

Effect of Pressure on the Melting Points of Eight Alkali Halides*

SYDNEY P. CLARK, JR.

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.

(Received June 15, 1959)

The melting curves of the alkali chlorides and the sodium halides have been determined at high pressures. The results can be represented within experimental error by Simon's equation. Comparison of the slope of the melting curve at low pressure with measurements of the changes of volume and entropy upon fusion suggests that the latter data are systematically in error.

I. INTRODUCTION

PREVIOUS investigations of the effect of pressure on melting points have largely been concerned with metals, organic compounds, and "solidified gases" (He, N₂, etc.). In the present work the list of substances studied is extended to include simple ionic compounds, thereby providing a further test of the validity of both Simon's equation of the melting curve and various interpretations of the parameters appearing in this equation.

The melting curves of the five alkali chlorides and of the remaining sodium halides have been followed to a maximum pressure close to 25 000 bars. Large changes in melting point were produced; in most cases the temperature of fusion was increased by 300 to 500°C. Experimental values of the initial slopes of the melting curves provide a measure of the internal consistency of the measurements of changes of volume and entropy upon fusion recorded in the literature. In addition, triple points at which two solid polymorphs and liquid coexist were located for KCl, RbCl, and CsCl.

II. EXPERIMENTAL METHOD AND RESULTS

Apparatus

Measurements at the higher pressures were made in the compound apparatus developed by Francis Birch at Harvard University. This equipment has been described previously.¹ Pressures were determined to within about 100 bars by the change in resistance of a coil of manganin wire. Temperatures were measured with Pt-Pt 10% Rh thermocouples. The charges were heated in a resistance furnace mounted inside the pressure vessel.

Temperatures of 1400°C have been reached in this apparatus by using small furnaces, but the present experiments required a furnace 0.25 in. in inside diameter. It was not possible to attain temperatures above about 1150°C without exceeding the capacity of the constant-voltage transformer which supplied the power.

Because of discrepancies between the results obtained in the high-pressure apparatus and thermochemical

data, the melting curves were redetermined up to 1300 bars in other equipment. This apparatus is a thick-walled tube, mounted in a horizontal position, containing a furnace that is somewhat larger than the vertically mounted one in the high-pressure equipment. Pressure was measured to within 10 bars with a Bourdon gauge, and temperature was measured with chromel-alumel thermocouples swaged in pressure-tight sheaths of inconel.

The power required to reach a given temperature roughly doubles as the pressure is raised from atmospheric to 1000 bars. The change over the remainder of the pressure range is less than this, even in the high-pressure apparatus. This is accompanied by changes in thermal gradients throughout the apparatus, and errors due to such causes should appear at the lower end of the pressure range. The low-pressure equipment was designed to make any such errors as different as possible from those in the high-pressure apparatus. Hence, the good agreement between the two sets of data can be taken as evidence that the results are free from instrumental bias.

Method

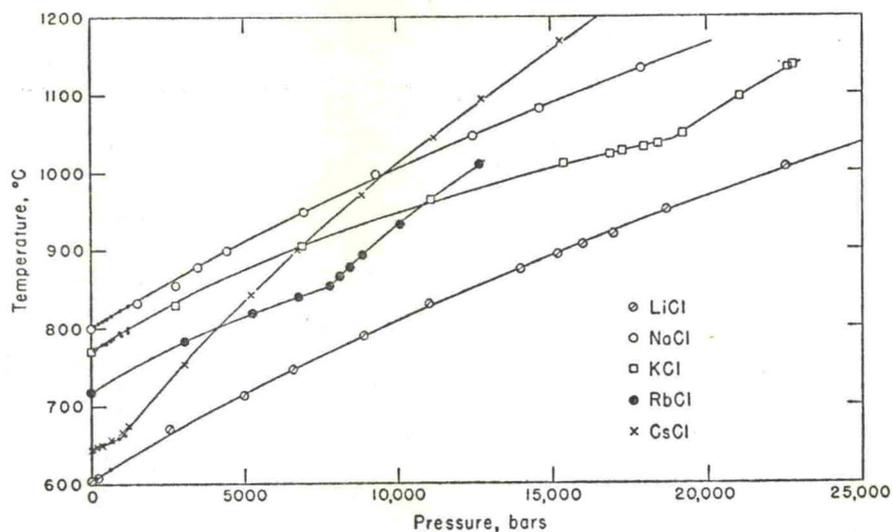
In the high-pressure apparatus, several Pt capsules containing the salt were packed around a thermocouple, and similar capsules, filled with Al₂O₃, surrounded another which was placed at the same level in the furnace. Melting and freezing were detected by changes in the rates of heating or cooling and by changes in the difference between the temperatures of the two thermocouples. Capsules with a reentrant tube in which the thermocouple was placed were used in the low-pressure apparatus. This improvement, and the greater sensitivity of the thermocouples, enabled the melting curve to be determined by arrests in heating and cooling without the use of a second thermocouple. In all cases the capsules were sealed by welding in order to prevent solution of the pressure media (nitrogen or argon) in the molten salt.

