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Experimental Measurement of the Lattice Energies of RbBr and NaCl*

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By measuring electrically the ion emission through an orifice in an equilibrium chamber at high temperature containing salt vapor the lattice energies are calculated. The values obtained are 151.3 kcal. for RbBr and 181.3 kcal. for NaCl. The probable error is about 3.0 kcal. for both measurements, and the maximum error in the neighborhood of 7.5 kcal. The corresponding electron affinities are 84.2 kcal. for Br and 88.3 kcal. for Cl.

INTRODUCTION

BECAUSE of the interest to chemists of the Born cycle for the calculation of energies involved in the formation of ionic salts, the experimental determination of the lattice energies of some alkali halides has been undertaken to extend the original work of one of us on KI and CsI.[1] Further improvements in the theoretical calculation of lattice energies[2,3] have made desirable experimental work of the greatest possible accuracy.

The method used for the experimental determination is essentially as follows. By determining the current carried by ions flowing out of a measured hole in an oven containing salt vapor, the equilibrium pressures of ions P_+ and P_- of the ions M^+ and X^- in equilibrium with the gaseous salt vapor MX at a pressure P_{MX} are measured. From these data the free energy change, ΔF, and by calculation of the entropies the energy change, ΔE, of the reaction (1) $MX_{gas} \rightarrow M^+_{gas} + X^-_{gas}$ are calculated. By employing known energies of other reactions the lattice energy, ΔE for the reaction $MX_{Cr.} \rightarrow M^+_{gas} + X^-_{gas}$, (0°K) and the electron affinity of the halogen, ΔE for $X_{gas} + e^-_{gas} \rightarrow X^-_{gas}$ (0°K), may be calculated. The actual handling of the data used in this paper, although in principle

assuming the same knowns as previously,[1] is such as to reduce greatly the uncertainty in the final lattice energies and electron affinities. The experimental procedure has also been greatly improved.

EXPERIMENTAL

The experimental arrangement has been altered from the original set-up of Mayer to give higher temperatures for the equilibrium (1) above. This was necessary in order to extend the measurements to the lighter alkali halides. One might instead use a more sensitive device for measuring the currents, but because of the difficulty of avoiding stray ion and electron currents this did not seem worth while. Modifications have also been made in the experimental technique to improve the accuracy of the experiments, since in Mayer's work the currents were not satisfactorily reproducible, and it seems probable, also, in view of our recent experiences that some unrecognized errors were inherent in the earlier procedure.

Fig. 1 shows the essential parts of the apparatus and may serve to illustrate how the measurements were carried out. The salt to be studied was placed in the lower half of the graphite oven (A) which was threaded into the upper part (B). (B) was heated directly by radiation. (A) was heated principally by conduction, so that its temperature could be adjusted by changing its position relative to the upper oven. The gaseous salt molecules, at a pressure determined by T_A, the temperature of the lower oven, diffused into B and then were

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[1] J. E. Mayer, Zeits. f. Physik **61**, 798 (1930).
[2] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).
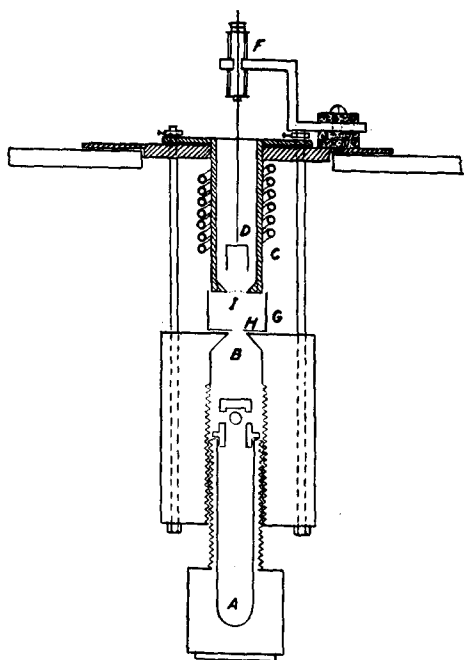[3] J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 19 (1932).

