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Author

Brewer, Leo.

Publication Date

1961-11-01

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UCRL-9952
UC-4 Chemistry
TID-4500 (16th Ed.)

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UNIVERSITY OF CALIFORNIA
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Berkeley, California
Contract No. W-7405-eng-48

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NOVEMBER 1961

UNIVERSITY OF CALIFORNIA
LAWRENCE RADIATION LABORATORY
BERKELEY, CALIFORNIA
TID-4500 (16th Ed.)

Printed in USA. Price 50 cents. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D.C.

THE THERMODYNAMIC PROPERTIES OF THE ALKALI HALIDES

Leo Brewer

Department of Chemistry and Lawrence Radiation
Laboratory, Berkeley, California

Abstract

The thermodynamic properties of the alkali halides
are reviewed.

Brewer and Brackett¹ recently reviewed the vaporization data of the alkali halides and present tables of free energy functions for both the condensed phases and the gaseous diatomic molecules. Enthalpies of sublimation and dissociation are also tabulated. The interest in alkali halides as liquids in nuclear reactors, as solvents for fuel processing, as plasma components in thermoelectric devices, and in many other applications makes the availability of complete and consistent thermodynamic data of considerable value. In combining thermodynamic data from many sources there is the hazard of introducing error into thermodynamic calculations due to the combination of inconsistent data. It is the purpose of this report to present those auxiliary thermodynamic data that would be needed in conjunction with the data tabulated by Brewer and Brackett to carry out a wide range of thermodynamic calculations involving the alkali halides.

Brewer and Brackett used the thermodynamic data for the alkali elements tabulated by Lewis, Randall, Pitzer and Brewer² who give in their Appendix 7 enthalpies of formation of the gaseous monatomic alkali metals. Stull and Sinke³ also present data for the alkali metals at closer temperature intervals and over a wider temperature range. However, if their tables are to be used, the enthalpies of sublimation of K and Rb must be corrected to be consistent with the values used by Brewer and Brackett. The ΔH_{298}° values for the sublimation of the monatomic alkali metals used are as follows: Li, 38.44; Na, 25.9; K, 21.45; Rb, 19.5; and Cs, 18.67 kcal/mole. The free energy functions given by Stull and Sinke must be corrected for changes in the S_{298}° values for Li, Na, K and Rb solids adopted by Lewis, Randall, Pitzer, and Brewer on the basis of the recent tabulation of entropies by Kelley and King.⁴

The first column of numbers in Table I presents the enthalpies of formation of the solid alkali halides at 298.15°K (see below) that were used by Brewer and Brackett and the second column of numbers of Table I presents the enthalpies of formation of the gaseous diatomic alkali halides at 298.15°K that result from the combination of the values in the first column with the enthalpies of sublimation given by Brewer and Brackett in their Table 7. (Due to a typographical error, the enthalpy of sublimation of CsI was given as 46.7 instead of the correct value of 45.7 kcal/mole.) All enthalpies of formation of the bromides and iodides are given here with respect to the liquid standard state of bromine and solid standard state of iodine.

The enthalpies of formation of the solid alkali halides were obtained from the tabulation of Lewis, Randall, Pitzer, and Brewer.² As they indicate on Pg. 678 of Appendix 7, the enthalpies of formation of all of the halides of cesium given by Rossini, Wagman, Evans, Levine, and Jaffe⁵ in U.S. Bureau of Standards Circular 500 were made more negative by 3.4 kcal/mole and all enthalpies of formation of the halides of rubidium were made more negative by 0.5 kcal/mole. They also indicate that all of the enthalpies of formation of the sodium and potassium halides should be made more negative by about 0.5 kcal/mole, due to newer values for the aqueous ions but this change was not made by Lewis, Randall, Pitzer, and Brewer or by Brewer and Brackett and the Circular 500 values were retained for all potassium halides and for all sodium halides with the exception of NaF. If the expected change in the enthalpies of formation of the solid halides of sodium and potassium is made in the revision of Circular 500, it is important to change the enthalpies of formation and enthalpies of dissociation

