the percentage of ionic micelle is not greatly affected by the addition of electrolytes.[10]

Summary

1.   We have calculated the activity coefficients of the various soaps.

2.   The activity coefficient so calculated offers evidence in favor of the micellar theory.

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THE VAPOR PRESSURES AND THERMAL PROPERTIES OF POTASSIUM AND SOME ALKALI HALIDES

BY ERNEST F. FIOCK[1] AND WORTH H. RODEBUSH

The physicists within the last few years have made a large number of measurements of energy changes in atoms and molecules by ionization and spectroscopic methods and have postulated various electron displacements and dissociations as accompanying these changes.   It is desirable to obtain direct thermal data for these postulated reactions for purposes of checking against the calculations of the physicists and verifying their postulates.   Thus, if the reaction Na + Cl ⟶ NaCl in the vapor state consists simply of the transfer of an electron from the sodium to the chlorine, the heat of this reaction should be calculable from the ionization potential of sodium and the electron affinity of chlorine.   The comparison of this calculated heat with the more directly determined quantity should decide whether the mechanism of the reaction is the simple one postulated above.

It is true that the physicists have not been able to agree upon a value for the electron affinity of chlorine but it seems probable that a satisfactory value will be established in the near future.   On the other hand, the classical calculation of this sort made by Foote and Mohler[2] for gaseous hydrogen chloride now appears to be in fortuitous agreement only with thermal data since Barker and Duffendack[3] have shown that the hydrogen chloride molecule does not dissociate on ionization as they supposed.   In fact, it seems likely that no chemical reaction is so simple as the elementary process that the physicist brings about in his measurement.   Thus the

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[10] Quick, *J. Chem. Soc.*, **127**, 1401 (1925).

[1] This communication is an abstract of a thesis submitted by Ernest F. Fiock in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Foote and Mohler, "The Origin of Spectra," Chemical Catalog Co., New York, **1922**, p. 185.

[3] Barker and Duffendack, *Phys. Rev.*, **26**, 339 (1925).

Einstein law of the photochemical equivalent applies only to the removal of an electron from an atom, a process which does not seem to correspond to any chemical reaction. Hence, the failure of any simple radiation theory of chemical action is not surprising. Nevertheless, there is still hope that thermal quantities may be calculated from the data of the physicist with high accuracy as, for example, heats of dissociation from band spectra.

On the other hand, the thermal data are far from complete. In his recent calculations of the energy of salt vapors Latimer[4] was compelled to estimate heat quantities of large magnitude in the absence of satisfactory data. In the case of the alkali metals and alkali halides the heats of vaporization are the most important quantities lacking. These can be calculated from vapor-pressure data of sufficient accuracy. Kröner's[5] data on potassium do not appear to be very concordant. Von Wartenberg,[6] Ruff,[7] Maier[8] and Jackson and Morgan[9] have made measurements on the alkali halides but the agreement is not good. Since the method devised by Rodebush and Dixon[10] for the measurement of vapor pressures at high temperatures promised to give accurate results on these substances, it has been used in the determinations of their vapor pressures.

Fig. 1.—Apparatus central element.

Experimental Part

The method of Rodebush and Dixon has been described in detail elsewhere.[10] The apparatus in which the substances were vaporized was made of pure nickel with welded joints by the American Nickel Corporation. The modified form of the apparatus is shown in Fig. 1. The reservoir A is 4.5 cm. in internal diameter and 2.5 cm. deep. The tubes B and C are 0.9 cm. in inside diameter. Instead of constrictions in the tubes, loose plugs were introduced. These plugs have a central hole 3 mm. in diameter for the ascent of the vapor and a slot E for the return of the condensed liquid. This proved to be a great improvement as it prevents clogging of the apparatus with drops of liquid.

The apparatus was heated in an electric furnace with an insulating cover and the regulation was accomplished by a hand rheostat. The temperature did not vary by more than 0.2–0.3°. Temperatures were measured
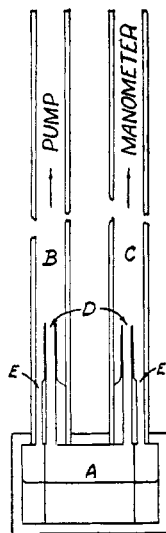
[4] Latimer, THIS JOURNAL, **45,** 2803 (1923); **48,** 1234 (1926).