The accuracy with which the melting points could be located was limited by rounding of the arrests in the rates of heating and cooling. The melting curve was crossed several times at each pressure, and the rates of heating and cooling were varied. Because of the small thermal inertia of the system it was not possible to

* Published with the partial support of the Committee on Experimental Geology and Geophysics, and the Division of Geological Sciences at Harvard University.

¹ Birch, Robertson, and Clark, *Ind. Eng. Chem.* **49**, 1965 (1957).

FIG. 1. Melting curves of the alkali chlorides. The small dots represent points obtained with the low-pressure apparatus.



change the temperature at a rate much less than 20°C per minute, but faster rates did not change the results. In the high-pressure apparatus melting points obtained from heating curves could be repeated to within 2°C. Cooling curves gave results that were irregularly lower because of supercooling. Arrests on heating rarely lasted more than a few seconds; they were accompanied by a pronounced maximum in the difference in temperature between the two thermocouples, which was taken as an equally good indication of the melting point. On the basis of the reproducibility of the data, a generous estimate of the uncertainty is $\pm 5^\circ\text{C}$ for most salts. For some unknown reason the melting curves of NaBr and NaI proved to be more difficult to locate in this apparatus, and the determinations of the melting points of these salts are uncertain by $\pm 10^\circ\text{C}$.

More accurate results were obtained in the low-pressure apparatus because of its greater sensitivity. Arrests on cooling were particularly sharp; the tempera-

ture remained constant to within 0.2°C for as long as 30 seconds in many instances. Results on heating and cooling rarely differed by as much as 1°C, and the data are almost certainly accurate to within $\pm 2^\circ\text{C}$. Results for NaBr were as sharp as those for the other salts in this apparatus.

The quantity that was actually measured was the change in melting point with pressure. Melting points of the salts at atmospheric pressure were measured in the pressure apparatus; the results served to calibrate the thermocouples *in situ*. The calibration always fell within a few degrees of the standard tables and did not change with time. Deviations from the tables varied smoothly with temperature for any particular thermocouple.

The melting points of the lots of salts used in the experiments were determined by conventional means with Pt-Pt 10% Rh thermocouples calibrated against the melting points of NaCl (800.5°C) and KCl (770°C).

FIG. 2. Melting curves of the sodium halides. The small dots represent points obtained with the low-pressure apparatus.