and ionization of the gaseous alkali halides by the same amount to insure consistency. The value given for NaF is that of Coughlin⁶ based on a recent heat of solution. It would be changed by the same amount as the other sodium halides if the enthalpy of formation of aqueous sodium ion is revised. The enthalpies of formation of the lithium halides are uncertain by several kilocalories. The values used by Brewer and Brackett for LiBr and LiI are those given in Circular 500. The values for LiF and LiCl of -145.7 ± 2 and -96 ± 2 kcal/mole given by Lewis, Randall, Pitzer, and Brewer are averages of determinations in the literature. Recent U.S. Bureau of Standards⁷ reports have reviewed more recent determinations, but there does not seem to be any basis for change until a decidedly more accurate determination becomes available. The enthalpies of dissociation of the gaseous alkali halides to the gaseous atoms given by Brewer and Brackett in their Table 8 required use of data for the alkali metals which have been listed above and data for the halogens. The enthalpies of atomization at 298.15°K of the halogens in their standard states are as follows: F, 18.9; Cl, 28.94; Br, 26.76; and I, 25.52 kcal/gram atom.² The halogen values used are consistent with those tabulated by Stull and Sinke except for iodine. Their enthalpy of sublimation of I₂ and their free energy functions for condensed I₂ at 298, 300, and 400°K must be revised to be consistent with $S_{298}^{\circ} = 27.76$ cal/deg mole for solid I₂.⁴

In the third column of numbers in Table I are given enthalpies of ionization of the gaseous diatomic alkali halides at 298.15°K. To obtain these values, the following ionization potentials of the gaseous atoms at 0°K from Moore⁸ were used: Li, 124.4; Na, 118.4; K, 100.0; Rb, 96.3; and Cs, 89.7 kcal/gram atom. Also the following electron affinities of the

gaseous halogen atoms at 0°K. were used: F, 80; Cl, 86; Br, 81; and I, 74 kcal/gram atom. ΔH_{298}° was taken equal to ΔH_0° for the reaction $M(g) + X(g) = M^+(g) + X^-(g)$. The electron affinities were obtained from the values tabulated by Cubicciotti⁹ by assuming that the deviations shown by potassium and rubidium salts were due to errors in the enthalpies of formation of the aqueous ions and by rounding off to the nearest kilocalorie. The electron affinities used by Brewer and Brackett were taken from a previous calculation of Cubicciotti which was slightly in error and the ionization enthalpies given here differ slightly from those used by Brewer and Brackett. Table II reproduces Table 9 of Brewer and Brackett with correction of the experimental values to agree with the electron affinities listed here. The calculated values given here are based on averaging the closely agreeing calculations of Berkowitz⁹ and Rothberg.¹⁰ Their tabulated energies have been corrected here for zero point energies.

It is hoped that the above summary will insure the use of consistent thermodynamic data in calculations of equilibria involving the alkali halides and will make easier the incorporation of new data as they become available.

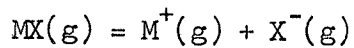
TABLE I

Enthalpies of Alkali Halides, kcal/mole

	Enthalpy of Formation at 298.15°K.		ΔH_{298}° for
	$\Delta H^{\circ}(\text{solid})$	$\Delta H^{\circ}(\text{gas})$	$\text{MX}(\text{g}) = \text{M}^{+}(\text{g}) + \text{X}^{-}(\text{g})$
LiF	-145.7	-80.2	181.9
LiCl	- 96.	-44.5	150.3
LiBr	- 83.7	-35.	143.6
LiI	- 64.8	-20.6	135.
NaF	-136.3	-69.2	152.4
NaCl	- 98.2	-42.7	129.9
NaBr	- 86.0	-34.	124.
NaI	- 68.8	-21.3	117.
KF	-134.5	-77.2	137.6
KCl	-104.18	-50.9	115.3
KBr	- 93.73	-42.7	110.
KI	- 78.31	-29.8	102.8
RbF	-131.8	-77.7	132.4
RbCl	-103.4	-52.3	111.
RbBr	- 93.5	-44.1	105.7
RbI	- 79.0	-31.7	99.
CsF	-130.3	-82.	129.3
CsCl	-106.9	-58.6	109.9
CsBr	- 97.7	-51.1	105.2
CsI	- 83.9	-38.2	98.

TABLE II

Comparison of experimental and calculated values of enthalpies of dissociation to the free ions



		$\Delta H_{\text{O}}^{\circ}$				
		Li	Na	K	Rb	Cs
		kcal.	kcal.	kcal.	kcal.	kcal.
F	calculated	171	150	136		128.5
	experimental	181	152	137	132	129
Cl	calculated	147	129	116	112	110
	experimental	149.5	129	115	110	109
Br	calculated	141	123	111	107.5	104
	experimental	143	123.5	109	105	105
I	calculated	133	117.5	105	102	99
	experimental	134	116.5	102	98.5	98

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