FIG. 1.

assumed to reach equilibrium with the ions and atoms at T_B, the temperature of the upper half.

The gaseous salt, ions, and atoms, diffused out of (B) through a measured hole in the platinum plate over a somewhat larger hole in the graphite oven. The pressure was such that Knudsen's equation could be used to calculate the numbers of ions diffusing out. The ions were caught by the Faraday cage D and the current measured by a sensitive galvanometer in series with it. A potential of a few volts was applied to the cage to collect either of the two ion types dependent on the sign of the potential.

The water-cooled shield C served to prevent ions and electrons from the heating elements and oven from reaching the cage, and also to select out a definite solid angle of the ion beam diffusing through II. Since salt collects on this part of the apparatus during an experiment the tube is water-cooled to prevent emission of ions or electrons from the surface which would otherwise be hot enough to permit this. A fine screen was placed at I to prevent the field of the Faraday cage from reaching through the opening and introducing uncertainty into the calculated solid angle of the ion beam that is collected. In practice the entire tube C was insulated and a

potential applied to it; in this way it was possible at fairly low voltages (2–5 volts) to collect effectively the entire ion beam, since the ions emerge from the oven according to a cosine law and with velocities only as high as 0.05 volt. The screen removed 40 percent of the ion beam.

The Faraday cage was insulated by two pieces of quartz tubing held against a brass support as shown in the diagram. The rod to the cage was threaded and nuts tightened to hold washers against the quartz which in turn was held rigid with respect to the brass support. The support was insulated from ground by three glass plates which were kept cool during an experiment and were also out of the path of diffusing salt molecules, so could not become coated and give rise to surface conduction. After each run the cage was tested for electrical leak and always when cool found to be well insulated. It is possible, however, that occasionally when the system was hot the leak may have been appreciable. This would only materially effect the reading of low currents.

Fig. 2 shows the apparatus as a whole. The system is mounted on a steel plate to which a bell jar about 30 cm in diameter and 40 cm tall
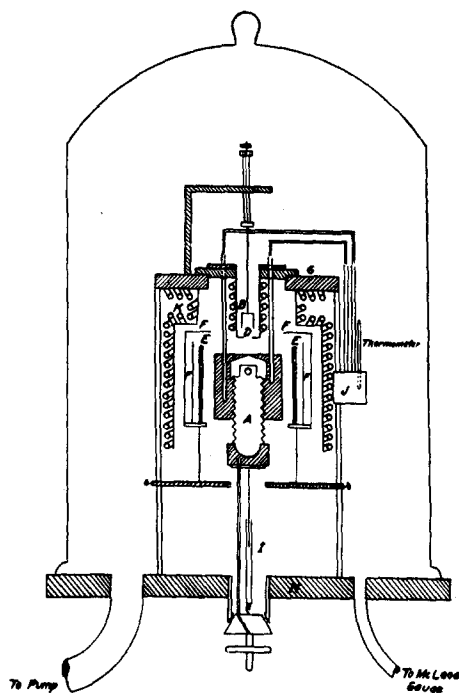

FIG. 2.

had been ground. With heavy grease it was found possible to hold the pressure to 10^{-4} mm Hg during runs with the temperature of the furnace as high as 1300°K. The leads are brought out through copper tubes soldered to the plate through Pyrex tubing held in place with picein.

A brass plate G held on three brass rods served to support the oven A, Faraday cage B and protecting tube D as well as the cooling jacket K. The cooling jacket was made from a large section of copper tubing 12 cm in diameter around the outside of which copper tubing was coiled and soldered in place.

