, thermal radiation spectrum, physical constants (speed of sound, specific heat, etc.) depend on temperature. Establishment of correlations between temperature and properties, as well as the physical mechanisms responsible therefore for a wide (perhaps larger) class of materials and properties is desirable from both a practical and theoretical viewpoint.

Of special theoretical interest as well as usefulness (considering the difficulty, expense, and insufficiently developed nature of techniques for their measurement) are such quantities as heats of fusion and vaporization, which characterize changes that occur at constant temperature.

Many approximate expressions of various complexities relating the heats of fusion and evaporation to the temperatures of such transitions are known [1, 2]. A relationship widely used in physics and chemistry which gives moderately satisfactory results can be formulated as follows: the entropy of liquid evaporation at the liquid's normal boiling point (the Truton constant) comprises about 20-22 cal/mole·deg (83,736 J/mole·deg), or mathematically

$$L_{ev}/T_{ev} \cong 21. \tag{1}$$

Materials which are intensely dimerized in the liquid state have an unusually high value for the Truton constant; for example, for nitrogen oxide the value is 27.1 cal/mole·deg. It was indicated in [4] that the most useful generalization from these data is that the Truton constant increases with increase in the complexity of the intermolecular forces. However, the relationship between the intermolecular forces which determine the physical properties and microscopic characteristics has not been studied sufficiently. For this reason establishment of a correlation between the Truton constant and other properties of the elements is of practical and theoretical interest.

We have performed calculations with the most general assumptions possible and obtained expressions relating the heat of phase transition to the temperature of the transition under normal conditions in the following form:

$$L_f = \frac{a}{n} T_f, \tag{2}$$

$$L_{ev} = 2aT_{ev}. \tag{3}$$

In essence Eq. (3) represents the known Truton law, and commencing from the calculation method used it requires introduction of a correction, which at present we lack necessary information to calculate, so that we must leave the expression in its present approximate form. Tables 1 and 2 present values of heats of fusion and evaporation calculated with Eqs. (2), (3) and experimental values taken from [1]. From top to bottom, each cell of the tables con-

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TABLE 1. Heats of Fusion

Period	Group																
	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	0
1	H_2 0,117 0,095 6																H_2	He
2	Li 3,01 3,11 6	Be 12,5 12,8 5											B 22,2 23,7 4	C	N_2 0,85 0,72 3	O_2 0,44 0,44 5	F	Ne 0,335 0,332 3
3	Na 2,6 2,6 6	Mg 8,95 9,52 4											Al 10,7 9,7 4	Si 4,65 35,5 2	P	S 1,7 2,0	Cl 64 71 1	Ar 1,176 1,153 3
4	K 2,33 2,31 6	Ca 8,66 9,27 5	Sc 16,01 17,26 4	Ti 15,5 16,2 5	V 17 5 16,5 5	Cr 14,6 14,9 5	Mn 14,6 15,6 4	Fe 15,5 14,9 4	Co 15,3 18,6 4	Ni 17,8 17,8 4	Cu 13,01 13,99 4	Zn 7,28 7,14 4	Ga 5,58 6,25 2	Ge 29,8 25,0 2	As	Se 5,4 5,0 4	Br 10,9 10,5 1	Kr 1,636 1,595 3
5	Rb 2,20 2,16 6	Sr 9,2 8,6 5	V 17,2 18,2 4	Zr 20,0 21,6 4	Nb 26,8 28,4 4	Mo 27,6 29,9 4	Tc 24,9 4	Ru 28,6 4	Rh 28 62 4	Pd 17,2 17,8 4	Aq 11,27 12,73 4	Cd 6,40 6,13 4	In 3,27 3,54 5	Sn 7 0 6,9 3	Sb 20,4 18,6 4	Te	J 15,7 15,1 1	Ve 3,295 2,218 3
6	Cs 2,18 2,08 6	Ba 7,66 8,13 5	La 11,3 12,3 4	Hf 21.8 20,52 5	Ta 31,4 33,7 4	W 35,2 37,7 4	Re 38,0 35,6	Os 36,8 4	Ir 27,92 4	Pt 21,7 21,1 4	Au 12,77 13,78 4	Hq 2,3 2,4 4	Te 4,2 4,7 5	Pb 4,7 4,1 5	Bi 10,9 11,2 2	Po 12,69 4	At 23,8 23,6 1	Rn 2,67 2,78
7	Fr 6	Ra 5	Ac 14,2 4	Ku														
Lanthanides					Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinides					Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md		Lr

TABLE 2. Heats of Evaporation

Period	Group Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII	Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	0
1	H_2														H_2	He
2	Li 148 131	Be 294 227									B 540 345	C	N_2 5,5 6,3	O_2 6,8 7,4	F 6,7 7,4	Ne 1,76 2,23
3	Na 89 96	Mq 131 115									Al 293 223	Si 394 217	P 12,4 45	S 90 54	Cl 20,4 19,7	Ar 6,52 7,21
4	K 78 84	Ca 151 145	Sc 305 344	Ti 430 293	V 458 301	Cr 349 240	Mn 224 195	Fe Co Ni 383 380 209 254	Cu 304 237	Zn 114 97	Ga 254 206	Ge 334 256	As 73	Se 768	Br 30 27	Kr 9,02 9,82
5	Rb 70 80	Sr 139 136	V 393 286	Zr 582 384	Nb 696 427	Ma 594 419	Tc 386	Ru Rh Pd 361 350 317	Aq 254 205	Cd 100 88	In 226 194	Sn 290 244	Sb 128 157	Te 114 104	J 41,7 37,6	Xe 12,64 13,62
6	Cs 66 79	Ba 151 158	La 400 301	Hf 661 451	Ta 753 469	W 779 480	Re 707 485	Cs Ir Pt 382 447 379	Au 324 245	Hq 59 52	Te 162 143	Pb 179 167	Bi 151 151	Po 103 102	At 90,4 53,6	Rn 16,4 17,4
7	Fr	Ra 150	Ac 397 297	Ku												
Lanthanides					Ce 314 262	Pr	Nd	Pm Sm Eu 248 146	Gd	Tb 253	Dy 237	Ho 277	Er 262	Tm	Yb	Lu
Actinides					Th	Pa 272	U 412 345	Np Pu 290	Am	Cm	Bk	Cf	Es	Fm	Md	Lr