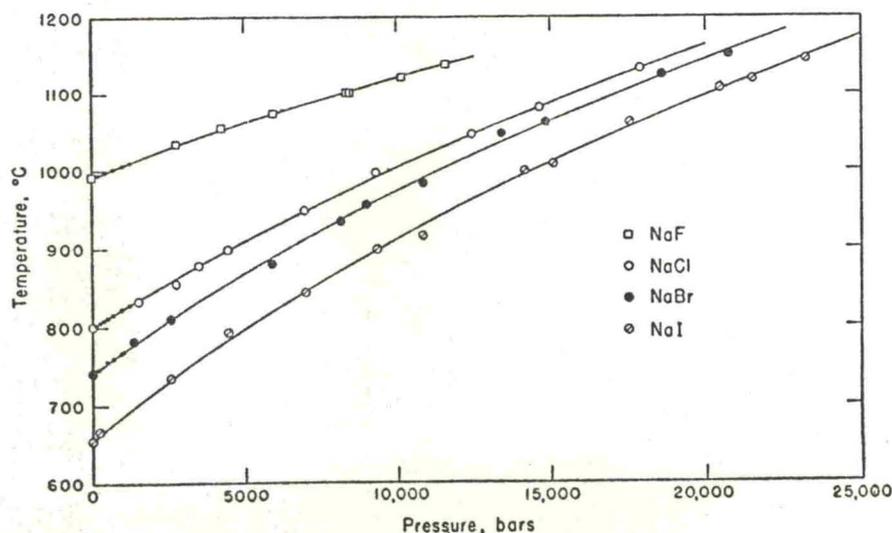


TABLE I. Parameters of the Simon equation.

Compound	T_0		P_0 bars	A bars	c	Standard deviation °C
	°K	°C				
LiCl	878	605±0.5	0	14 500±1000	2.5±0.1	2.6
NaF	1265	992±0.5	0	14 300±3000	5.5±1	1.3
NaCl	1073.5	800.5	0	16 700±900	2.7±0.1	3.3
NaBr	1014	741±0.5	0	12 200±500	2.9±0.1	5.6
Na I	928	655±0.5	0	10 100±400	2.8±0.1	6.1
KCl I	1043	770	0	6 900±700	5.7±0.5	2.3
KCl II	1315	1042±5	18,950	12 100	4*	1.0
RbCl I	990.5	717.5±0.5	0	6 600±700	6±0.3	0.6
RbCl II	1127	854±5	7,800	7 200±1000	4±0.3	1.9
CsCl I	917	644±0.5
CsCl II	933	660±5	950	8 400±600	2.3±0.1	1.5

* Assumed value.

These values were established by the careful work of Roberts.²

Since the thermocouples in the high-pressure apparatus are exposed to pressure, it is necessary to correct for its effect on their thermal emf. The correction is given by $\Delta T = 0.7 \times 10^{-6} PT$, where P is the pressure in bars, T is the centigrade temperature, and ΔT is the correction to be added to the measured temperature. The correction was determined by linear extrapolation of Birch's measurements,³ and its maximum value is 18°C in the present work. This is roughly ten times the maximum correction in Birch's range of pressure and temperature and the accuracy of the extrapolation cannot be high. The only alternative to the large extrapolation is to ignore this correction entirely, and this is felt to be the greater of the two evils.

Materials

Salts obtained from Mallinckrodt Chemical Works were used in the high-pressure experiments. All except RbCl and CsCl were of AR grade and all were used without further purification. The RbCl contained about 0.1% KCl and less than 0.1% NaCl. The CsCl contained less than 0.2% KCl and less than 0.1% NaCl and CaCl₂. Several different lots of salt were tried in the low-pressure apparatus. They included optical quality crystals of NaCl and KCl from Harshaw Chemical Company, CsCl from the Maywood Chemical Company, and several AR grade salts from the Fisher Chemical Company. The Maywood CsCl contained less than 0.1% KCl and the same amount of NaCl. All the analyses mentioned above were made with a flame photometer by Dr. P. M. Orville.

The influence of water on the melting curves was determined by partially dewatering the salts by heating them slowly to the melting point *in vacuo* and sealing the capsules in a dry box. Although this procedure does not remove all the water, it changes the water content, particularly for deliquescent salts such as NaBr or

LiCl. This treatment affected the melting points at atmospheric pressure and the initial slopes of the melting curves by less than the experimental error (0.5°C and 0.001°C/bar, respectively). Results from the different lots of salts agreed to within the same limits. One experiment with KCl was made in a gold capsule; it agreed with the others.

Results

The data are shown in Figs. 1 and 2. The breaks in slope of the melting curves of KCl, RbCl, and CsCl mark triple points between solid I (NaCl structure), solid II (CsCl structure), and liquid. The curves in the figures were calculated from the Simon equation,

$$P - P_0 = A[(T/T_0)^c - 1], \quad (1)$$

where T_0 is the melting point at pressure P_0 , and A and c are adjustable constants. P_0 differs from zero only for the high-pressure polymorphs of KCl, RbCl, and CsCl; in the latter cases P_0 and T_0 are the coordinates of the triple points.