The heating elements E of carborundum composition (Globar) were set in a framework which could slide on the three supporting rods and was capable of adjustment with respect to the oven. Six of the Globar rods, ground down to have a resistance of 30 ohms each, were mounted in parallel and gave fairly uniform heating at high temperatures. The resistance of these sticks decreases with temperature and they have the decided advantage over tungsten resistance elements that they are unaffected by residual oxygen pressure. Because of the amount of gas given off by the graphite furnace with rising temperature this fact was of great importance. As an example of the performance of the furnace: at 60 volts it carried 12 amperes and the oven temperature rose to 1225°K.

Several radiation shields (F) were interposed between the jacket and furnace to prevent loss by radiation. It was found particularly important to have the oven well shielded from above. Unless these precautions were taken differences of as much as 40° between the middle and the ends of the oven resulted.

The oven itself was turned out of a solid block of graphite with an outside diameter of 5 cm and drilled out on the inside to 1.5 cm. This gave a wall thickness that insured good conductivity and helped to prevent any large temperature gradient from the middle to the ends. In spite of this thickness and good shielding the differences rose as high as 10° at 1350°K. The influence of this on the results will be considered later. The lower half of the oven, also turned out of one block of graphite was 3 cm in diameter at the base with walls 1 cm thick, and served to keep the temperature of the solid salt fairly

uniform. The threaded walls of the tube connecting it with the equilibrium chamber were only effectively 1.5 mm in diameter so that large temperature differences could be maintained between A and B. A small cap (shown in Fig. 1) was made to fit over the opening from A into B to prevent molecules from diffusing directly out of the oven without first suffering collisions with the walls in the upper oven.

C indicates the method by means of which the lower half of the oven could be raised or lowered during an experiment without breaking the vacuum. The iron rod screwed to the bottom of the furnace was connected to a ground joint fixed in the base plate by means of a surrounding tube in which it could slide.

Three thermocouples were employed to measure the temperature of different parts of the oven. They were C.P. platinum-platinum 10 percent rhodium couples and were calibrated at five points up to 1083°C and a table of deviations from the Bureau of Standards table recorded. One at a depth 1/3 and another at depth 2/3 of the oven were used in the upper part to determine the temperature of the equilibrium and to check the uniformity of the temperature along the length of the oven. The cold junctions of these thermocouples were insulated and fastened to a brass block attached to the inlet cooling water. A thermometer inserted in the block in the same way enabled us to make a correction for the difference in cold junction temperature from the standard. This was usually 20 or 25°C.

The system was evacuated with a three stage steel mercury diffusion pump which was, of course, in continuous operation. It reduced the pressure to 10^{-5} mm when the system was cold. The pressure was determined by means of a McLeod gauge attached to the system as shown in Fig. 2.

The galvanometer was the best Leeds and Northrup type M 8. rated at 10^{-11} amperes per mm scale deflection at 1 meter. As set up in this experiment it gave a sensitivity of 2.17 $\times 10^{-11}$ amperes per mm on calibration. The lead to the galvanometer was carefully insulated and came in contact with glass only when it emerged from the vacuum system. It was sealed in with de Khotinsky cement. The rubidium bromide used was Kahlbaums which had been crystallized

three times by Professor Jones and used in conductivity work in the department. The sodium chloride was used as a standard in x-ray analysis.

CALCULATION OF RESULTS

From the observed ion currents and the knowledge of the two temperatures T_A and T_B of the solid salt in A, Fig. 1, and of the vapor in B, as well as the geometry of the holes and measuring system, it is possible to calculate directly the lattice energy. For the reaction taking place at A, the sublimation of the salt, we have

$$F_A^\circ(MX_{gas}) - F_B^\circ(MX_{cryst.}) = -RT_A \ln P_{AMX} \quad (1)$$

and for the equilibrium at B,

$$F_B^\circ(\text{ion gas}) - F_B^\circ(MX_{gas})$$
$$= -RT_B \ln (P_+P_-/P_{BMX}) \quad (2)$$

where F_T° is the standard free energy of the indicated substance at the indicated temperature, and P_+, P_-, and P_{MX}, the pressures of the positive and negative ions and of the salt molecules (in atmospheres). It is assumed that due to the Knudsen effect $P_{AMX} = (T_A/T_B)^{\frac{1}{2}}P_{BMX}$.

