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The Free Energies and Vapor Pressures of the Alkali Metals

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The free energies of the diatomic alkali vapors K_2, Na_2 and Li_2 are calculated from spectroscopic data, and the equilibrium constants for the dissociation into the monatomic form are computed. With the aid of these constants, equations are deduced from the observed vapor pressures obtained by various investigators, which give the partial pressures of atoms and molecules in the saturated vapors for temperatures up to the normal boiling point. In the case of sodium and potassium, the entropy of the solid metal is computed from the vapor pressure equation, and is compared with that predicted by the third law of thermodynamics.

I N spite of the numerous investigations that have been carried out to determine the vapor pressures of the alkalis, there has still been some difficulty in reconciling the results that have been obtained by various methods, and a corresponding uncertainty as to the correct form of the vapor pressure equation. One reason for this is that molecule formation may be appreciable in the vapor phase, and although attempts have been made both experimentally and by means of the Gibson-Heitler equation to determine the degree of such association, there has still been a chance of appreciable error in allowing for this effect. Thanks primarily to the work of Loomis and his associates,[1] however, there are available data sufficient to permit a precise calculation of the equilibrium between atoms and molecules in the vapors, and the results of such calculations, together with their application to the vapor pressure data are recorded briefly here.

The spectroscopic constants used in the calculation of $(F^0 - E_0^0)/T$ for K_2, Na_2 and Li_2 are listed in cm^{-1} in Table I; they are weighted averages computed for a nonisotopic gas from the table of Loomis[1] and the isotope abundance ratios of Brewer and Kueck,[2] by means of the familiar relations connecting the reduced mass of

a molecule with the spectroscopic constants.[3] Even for the highest temperatures considered here, only the normal $^1\Sigma$ state of the molecule need be taken into account, since the excited $^1\Sigma$ and $^1\Pi$ states make only negligible contributions to the state sum. The table also gives the values[1,4] of ΔE_0^0 in calories per mole for the reaction $M_2 = 2M$.

The resulting $(F^0 - E_0^0)/T$ are listed in Table II,[5] and were computed by methods already described;[6] because of the small values of the fundamental frequencies such calculations would be exceedingly laborious if integral approxima-

TABLE I.

	K_2	Na_2	Li_2
ω_e	92.49	159.2	352.0
$\omega_e x_e$	0.352	0.73	2.5
B_0	0.05593	0.1543	0.6776
$-D_0 \times 10^6$	0.0827	0.586	10.22
	0.000218	0.00082	0.00728
ΔE_0^0	11800	17515	26275

TABLE II.

$T^\circ K$	$-(F^0-E_0^0)/T$			$\log K = \log (P_M)^2/(P_{M_2})$		
	K_2	Na_2	Li_2	K_2	Na_2	Li_2
298.1	51.093	46.685	39.320	−5.247	−9.165	−15.540
300	51.148	46.738	39.369	−5.190	−9.081	−15.414
400	53.645	49.163	41.639	−2.962	−5.797	−10.500
500	55.606	51.077	43.447	−1.617	−3.816	− 7.539
600	57.224	52.659	44.953	−0.715	−2.490	− 5.558
700	58.603	54.009	46.246	−0.067	−1.538	− 4.138
800	59.807	55.188	47.379	+0.420	−0.823	− 3.070
900	60.877	56.235	48.388	0.800	−0.264	− 2.237
1000	61.841	57.178	49.298	1.105	+0.184	− 1.570
1200	63.53	58.83	50.89	1.562	0.857	− 0.564
1400	64.98	60.24	52.26	1.887	1.339	+ 0.155
1600	66.25	61.47	53.45	2.129	1.702	0.697
1800	67.39	62.58	54.52	2.315	1.981	1.118
2000	68.41	63.58	55.48	+2.464	+2.204	+ 1.456
$S^0_{298.1}$	59.706	55.024	47.081			

[1] Loomis, Phys. Rev. **38**, 2153 (1931). See this paper for a bibliography for the alkali molecular spectra.
[2] Brewer and Kueck, Phys. Rev. **46**, 894 (1934).