Simon's equation is not readily adapted to rigorous treatment by least squares, and an approximate procedure was adopted. The right side of Eq. (1) was evaluated with trial values of c , and A was then calculated by linear regression. The value of c which minimized the sum of the squares of the residuals was found by graphical interpolation. The equation was fitted to the measurements made in the high-pressure apparatus only.

The parameters of the Simon equation are given in Table I. The differences between the chaotic values in the literature for the melting points of these salts at atmospheric pressure, and T_0 as given in the table may be due in part to differing purity of material, but many discrepancies must be attributed to erroneous pyrometry.

The uncertainties in c and A were estimated by examining the trend of the residuals. Changing these parameters by more than the limits given in the table definitely impairs the fit of the experimental observa-

² H. S. Roberts, Phys. Rev. **23**, 386 (1924).

³ F. Birch, Rev. Sci. Instr. **10**, 137 (1939).

tions. This method of fitting and of estimating uncertainty assumes that the experimental points are perfectly accurate. Larger corrections might be required if neighboring points are in error in the same direction.

Small changes in c can be largely offset by changing A in the opposite direction. Hence the product cA is better determined than either quantity taken separately. The initial slopes of the melting curves are inversely proportional to this product, and they are fixed by the experiments within a few percent. But because the best value of A depends on the value adopted for c , extrapolation of the experimental results by means of the Simon equation is hazardous.

Agreement between the data from the low-pressure apparatus and the curves of Figs. 1 and 2 is excellent except for KCl. In this case the slope of the melting curve at $P=0$ is about $0.002^\circ\text{C}/\text{bar}$ higher than that found experimentally. Taking this slope as $0.0245^\circ\text{C}/\text{bar}$ from the low-pressure experiments and insisting that the curve pass through the triple point at 18 950 bars and 1315°K yields $A=8350$ bars and $c=5.1$ (cf Table I). The new parameters lead to a standard deviation roughly 50% greater than that given in the table. A discrepancy of this magnitude is hardly surprising, and it is difficult to say which pair of values of A and c is to be preferred.

The exponent c is considerably higher for NaF than for the other sodium halides. The values for LiCl and NaCl are smaller than those for KCl and RbCl. Since the properties of potassium and its compounds commonly show greater similarity to those of rubidium than to those of sodium, this result is perhaps not surprising. The high-pressure polymorphs have lower values of c than do the low-pressure forms, judging mainly from the data for RbCl.

The values of A are comparatively small when c is large. A is small for NaF and declines with increasing molecular weight for the remaining sodium halides. It reflects the changes in c for the alkali chlorides. The product Ac depends somewhat more regularly on molecular weight than either parameter by itself; this may be the result of the difficulty in uniquely fitting a two-parameter equation to the experimental results.

Other qualitative features of the data are the convergence of the melting curves of the sodium halides, and the crossing of those of several of the alkali chlorides. At 30 000 bars the order in which the four heaviest chlorides melt is reversed, and the melting points of all these salts increase with molecular weight.

III. DISCUSSION

Thermodynamic Calculations

The initial slope of the melting curve, $(dT/dP)_{P=0}$, is T_0/Ac according to Eq. (1). It is also equal to $\Delta V_f/\Delta S_f$, where ΔV_f and ΔS_f are the changes of volume and entropy on melting. Observed values of the initial slopes are compared with those calculated from Clapeyron's equation in Table II. The two sets of data agree

TABLE II. Melting parameters.