Multiplying Eq. (1) by T_B and (2) by T_A and adding, the relatively uncertain value of P_{MX} is eliminated, and the less uncertain difference

$T_B F^\circ{}_{T_A}(MX_{gas}) - T_A F^\circ{}_{T_B}(MX_{gas})$ introduced. For the various free energies the expression

$$F_T^\circ = E_0 + \int_0^T C_P dT - TS \quad (3)$$

is used, where E_0 is the energy at $T = 0^\circ$K. The energy $E_0(MX_{cryst.})$, the energy of the crystalline salt at the absolute zero, is arbitrarily chosen as zero, $E_0(\text{ions})$, the energy of the ions at the absolute zero, is then the lattice energy. The specific heat integral of the salt is calculated from a Debye function, $RTD(\theta/T)$, $\theta = h\nu_{max}/k$, and the entropy of the salt $RS_D(\theta/T)$ is similarly calculated assuming a Debye specific heat curve. Probable values for the ν_{max} have been taken from an article by the authors.[3] $E_0(\text{sub.})$, the energy at 0°K of the gaseous molecule, has been taken from the same source, as have the probable values for the frequencies of the molecular vibration. These latter values for the gaseous molecules are all of negligible importance, since, as before remarked, only the difference of $TF_T^\circ(MX_{gas})$ at two not very distant temperatures enters the equation. If ϵ is the energy $h\nu$ of vibration of the gaseous molecule, the integrated specific heat due to vibration may be written $RTP(h\nu/kT)$ and the vibrational entropy $RS_E(h\nu/kT)$ where $P(h\nu/kT)$ and $S_E(h\nu/kT)$ are appropriate well-known functions. The equation for the lattice energy then becomes

$$E_0(\text{ions}) = -\frac{T_B - T_A}{T_A}E_0(\text{sub.}) + RT_B\left[\left\{P\left(\frac{\epsilon}{kT_B}\right) - P\left(\frac{\epsilon}{kT_A}\right)\right\} - \left\{S_E\left(\frac{\epsilon}{kT_B}\right) - S_E\left(\frac{\epsilon}{kT_A}\right)\right\}\right.$$
$$\left. + 6\left\{D\left(\frac{\theta}{T_A}\right) - S_D\left(\frac{\theta}{T_A}\right)\right\} - 7.314 + 1.5 \ln W_M W_X + 2.0 \ln T_B + 3.0 \ln T_A - \ln P_+P_-\right]. \quad (4)$$

W_M and W_X are the atomic weights of the two ions. The ionic gas is assumed to be unimolecular with only the Stern-Tetrode entropy.

The pressure of the gaseous ion is related to the galvanometer deflection by the relation

$$P_{\text{ion}} = \frac{(2\pi WRT_B)^{\frac{1}{2}}}{1.013\times10^6} \cdot \frac{2.17\times10^{-11}\times\delta}{A\times F\times96,500} = 5.07\times10^{-18}(WT_B)^{\frac{1}{2}}\frac{\delta}{AF}. \quad (5)$$

Here δ is the galvanometer deflection in mm and 2.17×10^{-11} the sensitivity of the galvanometer in amperes per mm. A is the area in cm² of the oven opening, and F the calculated fraction of the ions recorded. F is of course dependent on the voltage placed on the screen and Faraday cage. The pressure is given in atmospheres. W is the atomic weight.