[3] For a discussion of the validity of averaging the spectroscopic constants for the various isotopic varieties of molecule present, and then treating the particular element as nonisotopic, see Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932); see also Gordon and Barnes, J. Chem. Phys. 1, 692 (1933).
[4] Loomis and Nusbaum, Phys. Rev. **40**, 380 (1932).
[5] As is now customary, none of the entries includes the nuclear spin contribution. The constants used were $hc/k = 1.4324$, $R = 1.9869$, additive constant for the translational free energy $= -7.267$. $(F^0 - E_0^0)/T$ can be interpolated using not more than second differences; in the case of the equilibrium constants, it is better to interpolate $T \cdot \log K$.
[6] Gordon and Barnes, J. Chem. Phys. 1, 297 (1933).

tions[7] were not used to avoid summation over all values of the vibrational quantum number. It should be noted in passing that with these molecules, the use of the rigid rotator-harmonic oscillator approximation to the energy levels (such as is employed in the simple Gibson-Heitler equation) would lead to very considerable errors. For example, in the case of potassium, it would predict for 2000° and 1000° 67.69 and 61.56, respectively, as the values of $-(F^0-E_0^0)/T$ instead of 68.41 and 61.84 as given in Table II; similarly for sodium, the entries for 2000° and 1000° would be 63.07 and 56.98 with resulting errors of 0.51 and 0.20 cal./deg., respectively.

Values of $(F^0-E_0^0)/T$ for the atoms can be readily computed since for $T<2000°$ only the normal ^2S state (of quantum weight 2) need be considered. From these and the values of ΔE_0^0 given in Table I, $\log K = \log (P_M)^2/(P_{M_2})$ for the three metals can be obtained, and is entered in the last three columns of Table II. As an example of the errors introduced by the use of the simple Gibson-Heitler equation for these vapors, it should be noted that for 1000° and 2000° in the case of sodium, the equation would give $K=1.69$ and $K=207$, respectively, as compared with the exact values from Table II, viz. 1.53 and 160. Experimental determinations of the degree of association of the alkali vapors have been made by Lewis[8] using a magnetic deflection method, but his values of the equilibrium constants are all considerably larger than those recorded in Table II.

Of the three alkalis, sodium has by far the most complete and concordant vapor pressure data; the work of Edmondson and Egerton,[9] of Thiele[10] and of Rodebush and his associates[11, 12, 13] covers a range of temperature of nearly 700° and a range of pressure from 1/10,000 of a millimeter to

nearly 500 millimeters. After allowing for the partial pressure of the molecules by means of Table II, the "best" equation[14] to fit the vapor pressures of the atoms (in mm of mercury) is given by

$$\log p_{Na} = 11.3245 - 26,087/4.575T$$
$$-1.174 \log T. \quad (1)$$

When used in conjunction with Table II, this leads to vapor pressures which in general agree with the results of experiment over the whole range to better than ±0.5 percent and with no drift in the deviations.

From Eq. (1), ΔE_0^0 for the reaction $Na(l) = Na(g)$ is 26,087 cal.; the latent heat of fusion of sodium[15] is 600 cal., and hence from the heat capacity data for crystalline sodium of Simon and Zeidler,[15] ΔE_0^0 for the reaction $Na(s) = Na(g)$ is 26,040 cal. Similarly, from Eq. (1), the entropy of $Na(g)$ and the data of Simon and Zeidler for the range 298°–371°, $S^0_{298.1}$ for crystalline sodium is 12.15 cal./deg.—in close but possibly fortuitous agreement with the "third law" value 12.2 cal./deg.

Fiock and Rodebush[16] have measured the vapor pressure of potassium for the range 679°–1033°K (pressures from 4.6 to 783 mm); molecule formation is less prominent than with sodium, but is still appreciable. After allowing for the partial pressure of K_2 by means of Table II, p_K (in mm) can be represented by the equation[17]

$$\log p_K = 11.410 - 22,210/4.575T$$
$$-1.275 \log T. \quad (2)$$

Eq. (2), in conjunction with Table II, predicts vapor pressures for this range which agree with Fiock and Rodebush's results within their estimated experimental error of ±1 percent. The agreement between these data for relatively high temperatures and those for the lower range (340°–470°K), however, is not nearly so satisfactory as in the case of sodium. For example,

[7] To ensure numerical accuracy in the integral approximations, the calculation was carried out for 2000° and 1000° for each gas with two different values of M, see reference 6, Eq. (12), p. 304. Note also the misprint in the expression for I_2 of Eq. (14), p. 304; the coefficient of the last term should be $(1/2r)$, not $(\frac{1}{2}r)$ as printed.

[8] Lewis, Zeits. f. Physik 69, 804 (1931).

[9] Edmondson and Egerton, Proc. Roy. Soc. A113, 520 (1927).

[10] Thiele, Ann. d. Physik (5) 14, 937 (1932).

[11] Rodebush and de Vries, J. Am. Chem. Soc. 47, 2488 (1925).

[12] Rodebush and Walters, J. Am. Chem. Soc. 52, 2654 (1930).

[13] Rodebush and Henry, J. Am. Chem. Soc. 52, 3159 (1930).

[14] The coefficient of the last term assumes with Thiele (reference 10) Rengade's value for heat capacity of liquid sodium—7.30 cal./deg./gram-atom (Rengade, Comptes rendus 156, 1897 (1913)).