Compound	ΔS_f cal/mol deg	ΔV_f cm ³ /mol	$\Delta V_f/\Delta S_f$ deg/bar	dT/dP observed deg/bar
A. At zero pressure				
LiCl	3.6 ^a	5.88 ^b	0.039	0.0242
	5.6 ^b		0.025	
NaF	5.5 ^b	4.64 ^b	0.020	0.0161
	6.2 ^a		0.016	
NaCl	6.3 ^a	7.55 ^b	0.029	0.0238
	6.7 ^b		0.027	
NaBr	5.9 ^a	8.07 ^b	0.033	0.0287
	6.0 ^b		0.032	
Na I	5.6 ^{a,b}	8.58 ^b	0.037	0.0327
KCl	5.8 ^a	8.35 ^c	0.034	0.0265 (0.0245)
	6.2 ^b		0.028	
RbCl	4.4 ^{a,b}	6.72 ^b	0.036	0.0249
CsCl	3.9 ^{a,b}	5.69 ^b	0.035	0.017
			5.5 ^d	
B. At the triple points				
KCl I	5.6 ^e	2.1 ^e		0.0089
KCl II	5.5 ^e	6.3 ^e		0.0272
RbCl I	5.1 ^e	2.8 ^e		0.0131
RbCl II	5.4 ^e	8.9 ^e		0.0391
CsCl I	4.2±0.6 ^e	3.0±0.4 ^e		0.017
CsCl II	5.0±0.7 ^e	10.0±1.4 ^e		0.0483

^a Rossini *et al.*⁶

^b H. Schinke and F. Sauerwald, *Z. anorg. u. allgem. chem.* **287**, 313 (1956).

^c G. J. Landon and A. R. Ubbelohde, *Trans. Faraday Soc.* **52**, 647 (1956).

^d Johnson, Agron, and Bredig, *J. Am. Chem. Soc.* **77**, 2734 (1955).

^e Estimated values. See text.

well for NaF. For most of the remaining salts the discrepancy is less than 20%, but RbCl and CsCl are inconsistent by factors of 1.5 and 2. Discrepancies of 20% are probably not surprising considering the present state of high-temperature thermochemistry, but it is disturbing to find that the observed slopes tend to be systematically lower than those calculated. ΔV_f has been consistently overestimated or ΔS_f consistently underestimated unless, improbably, unsuspected systematic errors affect the results obtained in both the high-pressure and low-pressure equipment by the same amount.

The source of the discrepancy for CsCl can be deduced from relations at the triple point. The I-II transition at atmospheric pressure takes place at 470°C ⁴; if the phase boundary is linear between this point and the triple point (which is probably nearly true for a solid-solid transition over the short range of P and T involved), its slope is $0.20^\circ\text{C}/\text{bar}$. Wagner and Lippert⁵ give $6\text{ cm}^3/\text{mole}$ for the volume change (ΔV_{tr}), and a compilation of data yields a value of $8\text{ cm}^3/\text{mole}$.⁴ These

⁴ Johnson, Agron, and Bredig, *J. Am. Chem. Soc.* **77**, 2734 (1955).

⁵ G. Wagner and L. Lippert, *Z. physik. chem.* **B31**, 263 (1936).

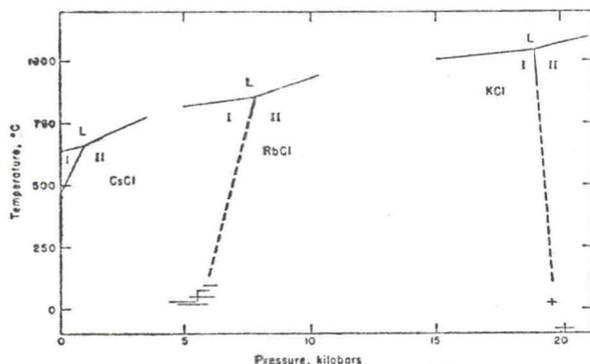


FIG. 3. Phase diagrams of KCl, RbCl, and CsCl near the triple points. The horizontal lines at low temperatures represent the ranges of pressure over which Bridgman observed the I-II transitions, and the vertical lines show his mean transition pressures.

data combined with the slopes of the melting curves at the triplet point serve to determine the remaining changes of volume and entropy (Table 2B). The uncertainties given in the table are only those arising from the uncertainty in ΔV_{tr} at atmospheric pressure; the slopes are assumed accurate.

Wagner and Lippert⁵ calculated the lattice energies of the two modifications of CsCl from the lattice constants. The difference between the two forms at the transition temperature, 1.8 kcal/mole, has crept into compilations of thermochemical data⁶ as the heat of transition. The value obtained from the mean slope of the transition line, 0.7 ± 0.1 kcal/mole, is to be preferred.

