phenyl compounds. Other than acidity constants, the fluorescence quenching rate constants can be studied utilizing these $\sigma^*$ constants.

These new $\sigma^*$ constants will be applied to the benzoic acid system to test and also to improve their generality. The work is in progress.

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# The Vacancies-in-Solid Model Applied to Solid Argon


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*(Received October 13, 1981)*


The molar volumes, the molar heat capacities and the molar entropies of solid argon are calculated from O K to the triple point using the vacancies-in-solid model. In the partition function, the central pairwise additive (Mie-Lennard-Jones 12,6) potential is used by introducing numbers, which is obtained by summing powers over all lattice points of a face-centred cubic in terms of the distance between nearest neighbours. A method of iteration is employed to evaluate the potential parameter, The results are compared with experimental values and other theoretical values. The results show a fair agreement with the experimental results.


## Introduction

The rare gas solids have long been used as model substances for testing theoretical studies of thermodynamic properties since the atomic interactions involve predominantly short ranged central forces which can be relatively accurately described for these substances. The representative theoretical studies are those of Herzfeld and Mayer[1], Rice[2], Henkel[3], Zucker[4] and Gupta *et al.*[5] Rice used Debye approximation to determine the thermodynamic properties of solid argon, assuming Grüneisen law be true. This gave best fit to the experimental specific heat data of Clusius[6]. But his cohesive energy expression showed large contributions from anharmonic terms even at low temperatures, which do not seem to be logical. Henkel used Einstein approximation and the effect of anharmonicity to calculate specific heats and

the equation of state of argon. Zucker extended this work to include zero point energy by a method of Domb and Salter[7]. The anharmonic Einstein theory for solid argon gives a better agreement with experimental results. However Zucker's validity for the much more complex physical problem has not been demonstrated[8], and the agreement between theory and experiments may be due to the result of the cancellation of many errors. Gupta *et al.* have theoretically studied the thermodynamic properties of the rare gas solids, taking into account the zero point energy. Their calculated values show a large discrepancy from observed values with increasing temperatures. Much has been written about the necessity for including anharmonic contributions to the free energy of a crystal lattice when calculating the thermodymanic properties of a particular model. The main purpose of this work is to emphasis that even a harmonic treatment predicts realistic values for the themodynamic properties. The present authors[9,10] have recently derived the solid partition function for monatomic crystals using vacancies-in-solid model which have taken account of two maximum phonon frequencies for the perfect oscillator and lattice vacancy defects, and then studied thermodynamic properties of solid krypton and xenon from 0 K to the triple point, using the Mie-Lennard-Jones (MLJ) 12,6 potential in a uniform field strength. The vacancies-in-solid theory is found to be successful in predicting the properties of rare gas solids over the whole temperature ranges, but discrepancies between calculated values and observed values at low temperatures may be due to an oversimplified model for the potential. This suggests that the potential function should be corrected. In the present work, the static lattice energy was employed, which is more realistic and theoretically justifiable. We report the theoretically calculated specific heats, molar volumes and entropies of solid argon over the whole temperature ranges in this work. We have compared our results with available experimental values and the other theoretical values. Finally, we are to test our validity of our vacancies-in-solid model.

## Theory

In the vacancies-in-solid moedl[9,10], we assume that regular lattice points of a real monatomic crystal are occupied by atoms ($N$) and vacancies ($n$) with a completely randomly distributed arrangement. Therefore we may consider the solid partition function as consisting of $x$ mole fraction of perfect crystal-like part and ($1-x$) mole fraction of imperfect crystal-like part together with a configurational part. The frequency distribution of an oscillator corresponding to a perfect crystal can be approximated to two peak frequencies Since an imperfect crystal contains lattice vacancies within it, an oscillator corresponding to it is able to make either an atom-vacancy link or atom-atom link, each corresponding to $\beta$-or $\alpha$-state arising from either appearance or disappearance of vacancies at the first neighboring site. The partition function of the imperfect oscillator in $\alpha$-state may be approximately equalized to that of a perfect oscillator. On contrary, the imperfect oscillator in $\beta$-state has only a lower frequency and a higher potential energy than those of the perfect oscillator. Summarizing discussions mentioned above, the canonical ensemble partition function $Q(N,V,T)$ for monatomic crystals is written as

$$Q(N, V, P) = Q_p Q_{imp} \tag{1}$$

where

$$Q_p = [2\sinh(\theta_{D\infty}/2T) \cdot 2\sinh(\theta_c/2T)]^{-(\frac{3}{2})N} e^{-\Phi_c/kT}$$

and

$$Q_{imp} = \frac{(N+n)!}{N!n!}(1+\Delta)^{(1-x)N}$$

with

$$\Delta = \left[\frac{\sinh(\theta_{D\infty}/2T)}{\sinh(\theta_C/2T)}\right]^{3/2} e^{-(\Phi_\beta - \Phi_c)/kT} \text{ and } x = V_0/V$$