[15] Simon and Zeidler, Zeits. f. physik. Chemie 123, 383 (1926).

[16] Fiock and Rodebush, J. Am. Chem. Soc. 48, 2522 (1926).

[17] The coefficient of the last term corresponds to a heat capacity for liquid potassium of 7.50 cal./deg./gram-atom; see reference 15.

for $373.2°K$, Eq. (2) predicts $P_K(=P)=1.32 \times 10^{-5}$ mm, while the equations fitted to their experimental results by Edmondson and Egerton,[9] Mayer [18] and Neumann and Völker[19] give 1.82, 3.01 and 1.89×10^{-5}, respectively.

From Eq. (2), from the heat of fusion of potassium (575 cal.) and from the thermal data of Simon and Zeidler,[15] $\Delta E_0{}^0$ for the reaction $K(s) = K(g)$ is 22,230 cal.; while from Eq. (2), the entropy of gaseous monatomic potassium and the heat capacity data of Simon and Zeidler, $S°_{298.1}$ for crystalline potassium is 14.60 cal./deg.—definitely *less* than the third law value, 15.2 cal./deg. The reason for this discrepancy is not immediately apparent, but it should be noted that the Neumann-Völker vapor pressure equation leads to a value of $S°_{298.1}$ in agreement with the third law value, but is in definite disagreement with Fiock and Rodebush's results even when al-

lowance has been made for the molecule formation.

In the case of lithium, Hartmann and Schneider[20] have measured the vapor pressure in the range $1204°–1353°K$ (pressures of from 17 to 94 mm); after correcting their observed pressures for p_{Li_2} by means of Table II, the pressure of the lithium atoms can be represented (as a rule to better than one percent by the equation)

$$\log p_{Li} = 11.889 - 38,900/4.575T - 1.174 \log T. \quad (3)$$

The normal boiling points for the three alkalis and the partial pressures of atoms and molecules at the boiling point in the saturated vapors, predicted by Eqs. (1), (2) and (3) and Table II are:

	K	Na	Li
T_B	1030°	1162°	1599°
p_M	716 mm	658 mm	648 mm
p_{M_2}	44 mm	102 mm	112 mm

[18] Mayer, Zeits. f. Physik **67**, 240 (1931).
[19] Neumann and Völker, Zeits. f. physik. Chemie **A161**, 33 (1932).

[20] Hartmann and Schneider, Zeits. f. anorg. Chemie **180**, 275 (1929).

Electron Distribution in (NH₄)₂C₂O₄·H₂O and the Structure of the Oxalate Group

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The electron distribution of $(NH_4)_2C_2O_4 \cdot H_2O$ projected on (001) was obtained by a Fourier analysis making use of quantitative intensity measurements of x-ray scattering from ($hk0$). This analysis combined with a determination of the atomic parameters perpendicular to (001) gave the complete structure. Separations of covalently linked atoms in the $C_2O_4{}^{--}$ group are $C-C$, $1.581\pm0.01A$; $C-O$, $1.25\pm0.02A$; and $C-O$, $1.23\pm0.02A$ with the angle $O-C-O = 129°\pm2°$. In this compound the $O-C-O$ parts of an oxalate group are in planes at an angle of 28° while in $H_2C_2O_4 \cdot 2H_2O$, α and β $H_2C_2O_4$ the parts are coplanar.

INTRODUCTION

THE crystal structures of a number of oxalates have been determined by the usual methods of analysis of x-ray diffraction data. In $H_2C_2O_4 \cdot 2H_2O$,[1] α $H_2C_2O_4$ and β $H_2C_2O_4$[2] the oxalate group apparently has a center of symmetry and thus the four oxygen atoms of the group must be coplanar but cannot be crystallographically equivalent. Atomic separations as

found for these compounds and for KHC_2O_4, $RbHC_2O_4$, $K_2C_2O_4 \cdot H_2O$, and $Rb_2C_2O_4 \cdot H_2O$ are $C-C$, 1.57 to 1.60A; $C-O$, 1.20 to 1.30A; and angle $O-C-O$, 125°–134°.[3] A more accurate determination of these values and a knowledge of the possible equivalence of the oxygen atoms can be obtained from a Fourier analysis of the electron distribution on a given plane.

[1] W. H. Zachariasen, Zeits. f. Krist. **89**, 442 (1934).
[2] S. B. Hendricks, Zeits. f. Krist. **91**, 48 (1935).

[3] Note *X-rays in Theory and Experiment*, by A. H. Compton and S. K. Allison (New York, 1935), p. 444 *et seq.*, for a logical development of the subject.