A similar analysis of the relations at the triple points of KCl and RbCl is subject to greater uncertainties because of the longer extrapolation required and because of the inferior purity of the RbCl used in this investigation. Assume, however, that the I-II transition can be represented by straight lines connecting the triple points with Bridgman's data at about room temperature (Fig. 3), and that $\Delta V_{tr} = 4.2$ cm³/mole for KCl⁷ and 6.1 cm³/mole for RbCl.⁸ The parameters of the melting curves are then those given in Table IIB.

The results suggest that the calorimetric value of ΔS_f is too low for RbCl, since this quantity decreases along the melting curves of other substances,⁹ and decreases initially for KCl. The large decrease in ΔV_f is to be expected in view of the high compressibility of molten salts.¹⁰ But these suggestions, depending as they do on assumptions about ΔV_{tr} and the slopes of the I-II transition curves, must be considered tentative.

⁶ Rossini *et al.*, Natl. Bur. Standards Circ. 500 (1952).

⁷ P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **74**, 21 (1940).

⁸ P. W. Bridgman, Z. Krist. **67**, 363 (1928).

⁹ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, England 1952), revised edition, p. 201.

¹⁰ J. O'M. Bockris and N. E. Richards, Proc. Roy. Soc. (London) **A241**, 44 (1957).

Parameters in the Simon Equation

Salter¹¹ has argued that $A = (\partial U/\partial V)_{T=0}$ for the solid. This result is the automatic consequence of the fact that both quantities equal the negative of the pressure required to cause melting at 0°K. But there is no *a priori* reason to single out the solid for emphasis, and by definition $A = (\partial U/\partial V)_{T=0}$ for the liquid as well. Besides, there is no guarantee that Eq. (1) is valid at temperatures near zero and at negative pressures.

The parameter A is compared with $(\partial U/\partial V)_T$ at atmospheric pressure and the melting point in Table III. It is smaller than the latter quantity for the solids, but agrees better with the values for the liquids and with the differences between solids and liquids. The interpretation of A as the difference between the "internal pressures" of solid and liquid at low external pressure has intuitive appeal; it apparently fails in the case of the alkali metals, however, since A has been found to be larger than $(\partial U/\partial V)_T$ of these solids.¹² There is a distinct possibility of experimental error here, since the chemical activity and mechanical softness of the alkali metals makes measurement of their properties near the melting point difficult.

Theoretical values of c given by Domb,¹³ de Boer,¹⁴ and Salter¹¹ are near unity for these salts. This is definitely too low. They fit experimental data for the rare gases better, but also fail for the alkali metals. Gilvarry's theory¹⁵ predicts values of A which are too high by a factor of 2 or 3 for NaCl and KCl. All these theories contain approximations which are not strictly valid for ionic crystals, and the disagreement is perhaps to be laid to their account.

The present work demonstrates that the Simon equation can represent the melting curves of ionic compounds at high temperatures. But this does not imply that this representation is unique or even the best at

TABLE III. $(\partial U/\partial V)_T$ and A .

	$(\partial U/\partial V)_T$ solid	$(\partial U/\partial V)_T$ liquid	Difference	A
NaCl	26 000 ^a	13 250 ^d	12 750	16 700
NaBr	22 200 ^b	10 100 ^d	12 100	12 200
NaI	14 800 ^b	8 950 ^d	5 850	10 100
KCl	17 700 ^c	10 800 ^d	6 900	6 900 (8 350)

^a Thermal expansion from A. Eucken and W. Dannohl, Z. Elektrochem. **40**, 814 (1934); compressibility from L. Hunter and S. Siegel, Phys. Rev. **61**, 84 (1942).

^b Extrapolated from room-temperature data.

^c Thermal expansion from R. E. Glover, Z. Physik **138**, 222 (1954); compressibility from C. B. Cooper and F. D. Enck, Department of Physics, University of Maryland Technical Report No. 11 (1955).

^d Bockris and Richards.¹⁰

¹¹ L. Salter, Phil. Mag. **45**, 369 (1954).

¹² F. E. Simon, Nature, **172**, 746 (1953).

¹³ C. Domb, Phil. Mag. **42**, 1316 (1951).