The pressures may be replaced in (4) by deflections, changing to $\log_{10}$ we obtain

$$E_0(\text{ions}) = -\frac{T_B - T_A}{T_A}E_0(\text{sub.}) + 4.598T_B\left[31.36 + \frac{1}{2.303}\left\{P\left(\frac{\epsilon}{kT_B}\right) - P\left(\frac{\epsilon}{kT_A}\right)\right\}\right.$$

$$-\frac{1}{2.303}\left\{S_E\left(\frac{\epsilon}{kT_B}\right) - S_E\left(\frac{\epsilon}{kT_A}\right)\right\} + 2.605\left\{D\left(\frac{\theta}{T_A}\right) - S_D\left(\frac{\theta}{T_A}\right)\right\}$$

$$\left. + \log W_M W_X + \log T_B + 3\log T_A + 2\log A + 2\log F - \log \delta_+\delta_-\right]. \quad (6)$$

This method of calculation, due to the partial elimination of the constants of the molecule gas, considerably reduces errors present in the original work on CsI and KI.

DISCUSSION OF THE METHOD AND ERRORS

In order to give an idea of the relative importance of the factors involved in the calculations the numerical values for experiment (1) in Table II are reproduced in Table I.

TABLE I.

$[(T_B - T_A)/T_A]E_0$ (sub.)	= 26.0 kcal.
4.598 T_B	= 6.04 kcal./2.303
numerical constant	= 31.36
log $W_M W_X$	= 3.83
log T_B	= 3.12
3 log T_A	= 8.80
$2.6[D - S_D]_{T=T_A}$	= -6.87
$(1/2.3)[(P_B - P_A) - (S_A - S_B)]$	= -0.12
2 log A	= -5.85
2 log $F - \log \delta_+\delta_-$	= -4.68
sum	= 29.59
4.598 $T_B \times$ sum	= 178.5 kcal.
Lattice energy	= 152.5

It is evident that an error of 5 percent in $\int_0^T C_p dT - TS$ for the crystalline salt, corresponding to the same percentage error in $S(\theta/T) - D(\theta/T)$ would introduce about 2 kcal. error into the final lattice energy. This is possible, and the greatest single questionable item in the calculations alone. A fairly large error in the frequency of the gaseous molecule would have a negligible effect.

The 5 percent uncertainty (2.5 kcal.) in the energy of sublimation, $E_0 MX$, introduces only 1 kcal. uncertainty in the lattice energy. About 3 kcal. maximum error, and probably considerably less, is then introduced by uncertainties in data unconnected with the experiment itself.

The temperatures are undoubtedly measured correctly in the experiment to better than 5°, which would introduce about 0.25 percent or about 0.5 kcal. uncertainty. Although the deflections are measured with considerable accuracy the fraction of the beam measured, and diameter of the hole necessarily introduce some 25 percent error in this term, or about 1 kcal. in the lattice energy.

One may then expect a maximum error of ±3 kcal. due to uncertain values used in the calculations ±1.5 kcal. due to inherent experimental errors, *provided only* that the current measured is due to ions emitted from the oven and *provided* Eq. (5) relating the current measured to the pressure of ions in the oven holds correctly.

It is difficult to state exactly all the reasons adduced by the authors for believing that actually only ion currents from the oven were measured in the experiments reported. In various experiments not here reported stray currents undoubtedly existed. In many runs when salt had previously coated the outside of the oven at H in Fig. 1 abnormal positive currents and some negative currents were observed at even comparatively low temperatures. These currents dropped rapidly with time, presumably as the salt and other possible impurities distilled off the platinum plate. In other experiments when the shield G of Fig. 1 was absent abnormal stray currents were observed. Certain elementary reasons for believing that the currents observed in the reported experiments were due only to ions from the oven orifice may be given.

(1) The experiments were reproducible when no obvious difficulty arose.

(2) Without salt in the oven no deflections were observed. In one case during a run the salt

completely evaporated from the oven and the deflections fell to zero.

(3) Over a range of 125° and sevenfold change in current no systematic change in the calculated lattice energies is observable.

(4) Variations of the current with voltages applied to the screen I and Faraday cage D of Fig. 1 agreed qualitatively with the expected behavior of ions emerging from the hole H with about 0.05 volt energy and directions distributed according to a cosine law.

(5) Current with NaCl and RbBr in the oven differed by 35-fold in agreement with probable theoretical values of the lattice energies.