TABLE 3. Elements Arranged by Groups

Period	Group																	
	VIII	VIII	VIII	VIIIa	VIa	Va	IVa	IIIa	IIa	Ia	0	VIb	VIb	Vb	IVb	IIIb	IIb	Ib
1										H_2 6	He 3	H 1						
2									Be 5	Li 6	Ne 3	F 1	O	N	C	B 4		
3									Mg 4	Na 6	Ar 3	Cl 1	S	P	Si	Al		
4	Ni 4	Co 4	Fe 5	Mn 4	Cr 5	Y 5	Ti 5	Sc 4	Ca 5	K 6	Kr 3	Br 1	Se	As	Ge	Ga 1	Zn 4	Cu 4
5	Pd 4	Rh 4	Ru 4	Tc 4	Mo 4	Nb 4	Zr 4	Y 4	Sr 5	Rb 6	Xe 3	T 1	Te	Sb	Sh	Tn 5	Cd 4	Aq 4
6	Pt 4	Jr 4	Os 4	Re 4	W 4	Ta 4	Hf 5	La 4	Ba 5	Cs 6	Rn 3	At 1	Po 4	Bi 2	Pb 5	Tl 5	Hq 4	Au 4
7							Ku 4	Ac 4	Ra 5	Fr 6								

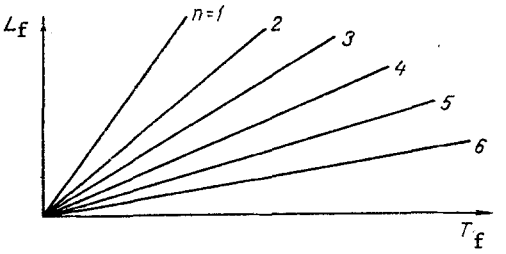

Fig. 1. Distribution of elements over groups

tains the name of the element, the experimental value, the calculated value, and the corresponding value of n. Since for hydrogen, fluorine, nitrogen, and chlorine information on the phase transition temperature [1] was available only for a molecular composition, the calculation was performed for such a composition.

Comparison of calculated and experimental values of the heat of fusion (Table 1) shows that the values are described satisfactorily by Eq. (2) with the number n correlating to the element's group number in the periodic table. The greatest uniqueness is shown by elements forming a square in the periodic table with corners at Ba, Bi, Br, and N. Careful study of the relationships among these elements and their nature permits a clearer description of the nature of the relationships involving the other elements.

If we depict the equation for heat of fusion, Eq. (2), in graphical form in the coordinates fusion temperature—heat of fusion, then as a function of n we obtain a family of curves which pass through the origin. For the elements of the periodic table we have a family of six curves (Fig. 1).

All the elements of the periodic table can be divided into six groups (Fig. 1), although quite nonuniformly (as regards the number of elements per group). In the group corresponding to n=1 we have only halogens; in the group n=2 are Bi, Ga, Ge, Si; group n=3 consists of the inert gases, as well as N_2; group n=6 has the alkali elements and H_2; groups n=4, 5 contain all remaining elements of the periodic table, these being the largest in number of elements.

In the presence of experimental values of temperature and heat of fusion, Eq. (2) may be used to determine the value of n, i.e., to determine the group into which the compound falls:

$$n = \frac{aT_f}{L_{ev}} . \qquad (4)$$

All inorganic and organic compounds on which information is provided in [1] are, according to Eq. (4), distributed over the same six groups, but with somewhat greater scattering than the elements of the periodic table. The majority of organic compounds from [2] fall into the group n=1, although there is a small number of compounds falling into the remaining groups.

In view of the structural peculiarities of the elements of the first short period of the periodic table their chemistry must be considered individually, and as is indicated in [3], they may not be regarded as analogs of the other elements of the group.

It follows from this that the features of an element responsible for its chemistry do not play a significant role in formation of its solid state structure, and Eq. (2) can be used for preliminary estimation of the properties and structure of compounds by using the properties of the periodic table elements as a test.

As follows from Eq. (4) and Fig. 1, the values of the ratio $\alpha T_f/L_f$ for the elements are limited (located in the region of the values for the alkali elements and the halogens), i.e., to the values of the elements with electron shells differing least from inert gas shells (inert gas electron shell+one electron and inert gas electron shell—electron (hole)). If we arrange the elements of the periodic table according to Eq. (4) with consideration of our remarks on the electron shell, then the table of elements takes on a quite interesting form with the appearance of a symmetry relative to the inert gas column (Table 3, elements C, P, O, H-Ku, La, Ra, ...).

NOTATION

L_f, L_{ev}, heats of fusion and evaporation, kJ/K·mole; T_f, T_{ev}, fusion and evaporation temperatures, K; α, constant, 41.28 J/K·mole; n, integers in range 1-6.

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