Here $Q_p$ and $Q_{imp}$ represent thecanonical ensemble partition function of the perfect crystal-like part and the imperfect crystal-like part, respectively $\Phi_c$ and $\Phi_\beta$ are the static lattice energy per mole of the perfect oscillator and the imperfect oscillator, respectively. $\theta_{D\infty}$ is the limiting vlue of $\theta_D$ at high temperatures although from theoretical considerations $\theta_D \rightarrow \theta_{D\infty}$ rapidly for $T > \theta_{D/5}$ Other symbols have as the same meanings as in the previous paper. In this work we use the following interatomic potential $\phi(a)$ for a pair of atoms separated by a distance $a$,

$$\phi(a) = \frac{-\varepsilon}{n-b}[n(a_0/a)^6 - 6(a_0/a)^n] \tag{2}$$

In the case of argon, $n=12$, The static lattice energy is given by

$$\Phi_c = \frac{1}{2}N\varepsilon\left[S_{12}(a_0/a)^{12} - 2S_6\left(\frac{a_0}{a}\right)^6\right] \tag{3}$$
$$= D_e(S_{12}x^4 - 2S_6x^2)$$

with

$$x = (a_0/a)^3 = V_0/V \text{ and } D_e = \left(\frac{1}{2}\right)N\varepsilon$$

where $a_0$ and $a$ are the equilibrium nearest neighbor distance between two atoms at 0 K and a given temperature, respectively, and $\varepsilon$ is the depth of the potential well for two molecules at equilibrium separation. The $S_6$ and $S_{12}$ are numbers obtained by summing powers over all lattice points of a face-centred cube in terms of the distance between nearest neighbours. Here we will think the potential energy ($\phi_\beta$) of $\beta$-oscillator. Calculations of the vacancy formation enthalpy in rare gas solids have been made by Hall[11], Burton *et al.*[13,14] and Cotterill *et al.*[15,16] using a wide variety of potential. All these calculations find that there is little relaxation of the atoms around a vacancy independent of the model potential used. Their calculated vacancy formation energy of argon remain remarkably close to the available cohesive energy value per atom. Therefore the static potential energy per mole of the $\beta$-oscillator is given as follows

$$\Phi_\beta = \left(1 - \frac{n_1}{z}\right)\Phi_c \tag{4}$$

Here $z$ is the number of the nearest neighboling site. The structure of argon is a face centred cubic, $z$ is 12 in

the face centred cubic crystal. $n_1$ is the number of the vacancy in the nearest neighboring lattice site. In the case of Schottky defect crystals, the number of lattice vacancy is so small as to make it improbable that two vacancies on the average occupy neighboling sites, so that it is natural for us to assume only existence of a monovacancy around a given central atom.

## Results and Discussion

*Determination of Parameters.* According to Wallace and Patrick[17], the required lattice sums for the *fcc* lattice are $S_{12}$= 12.1318802 and $S_6$=14.4539211. The potential parameter ($D_e$) is determined by solving the equation of state for the solid by a method of iteration, using the observed properties, *i.e.* the triple point temperature, the molar volume at 0K and the triple point, and the Debye temperature ($\theta_{D\infty}$). According to our present model, the zero point energy ($E_z$) is given as follows

$$E_z=\left(\frac{3}{4}\right)R(\theta_{D\infty}+\theta_c) \tag{5}$$

This equation can be used to determine the characteristic temperature ($\theta_c$) of a low maximum phonon frequency. Beaumont *et al.*[18] show that $\theta_{D\infty}$ for argon probably lies between 82 and 85K. The zero point energy and the recent observed crystal properties for the argon have been taken from the reviewed paper of Pollack[19] and the review book of Klein *et al.*[20], respectively, The following physical properties are used: $T_t$=83.806 K; $V_t$=24.633 cm$^3$/mol; $V_0$=22.557 cm$^3$/mol; $\theta_{D\infty}$=83.5 K and $E_z$=187 cal/mol. For the calculations of thermodynamic properties, the following parametric values are estimated; $\theta_c$=42 K and $D_e$=43.502 cal/mol. The following calculations were carried out with the Hewlett packard 3000 computer.