With regard to the second factor, the validity of Eq. (5) only negative remarks can be made. It is to be expected that what may be called a contact potential will exist between the gas in the interior of the oven and the platinum surface surrounding the hole H. An ion sheath will clothe the surface. An ion will then, depending on its sign, either be accelerated toward the hole H or repelled from it. It is consequently not to be expected that exactly equal numbers of negative and positive ions, or exactly numbers in the ratio of the square roots of the molecular weights, will emerge. For one ion species the deflection will be larger than that corresponding to the existing pressure, and for the other smaller. This effect is actually observed. The positive ion currents are always considerably larger than the negative ion currents, and the factor is in some cases as large as three. However, if this interpretation is correct the approximation of using the product of the two deflections in Eq. (6) will not be greatly in error. It is to be emphasized here that a threefold error in the estimation of the pressure of one of the ion species introduces only a 3 kcal. error in the final lattice energy, an error of 2 percent.

It is hoped that a slightly altered experimental technique and apparatus will enable us to completely obviate this uncertainty.

Little has been said in the above about the factor F in Eq. (5) giving the fraction of the ions caught by the Faraday cage. The screen I transmits only a certain fraction dependent on its transparency. If the true potential difference between H and I (Fig. 1) were exactly zero, a certain fraction calculable from cosine law

emission and the geometry of the apparatus would hit the screen. As was to be expected this true zero of potential difference was found not to be zero as read on a voltmeter, but different (by 0.3 volt) due to the contact potentials and high temperature gradients existing at the connecting parts. If the potential of I were raised with respect to H (in either direction) one of the ion species would be accelerated perpendicular to the oven face and the fraction of these ions striking within the diameter of the hole at I should rise asymptotically to 1. This fraction should approach very nearly 1 at about 1 or 2 volts. This behavior was observed. By this method the authors believe that they were able to estimate the deflections when 100 percent of each of the ion species were striking within the hole radius I to within better than 20 percent.

RESULTS

The result of 10 experiments on RbBr and 2 experiments on NaCl are given in Table II. The lattice energies of RbBr and NaCl deduced from the experiments, 151.3 and 181.3, respectively, agree well with the theoretical values 153.5 and 183.1 previously calculated by us.[3] The authors would be inclined to set an upper limit of 4.5 kcal. on the possible error of the experimental values, about 3 kcal. of which are due to uncertain data for the specific heat of the salts and the heat of sublimation. In addition there is, however, a *possible* error of some ±3 kcal. due to possible faulty interpretation of the results, which error, however, if it exists, will be

TABLE II. *Lattice energies of RbBr and NaCl.*

Salt	T_B (°K)	T_A (°K)	Deflections (δ_+ mm)	(δ_- mm)	Lattice energy (kcal.)
RbBr	1316	860	169	103	152.5
"	1319	868	188	116	153.2
"	1262	831	84	45	149.4
"	1260	837	91	32	152.2
"	1251	827	61	22	150.1
"	1244	830	39	14	152.0
"	1230	827	32	9	152.0
"	1226	827	31	6	151.7
"	1211	810	33	16	149.5
"	1197	824	25	15	150.3
NaCl	1264	945	13.5	11	181.7
"	1160	932	2.3	1.5	181.0

Average lattice energies, RbBr 151.3, NaCl 181.3 kcal.

systematic in the sense that it has the same sign and closely the same order of magnitude for both salts. The usual method of calculating probable error by root-mean-square method leads to ±2.5 kcal. neglecting the possible systematic error, and ±4 kcal. including this. Owing to the small number of experiments carried out on NaCl there is an additional uncertainty in this case.

With the Born cycle, and the particular values of ΔE for the involved reactions previously used by us, the electron affinity, ΔE for the reaction $X_{gas} + e^-_{gas} \rightarrow X^-_{gas}$ 0°K, is calculated to be 84.2 kcal. for Br and 88.3 kcal. for Cl.