¹⁴ J. H. de Boer, Proc. Roy. Soc. (London) **A215**, 5 (1952).

¹⁵ J. J. Gilvarry, Phys. Rev. **102**, 325 (1956).

tainable with two disposable constants. The significance of the parameters appearing in this equation cannot be determined because theory has failed thus far to predict the experimentally determined values.

Present experimental evidence is consistent with the conclusion that the melting curve rises indefinitely with increasing pressure, and the Simon equation contains this feature. It has been suggested that the melting curve passes through a maximum temperature, approaches an asymptomatic temperature, or ends at a critical point. None of these alternatives has been

realized experimentally in one-component systems, and Bridgman's arguments⁹ against them, which are based on the behavior of melting curves at lower temperatures, are still valid.

ACKNOWLEDGMENTS

I wish to express my appreciation to Professor Francis Birch of Harvard University for his support and encouragement of this work. I have benefited from helpful discussions of thermochemical data with Dr. R. A. Robie of the U. S. Geological Survey.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 31, NUMBER 6

DECEMBER, 1959

Contribution of Bound, Metastable, and Free Molecules to the Second Virial Coefficient and Some Properties of Double Molecules*

DANIEL E. STOGRYN† AND JOSEPH O. HIRSCHFELDER

Theoretical Chemistry Laboratory, University of Wisconsin, Madison 5, Wisconsin

(Received May 19, 1959)

The second virial coefficient for molecules interacting with a spherically symmetric potential is divided into three parts: (1) a contribution B_b , related to the equilibrium constant for the formation of bound double molecules; (2) a contribution B_m , related to the equilibrium constant for the formation of metastably-bound double molecules; and (3) a contribution B_f , due to molecules which interact but are free to separate after the interaction. Equations are given for determining each of the three parts of the second virial coefficient. A detailed treatment of these three contributions together with numerical tables on a reduced temperature basis is given for the square-well, Sutherland, and Lennard-Jones (6-12) potentials.

The mean lifetimes of metastably bound double molecules are discussed, and numerical values are given for the special case of argon. Tables for computing mean lifetimes in other Lennard-Jones gases are given. It is found that most metastably bound double molecules have mean lifetimes considerably longer than the mean time between collisions at ordinary pressures. Finally, an equation is developed for the number of vibrational levels of a double molecule.

I. INTRODUCTION

THE equation of state of a dilute gas can be expanded in the virial form

$$PV/RT = 1 + B(T)/V + C(T)/V^2 + \dots \quad (1)$$

Here $B(T)$, the second virial coefficient, can be expressed in terms of the energy of interaction between pairs of molecules. If the intermolecular potential, $\phi(r)$, depends only on the separation r and not on the relative orientations of the two molecules, then

$$B(T) = 2\pi N \int_0^\infty \{1 - \exp[-\phi(r)/kT]\} r^2 dr. \quad (2)$$

This relationship is easy to derive from statistical mechanical arguments and has been used¹ since 1908

* This work was carried out at the University of Wisconsin Theoretical Chemistry Laboratory under the Office of Naval Research Contract N7-onr-28511.

† Dow Chemical Company Fellow, 1957-1958. Present address: Lockheed Aircraft, Physics Research Department, Burbank, California.

¹ L. S. Ornstein, thesis, Leiden, 1908.

and maybe earlier. The simplicity of the second virial coefficient in terms of the intermolecular potential arises from the fact that the equation of state is an equilibrium property.

The second virial coefficient can be broken up into three parts,

$$B(T) = B_f(T) + B_b(T) + B_m(T). \quad (3)$$

Here $B_f(T)$ arises from collisions between free molecules; $B_b(T)$ is related to the equilibrium constant for the formation of bound double molecules (or dimers) in the gas; and $B_m(T)$ is related to the equilibrium constant for the formation of metastable double molecules (or dimers) which, according to quantum mechanics, can dissociate but which, according to classical mechanics, are firmly bound. Terrell Hill² has derived the equation for $Q_{2b}(T)$, the partition function for bound double molecules, and from this we

² T. L. Hill, *J. Chem. Phys.* **23**, 617, (1955); *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 5.