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

THE MASS EFFECT IN THE ENTROPY OF SUBSTANCES

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The entropies of perfect monatomic gases at any standard temperature and pressure are given accurately by equations of the form[1]

$$S = 3/2\ R\ ln\ A + S_0, \qquad (1)$$

where S represents the molal entropy of the gas, A its atomic weight, and S_0 is a general constant. Similar equations are known to hold, approximately at least, for many solids.[2] To propose and test the hypothesis that the mass effect is the same in *all* substances is the object of the following notes.

The hypothesis will be restricted to substances in which equipartition of energy obtains and, to avoid complications from the effects of other factors contributing to entropy, it will be applied only to groups of substances in which the atomic arrangement is similar, and atomic amplitudes approximately equal or calculable. Its test then will consist in the comparison of experimentally determined entropies with those calculated from equations of the type

$$S = 3/2\ R\ ln\ A_1 A_2 A_3 \ldots A_n + k, \qquad (2)$$

n being the number of atoms per molecule and k a constant, empirically determinable and characteristic of each group of substances.

In the case of diatomic gases Equation 2 becomes

$$S = 3/2\ R\ ln\ A_1 A_2 + k_3, \qquad (3)$$

which fits the existing experimental data quite closely without any term involving amplitude of atomic vibration within the molecule. There appears, however, to be a small trend in k_3 with increasing molecular weight, which is perhaps traceable to this factor. A partial correction of this variation is obtained by the introduction of an arbitrary term involving the molecular weight M, and an empirical constant a, giving

$$S = 3/2\ R\ ln\ A_1 A_2 + a\ ln\ M + k_4. \qquad (4)$$

Table I has been constructed for the comparison of these equations and that proposed by Latimer[2] for diatomic gases, namely,

$$S = 3/2\ R\ ln\ M + {}^1/_2 R\ ln\ A_1 A_2 + k_5. \qquad (5)$$

Under S_3, S_4 and S_5 of the table are given the entropies calculated by Equations 3, 4 and 5, respectively. The constants used in these calculations are $k_3 = 31.4$, $a = 0.7$, $k_4 = 29.0$ and $k_5 = 31.1$. They are in each case averages determined from all of the data (graphically in the case of a and k_4). The average deviation of the calculated results from the ex-

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[1] Lewis, Gibson and Latimer [THIS JOURNAL, **44,** 1008 (1922)] outline the previous development and calculate the constant of this equation.

[2] Latimer, THIS JOURNAL, **43,** 818 (1921).

perimental is given in the last row of the table. Equation 4 is seen to be in particularly good agreement with experiment.

Table I

Molal Entropies of Diatomic Gases

Cal./deg. at 25° and one atmosphere

Gas	S	S_3	S_4	S_5
H_2	29.2	31.5	29.6	33.2
N_2	45.6	47.2	47.1	46.3
O_2	48.0	47.9	47.9	46.9
Cl_2	52.6	52.7	53.3	50.9
Br_2	(55.4)	57.5	58.7	54.9
I_2	61.8	60.3	61.8	57.2
HCl	43.3	41.1	42.2	45.4
HBr	(47.0)	44.5	45.2	48.6
HI	47.5	45.9	46.9	50.4
CO	45.6	47.1	47.0	46.3
NO	49.3	47.5	47.5	46.6
Av. Dev.	....	1.2	0.9	2.3

The experimental values, S, for the elements in Table I are taken from the paper of Lewis, Gibson and Latimer.[1] The value of these authors for hydrogen, 29.4, has been slightly modified, as a repetition of their calculation gives a value 0.2 unit lower. With the exception of the constant used for Equation 1, this repetition checks the result of Tolman.[3] The entropies of hydrogen chloride, hydrogen iodide and nitric oxide (NO) have been calculated from their heat contents and free energies, given by Lewis and Randall,[4] combined with the data for the elements. The figure for carbon monoxide is that of Lewis and Gibson.[5] The value of Lewis, Gibson and Latimer given in the table for bromine is not an experimental one. It is thought that the figure calculated by Equation 4 is more reliable. Using the latter value, the "experimental" entropy of hydrogen bromide may be obtained from Lewis and Randall's data. This, with bromine, is given in parentheses in the table and not used in determining the constants.

For polyatomic gases the data are few and inaccurate. Heat contents and free energies of substances obtained from Lewis and Randall, together with some third law calculations (combined with entropies of vaporization) give approximate figures for 9 triatomic, 4 tetraatomic, and 6 pentaatomic gases. The detailed results of these calculations will not be given. It will only be said that for each of these groups an equation of the type of Equation 2 fits the experimental data with an average deviation of about 3.5 units. This is not much greater than the uncertainty in the

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[3] Tolman, This Journal, **42,** 1185 (1920).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company (in press).

[5] Lewis and Gibson, This Journal, **39,** 2554 (1917).

experimental figures, though the differences among the various gases appear to be traceable in some instances to relative amplitudes of vibration (looseness of constraints) of the atoms in the molecules. It may be noted also that if any effect due to differences in arrangement of atoms in the molecules is present, it is less in these cases than the other causes of differences.