[5] Kröner, *Ann. Physik,* **40,** 438 (1913).

[6] Von Wartenberg and Albrecht, *Z. Elektrochem.,* **27,** 162 (1921). Von Wartenberg and Schulz, *ibid.,* **27,** 568 (1921).

[7] Ruff and Mugdan, *Z. anorg. allgem. Chem.,* **117,** 147 (1921).

[8] Maier, *Bur. Mines Tech. Papers,* No. 360.

[9] Jackson and Morgan, *J. Ind. Eng. Chem.,* **13,** 110 (1921).

[10] Rodebush and Dixon, *Phys. Rev.,* **26,** 851 (1925).

by a platinum—platinum–rhodium thermocouple which was repeatedly calibrated against the boiling point of sulfur and the melting points of potassium chloride and potassium sulfate.[11] The apparatus was sealed to the glass pump and manometer system with de Khotinsky cement. Argon was used to furnish an inert atmosphere. Sulfuric acid was used in the manometer. The levels in the manometer were read to 0.02 mm. with a cathetometer and the density of the sulfuric acid was determined after each run. About 25 g. of material was introduced into the apparatus for a determination.

The boiling point of potassium in the neighborhood of one atmosphere was determined by boiling the metal in a nickel tube and measuring the temperature of the vapor with a thermocouple protected by a nickel shield. The lower end of the tube was heated in an electric furnace and a heating jacket was placed around the tube above the liquid line to prevent excessive cooling of the vapor. Argon was used as an inert atmosphere and the total pressure was obtained as the sum of the readings of a mercury manometer and the barometer. A constant temperature could be obtained in the vapor even while the rate of heating of the liquid and vapor jackets was varied considerably.

Purity of Materials

Mallinckrodt's metallic potassium was used. It was freed from oil and oxide and introduced into the apparatus in a clean state by repeated filtering and distillation in a vacuum. Spectroscopic tests indicated less than 0.1% of sodium in the initial material. The salts used were recrystallized from products purchased as being of high purity and with one or two exceptions probably contained negligible amounts of impurity. The sample of potassium bromide was furnished by Professor Braley of this Department. It had been recrystallized twice but was not known to be free from chlorides. The cesium chloride was purchased as pure from Eimer and Amend, but it was not recrystallized. Tests showed it to be free from any considerable amounts of sodium and potassium. Tests on the material after a run showed that no appreciable amounts of nickel were dissolved.

Results

The results are given in the tables. In addition, an empirical equation has been fitted to each set of data. This equation is linear in $\log p$ and $1/T$ in every case. This is not surprising in the case of the salts since the measurements cover a comparatively short range of temperatures. In the case of potassium, however, where the range is considerable, the absence of curvature is surprising since the difference in the heat capacities of the liquid and vapor must be two or three calories. The authors have noticed, in fitting equations to vapor-pressure data for other metals, that a linear equation often seems to fit as well as one that contains a term for ΔC_p and they are at a loss to explain this. It may be due to deviations of the saturated vapor from the perfect gas law at higher pressures.

[11] Roberts, *Phys. Rev.*, **23**, 386 (1924).

Previous tests of the experimental method on substances of known vapor pressure, such as mercury, have indicated that the accuracy of the method is limited only by the uncertainty of the temperature control. The plot shows the data to be highly consistent and the absolute error of the measurements is believed to be less than 1% on the average.

TABLE I

VAPOR PRESSURES OF METALLIC POTASSIUM

Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.	Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.
406.2	4.60	4.57	509.5	32.80	33.2
427.9	7.27	7.26	528.5	44.83	45.9
448.6	11.18	11.0	754.3	744.0	741.7
469.1	16.23	16.3	757.0	763.1	761.2
489.4	23.35	23.5	759.8	783.3	782.0

$\log_{10} p = -4433/T + 7.1830$

$\Delta H = 20,260$ cal. per gram atom

TABLE II

VAPOR PRESSURES OF SODIUM CHLORIDE

Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.	Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.
976.5	6.12	6.19	1079.5	23.21	23.23
1002.5	8.71	8.83	1105.0	31.25	31.25
1028.4	12.37	12.38	1130.2	41.27	41.46
1054.1	17.07	17.09	1155.4	54.16	54.45

