

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*

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(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.

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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.