As applied to solids, Equation 2 has previously been obtained and tested by Latimer.[2] He found that it holds closely for some 18 salts,—evidence that these substances are similar from an atomic-kinetic standpoint. Latimer also points out that the simple equation fails in the case of the metals. He has recently found, however, that a corrective term involving coefficients of expansion, atomic volumes and specific heats eliminates large discrepancies. This alone is probably enough to bring the metals into the groups whose entropies are affected in similar ways by the atomic masses. The following considerations substantiate this view and are of some interest in themselves.

Lindemann[6] and Einstein[7] have suggested approximate equations connecting the frequency of atomic vibration with other properties of metals. Assuming equipartition, and that the oscillations are harmonic in character, it is possible to use these equations to determine amplitudes and hence the volume, v, through which oscillation occurs. Assuming that the entropy term involving this volume takes the form $R \ln v$, modifications of Equation 2 are obtained. Lindemann assumes that at the melting point, T_m, v is proportional to the atomic volume V, and the resulting entropy equation is

$$S = 3/2\, R \ln A + R \ln V T_m^{-3/2} + k_6. \tag{6}$$

Einstein introduces certain plausible assumptions connecting atomic volume and compressibility, β, with frequency (or amplitude). The equation which is finally obtained for entropy is

$$S = 3/2\, R \ln A + R \ln V^{-1} \beta^{3/2} + k_7. \tag{7}$$

Using atomic volumes (at ordinary temperatures) in cubic centimeters, and taking Richards'[8] values and units for compressibility, k_6 and k_7 are found to be about 13.0 and 42.1, respectively. The values S_6 and S_7 calculated from the corresponding equations are compared with the experimental ones, S, given by Lewis, Gibson and Latimer[1] in Table II.

The corrections due to the new terms in Equations 6 and 7 vary in each case over a range of about 11 units. The fidelity with which the experimental values are reproduced is about the same for each equation and is on the average within experimental error. What choice there is between the two seems to lie with Equation 6, for some of the larger

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[6] Lindemann, *Physik. Z.*, **11**, 609 (1910).

[7] Einstein, *Ann. Physik*, [4] **34**, 170 (1911).

[8] Richards, THIS JOURNAL, **37**, 1646 (1915).

deviations from it as, for example, in the case of the alkali metals, are explainable on other grounds.

TABLE II

ATOMIC ENTROPIES OF METALS

Cal./deg. at 25°

Metal	S	S_6	S_7	Metal	S	S_6	S_7
Li..........	7.6	5.6	8.1	Rh.........	7.6	8.0	..
Na..........	12.2	10.9	12.1	Pd.........	8.9	9.1	8.5
Mg..........	8.3	7.2	8.4	Ag.........	10.25	10.3	10.2
Al..........	6.82	6.9	7.3	Cd.........	11.80	13.0	12.0
Si..........	4.7	5.7	2.6	Sn.........	11.17	14.1	11.5
K..........	16.6	14.1	14.5	La.........	13.7	13.0	..
Ca..........	10.6	9.6	10.7	Ce.........	13.8	13.3	..
Ti..........	6.6	6.3	..	W.........	8.4	8.6	8.1
Cr..........	5.8	6.3	8.3	Os.........	7.8	9.0	..
Mn..........	7.3	6.9	8.2	Ir.........	8.7	9.3	..
Fe..........	6.71	6.5	7.0	Pt.........	10.0	10.2	9.3
Co..........	7.2	6.5	..	Au.........	11.0	11.8	10.6
Ni..........	7.2	6.5	6.7	Tl.........	14.6	15.6	13.6
Cu..........	8.18	7.7	8.5	Pb.........	15.53	15.5	13.6
Zn..........	9.83	10.3	10.5	Th.........	13.6	12.4	..
Mo..........	7.5	7.5	7.4	U.........	11.1	10.5	..
Ru..........	6.9	7.9	..	Av. Dev.	...	0.8	0.7

The entropy of liquids may be approached either through the entropy of condensation of their vapors, or of fusion of the solids. That substances which obey the above law of the mass effect as gases or solids, also do as liquids, follows if the entropy change in the transition is constant for the different classes. Trouton's rule may be cited for the gas-liquid change. A similar rule holds for the entropy of fusion of substances which are analogous in structure both in the solid and liquid state.[9] In illustration, a review of the data concerning this quantity for the metals, bringing in recent results, shows that 19 metals, including very diverse types, average 2.15 ± 0.36 cal./deg. per gram atom at their melting points.

Summary

The hypothesis that the expression for the mass effect in the entropy of all substances in which equipartition holds takes the same form as for monatomic gases is tested for all cases for which data are available. Much evidence is found supporting the hypothesis, and none definitely contradicting it. Several approximate equations are given for the calculation of the entropy of diatomic gases and of metals.

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[9] Harkins, *Proc. Nat. Acad. Sci.*, **5**, 539 (1919), summarizes the earlier literature on entropy of fusion.