*Molar Volumes.* The themodynamic pressure ($P$) of a crystal is equal to the negative isothermal volume derivative of the Helmholtz free energy A. Hence, the equation of state, which connects the state parameters, $P$,$V$ and $T$ of a solid, is

$$P(V,T)=P_{sl}(V)+P_{conf}(V,T)+P_{deg}(V,T)+P_{vib}(V,T) \tag{6}$$

where $P_{sl}$, $P_{conf}$, $P_{deg}$, and $P_{vib}$ are called static lattice, configurational, degenerate and vibrational pressure, respectively, and the vibrational pressure is assumed to be negligible, *i.e.* the vibrational frequency is assumed to be independent of the volume of a crystal. Finding the molar volume is equivalent to finding the equilibrium molar volume under zero pressure at various temperatures. By trial and error method, we may obtain $x(T)$ values for given temeperatures, then a molar volume ($V$) for a given temperature is estimated from the molar volume ($V_0$) at 0 K over the whole temperature since $x(T)=V_0/V$. Thus our theoretical curve is given in Figure 1 along with recent experimental data, and theoretical curves of Gupta *et al.*[5b] and Zucker[4] for comparisons. The experimental molar volumes are taken from X-ray measurements of Peterson *et al.*[21] and the bulk data of Smith *et al.*[22,23] The original experimental error has been given to be ±0.07 %. As shown in Figure 1, it is not surprising that our theoretical and the observed values agree

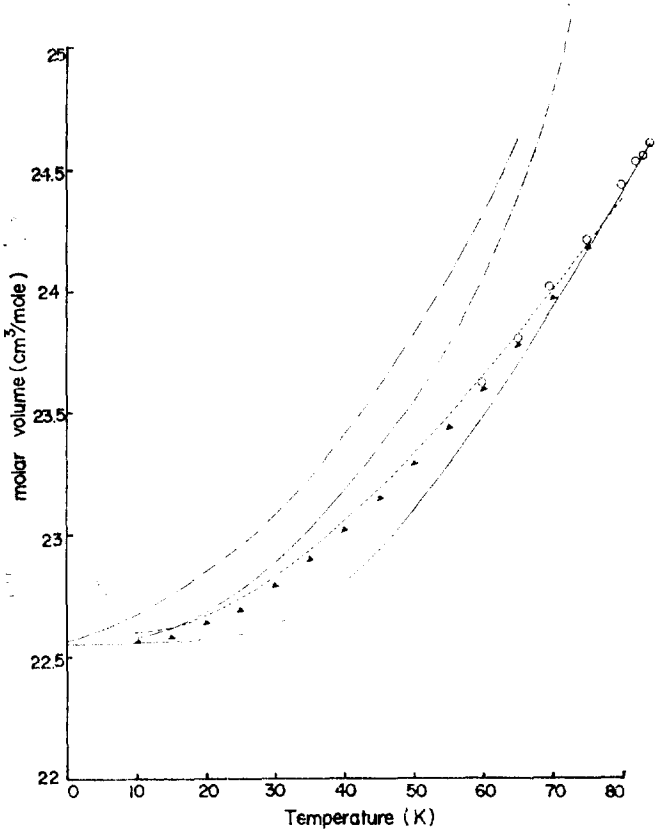


**Figure 1.** Molar volume–temperature curve for solid argon. Full triangles: obtained from X-ray measurements by Peterson *et al.*[21] Open circles: bulk data by Smith *et al.*[22,23] –··–: theoretical curve of Gupta *et al.*[5b] – · –: theoretical curve of Zucker's *quasi*–Debye theory[4]. – – –: theoretical curve of Zucker's anharmonic Einstein theory[4]. —: the present theoretical curve.