$\log_{10} p = -9419/T + 8.3297$

$\Delta H = 43,050$ cal. per gram molecule

TABLE III

VAPOR PRESSURES OF POTASSIUM CHLORIDE

Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.	Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.
906.0	4.30	4.19	1036.9	24.85	24.81
932.0	6.26	6.15	1062.6	34.00	33.69
959.0	9.03	9.01	1088.0	45.39	45.27
985.2	12.84	12.85	1105.0	54.54	54.75
1011.1	18.09	17.98			

$\log_{10} p = -9115/T + 8.3526$

$\Delta H = 41,660$ cal. per gram molecule

TABLE IV

VAPOR PRESSURES OF POTASSIUM BROMIDE

Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.	Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.
906.0	6.32	6.32	993.9	20.82	20.76
923.8	8.15	8.16	1011.1	25.69	25.70
941.4	10.44	10.42	1028.4	31.69	31.70
959.0	13.23	13.21	1045.6	38.68	38.81
976.5	16.60	16.62	1062.6	46.74	46.10

$\log_{10} p = -8780/T + 8.2470$

$\Delta H = 40,130$ cal. per gram molecule

<div align="center">

TABLE V

VAPOR PRESSURES OF POTASSIUM IODIDE

</div>

Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.	Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.
842.9	5.29	5.27	950.2	23.37	23.38
852.0	6.07	6.05	976.5	32.25	32.39
879.0	9.00	8.98	1002.5	43.88	43.13
897.0	11.53	11.56	1028.4	60.08	59.30
923.8	16.62	16.62			

$\log_{10} p = -8229/T + 8.0957$

$\Delta H = 37,610$ cal. per gram molecule

<div align="center">

TABLE VI

VAPOR PRESSURES OF CESIUM CHLORIDE

</div>

Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.	Temp., °C.	Pressure, mm. of Hg Obs.	Calcd.
824.7	4.15	4.30	959.0	28.60	28.54
852.0	6.49	6.55	985.2	39.42	39.39
879.0	9.77	9.74	1011.1	53.13	53.46
906.0	14.18	14.23	1019.9	58.48	59.14
932.0	20.32	20.18			

$\log_{10} p = -8282/T + 8.1772$

$\Delta H = 37,854$ cal. per gram molecule

<div align="center">

TABLE VII

DEVIATIONS OF CALCULATED VALUES FROM OBSERVED VALUES

</div>

Substance	Total observations	Max. dev., mm.	Av. dev., mm.	Max. dev., %	Av. dev., %
K	17	2.7	0.71	3.3	1.1
NaCl	23	0.70	.11	1.7	0.5
KCl	24	.40	.10	4.6	.8
KBr	10	.64	.09	1.4	.3
KI	22	.78	.14	1.5	.4
CsCl	23	.34	.09	3.5	.7

Thermal Properties

In Table VIII are shown the principal thermal data for the substances investigated. The entropies of the solid at 298° K. have been calculated from specific-heat data except in the case of potassium iodide and cesium chloride, for which the values were estimated. The heat of fusion of po-

<div align="center">

TABLE VIII

HEATS OF SUBLIMATION

</div>

	K	NaCl	KCl	KBr	KI	CsCl
$S_{solid\ 298°K.}$	16.5	17.6	19.8	22.6	24.4	23.3
T_f	336.6	1073	1043	1001	950	918
ΔS_f	1.6	6.7	6.1	6.2	6.2	6.2
$\Delta S_{vaporization\ to\ 1\ atm.\ at\ T_f}$	19.65	24.9	25.0	24.5	23.8	24.2
$\int_{T_f}^{298} \Delta C_p\ d\ ln\ T$	0.24	6.4	6.3	6.1	6.8	5.6
$S_{vapor\ 298°K.\ 1\ atm.}$	38.0	55.6	57.2	59.4	60.2	59.3

tassium is given by Bernini,[12] and for sodium and potassium chlorides by Plato.[13] The other heats of fusion have been estimated. The heats of vaporization are calculated from our data by the Clapeyron relation. ΔC_p is assumed to be —5 cal.