at 0 K and the triple point because molar volumes at 0 K and the triple point are used in determing potential parameter ($D_e$). The triple point is in fact the only fixed point in the calculations of the parameter. The comparison of the theoretical equation of state with experimental $V(P,T)$ is an especially sensitive test for anharmonicity. Our ($V$, $T$) curve refers to zero pressure. Our estimated molar volumes closely equal to observed molar volumes near the triple point, but with decreasing temperatures deviate more from observed molar volumes. It can be seen that our theoretical molar volumes are somewhat less than observed volumes between 0 K and the triple point. Our results of molar volumes show a maximum discrepancy near about $T \leq T_t/2$. The maximum relative discrepancy of the molar volume is 0.95 %. This discrepancy may be due to an inadequacy of the short range repulsive term in the potential function. Our results are in better agreement than those of Zucker based on *quasi*–Debye theory and Gupta *et al.*, using an exponential interatomic potential and zero point quantum effects. The theoretical molar volumes of Gupta *et al.* and Zucker[4] are all too high compared with observed values at high temperatures. The theoretical molar volumes of Zucker based on the anharmonic Einstein theory give a better agreement with observed values. However Zucker's validity for the much more complex physical problem has not been demonstrated.

*Heat Capacities.* In order to check on the accuracy of the

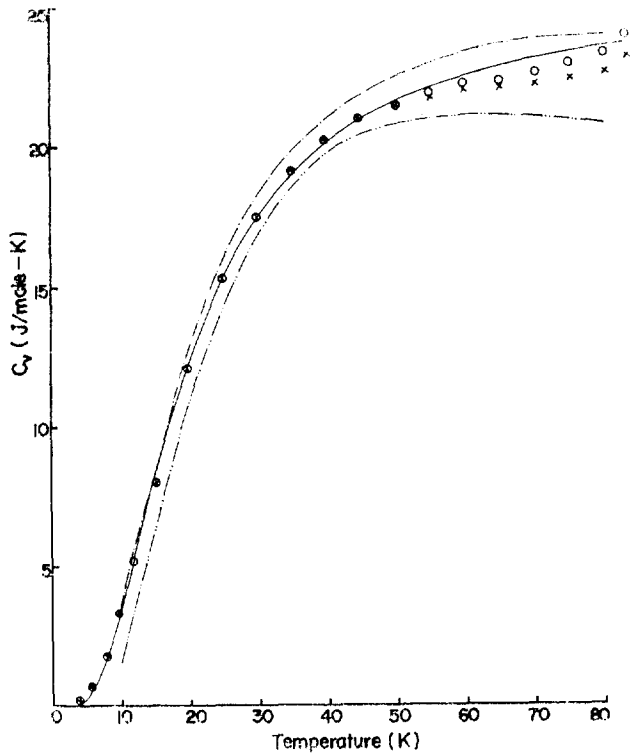


**Figure 2.** $C_v$–temperature curve of solid argon open circles: obtained by Peterson *et al.*[21] Crosses: obtained by Crawford *et al.*[25] – · –: theoretical curve of Zucker's *quasi*–Debye theory[4]. –··–: thoretical curve of Zucker's anharmonic Einstein theory. —: the present theoretical curve.

second derivatives of the partition function, the heat capacities are calculated up to the triple point. The isochoric heat capacity and the isobaric heat capacity are related to the partition function by the following equations

$$C_v=\left[\frac{\partial}{\partial T}\left(kT^2\frac{\partial}{\partial T}\ln Q\right)\right]_v \tag{7}$$

and

$$C_p=C_v-k\left[\frac{\partial}{\partial T}\left\{T\left(\frac{\partial}{\partial V}\ln Q\right)_T\right\}_v\right]^2\Big/\left(\frac{\partial^2}{\partial V^2}\ln Q\right)_T \tag{8}$$

The calculated results are presented in Figure 2 and 3 along with experimental data and the other theoretical results for comparisons. The observed isobaric heat capacities for argon have been taken from the measurements of Flubacher *et al.*[24] The original estimated accuracies of these $C_p$ data are ±2% at the lowest temperatures, decreasing 0.2 % at intermediate temperatures, and increase to ±0.5% at the highest temperatures near the triple point. The isochoric heat capacities for argon have been taken from Crawford *et al.*[25] and Peteraon *et al.*[21] The uncertainties in the $C_V$ data are large compared with the experimental $C_p$ data since they have been calculated using

$$C_v=C_p-TV\beta^2B_T \text{ and } C_v=C_p-TV\beta\left(\frac{\partial P}{\partial T}\right)_v \tag{9}$$

An original estimated uncertainties of $C_v$ data including all possible source of errors are ±0.3% at the low temperatures, increasing to ±2.2 % at the triple point. The theoretical curves of Zucker[4] using a *quasi*–Debye theory