TABLE IX

HEATS OF SUBLIMATION

	$\Delta H_{\text{sublimation at 298°K.}}$	Lattice energy	Heat of soln. of gaseous ions
NaCl	54	182	248
KCl	52	163	235
KBr	50	156	216
KI	47	144	195
CsCl	47	...[a]	225

[a] The crystal structure of cesium chloride is not simple cubic and Born does not calculate its lattice energy.

In Table IX are given the values in kilogram calories of the heats of sublimation of the crystals at 298°K. calculated by us, the values of the lattice energies as calculated by Born[14] and the heats of solution of the gaseous ions calculated by Born's[15] formula

$$\Delta E = (Ne^2/2r)[1 - (1/D)] \tag{1}$$

The figures for the lattice energies are the original calculations of Born and would be changed somewhat by new values of the constants involved. The calculation of the heat of solution involves the arbitrary choice of the "atomic radii." Born himself does not claim a high accuracy for his lattice energy value but apparently the only test of his theory that has been made with dependable data is the comparison made by Richards and Saerens[16] of experimental compressibilities with those calculated by Born and here the agreement seems as good as one could expect. All other tests of his theory involve uncertain ionization potentials or "electron affinities." Latimer[4] has recently attempted to verify the formula for the heat of solution of gaseous ions by the use of very uncertain data. It seems rather more plausible to assume that the formula is correct and draw what inferences we may. When we examine Table VIII we notice first a satisfactory parallelism between the values for the heat effects in the three columns. By far the most striking features, however, are the extremely small values of the heats of solution of the solid alkali halides in spite of the large values of the heats of vaporization and the lattice energies. This means that the lattice energy is nearly equal to the heat of solution of the

[12] Bernini, *Physik. Z.*, 7, 168 (1906).

[13] Plato, *Z. physik. Chem.*, 55, 737 (1906); 58, 369 (1907).

[14] Born, *Verh. deut. physik. Ges.*, 21, 13 (1919). The lattice energy is the energy increase involved in the separation of the ions of the crystal to an infinite distance from one another.

[15] Born, *Z. Physik*, 1, 45 (1920).

[16] Richards and Saerens, THIS JOURNAL, 46, 934 (1924).

gaseous ions or, in other words, that the electrical forces of the ion are neutralized to about the same extent in solution as in the crystal lattice. This would seem to justify Born's tacit assumption that the energy relations of an ion depend only upon its charge and its "effective atomic radius." If we assume the dielectric constant of water infinite in Equation 1 for the heat of solution of gaseous ions, the energy value given is not altered appreciably, but the expression becomes identical with that for the neutralization of the ions in question by the closest approach of an ion of opposite sign and equal radius. This approximates the energy change in the condensation of a gaseous ion in the lattice[17] and hence it appears plausible that the two heat effects should be so nearly equal. In the process of the hydration of an ion, water is not to be pictured as a homogeneous medium of high dielectric constant. Rather the process consists of the neutralization of the ionic charge by the more or less polar molecules. In Equation 1 no correction is made for the radii of the water molecules nor for repulsive forces, and hence it is not surprising that the values in Col. 3 are larger than in Col. 2.

Latimer has pointed out the apparent lack of specific action between the ion and the solvent. It seems certain, however, that the tendency to coordinate the solvent molecules as auxiliary valence groups is a function of the charge and effective radius of the ion and hence a specific property. Likewise, the tendency of a solvent to become coördinated is a function of the effective radius and the potential polarity of its molecules.

A final point for comment on the data in Table VIII is the small value of the heat of sublimation of a salt compared to its lattice energy. This must mean that when a molecule vaporizes from the lattice, the two ions approach more closely and the molecule becomes less polar.

If we subtract the heat of sublimation from the lattice energy, we have the heat of ionization of the salt vapors. The values in Col. 3 must certainly represent a maximum value for the lattice energy, while we suspect the figures in Col. 2 to be near the right value. This would indicate that the heat of dissociation of sodium chloride vapor into sodium and chloride ions is in the neighborhood of 128 calories.

Summary

The vapor pressures of potassium and five alkali halides have been measured.

The thermal data have been calculated for these substances.

Some inferences favorable to Born's theory of lattice energy have been drawn.

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[17] Neglecting repulsive forces the potential energy of the lattice is $(0.145\ e^2)/(r_+ + r_-)$ (where r_+ and r_- are the respective radii) per bond, per ion, and each ion has six bonds.