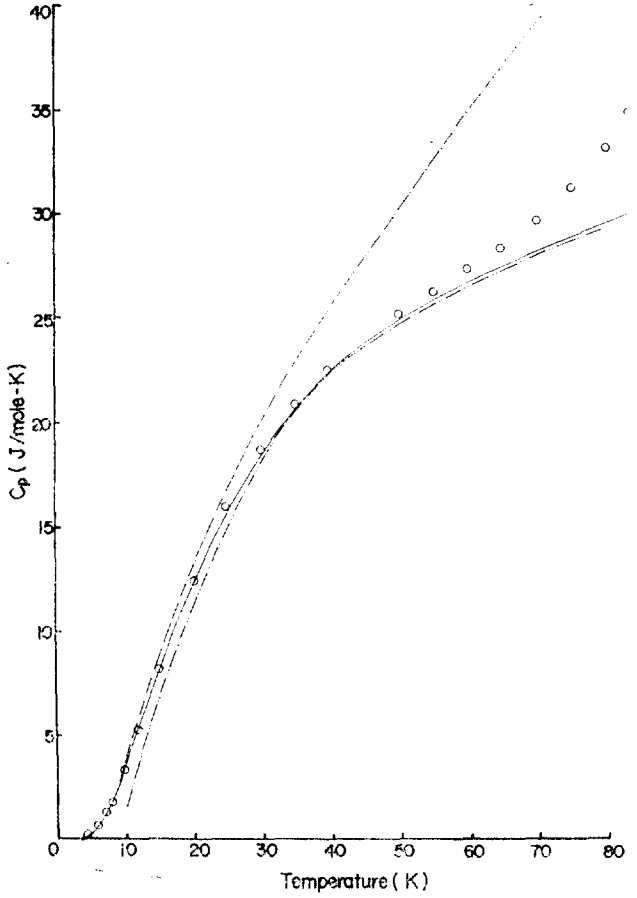


**Figure 3.** $C_p$–temperature curve of solid argon open circles: obtained by Flubacher *et al.*[24] – · –: theoretical curve of Zucker's quasi–Debye theory[4]. –··–: theoretical curve of Zucker's anharmonic Einstein theory. —: the present theoretical curve.

and an anharmonic Einstein theory have been drawn. The theoretical $C_v$ curve by Gupta *et al.* using a Born-Karman theory and a modified (exp, 6) potential have also been drawn. As shown in Figures 2 and 3, the present isochoric and isobaric heat capacities are in agreement with the experimental values except below about 6 K and near the triple point within experimental errors. At low temperatures the present heat capacity is slightly less than the observed values. As vacancies-in-solid theory is just a modified Einstein theory which have taken account of two maximum phonon frequencies for the perfect oscillator and lattice vacancy defects, this is just as might be expected. But as the temperature rises, the present $C_v$ does not approach $3R$ as the heat capacity of the Debye theory and the Einstein theory do. This is undoubtedly due to the effect of lattice vacancy defects and two maximum phonon frequencies. As approching to the triple point, our heat capacities do slightly deviate from the experimental values. This may be due to taking no thought of the effect of anharmonicities which are expected to be more prominent at more high temperatures. Our theoretical $C_v$ is in agreement with theoretical values of Gupta and Dayal[5a] up to an intermediate temperature (50 K) which they have calculated. Gupta *et al.* have not mentioned any heat capacity above the intermediate temperature. Our theoretical heat capacities are more in better

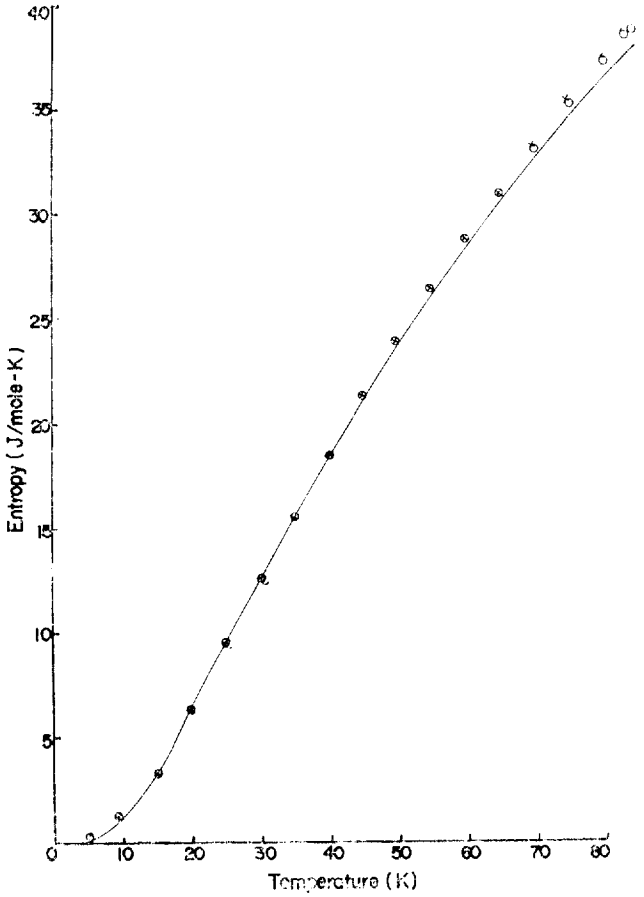


**Figure 4.** Entropy–temperature curve of solid argon Open circles: obtained by Crawford *et al*[25]. Crosses: obtained by Kuebler *et al.*[26] —: the present theoretical curve.

agreement with observed values than theoretical values of Zucker[4]. $C_v$ of Zucker's anharmonic Einstein theory is less than experimental values over the whole temperature range, and is especially much less than experimental values as approaching the triple point. This may be due to the excessive anharmonicities. $C_p$ of Zucker's *quasi*–Debye theory are also much greater than experiment and our heat capacities at high temmperatures. The present vacancies–in–solid model indicates that the magnitude of an anharmonicity contribution to heat capacities is not as great as what other workes[2-4] have mentioned. But the behavior of observed $C_v$ seems to be anomalous near the triple point.

*Solid Entropy.* The solid entropy is calculated by the relation.

$$S=k\ln Q+kT\left(\frac{\partial}{\partial T}\ln Q\right)_v \tag{10}$$

Our calculted resulats are presented in Figure 4 along with entropies which Crawford *et al.*[25] and Kubebler *et al.*[26] have determined. They evaluated the entropy of solid argon by a Simpson's rule integration of the smoothed heat capacity curve at constant pressure of Flubacher *et al.*[23] Two sets of entropy determined by them agree excellently at temperatures up to 65 K, but at higher temperatures the entropies of Kuebler *et al.* are somewhat larger than those of Crawford *et al.* The original estimated uncertainties of solid entropy determined by Crawford *et al.* are $\pm 0.2\%$ below 60 K and increase to $\pm 0.5\%$ at 83 K. All calculated entropies are in good agreement with entropies derived by the thermodynamic relation within the estimated uncertainties except near the triple point. Our theoretical entropy is somewhat less than derived entropy near the triple point. This may be due to taking no accout of the effect of anharmonicity. The large discrepancy on Gupta's and Zucker's values shows a general tendency to be found in all the theoretical values computed on the basis of a perfect crystal structure. Perhaps this will be arised from the fact that they have taken no account of lattice vacancy in contrast with our present theory. The present calculations show an agreement with the experimental results with approaching the triple point, compared with other theories. At the higher temperatures, these agreements between theoretical and experimental data may be interpreted as justifying our present theory.

## Conclusions

The solid partition function, based upon the vacancies–in–solid model, gives the equation of state, and equations of the heat capacity and the entropy which may be applied to their predictions over a wide range of temperatures. The critical test of any chosen potential function is how well this potential function provides the experimental crystal data beyond the points at which they are fitted. In all cases the present theory gives results agreeing more closely with available experimental data. This agreement may be interpreted as justifying the vacancies–in–solid model. Thus we may deduce some conclusions from present results as follows:

(1) The magnitude of anharmonicity contribution on thermodynamic properties is not as great as what other worker have mentioned.

(2) The two maximum frequency model ($\theta_D$ and $\theta_c$) for a perfect oscillator gives a better results to an estimation of the heat capacity and the entropy rather than an Einstein or Debye model.

(3) Although a perfect crystal exists at considerably low temperatures, it is required that the complete description of the solid takes account of the presence of vacancy defects.

(4) Ordinary equation of state of the solid based upon standard lattice theories involve pressures expressed in terms of the sum of the static lattice pressure and the vibrational pressure which is ignored by our model. Our model, however, indicates that the contribution of the configurational and isomeric degenerate pressure are more of importonce, especially near the triple point, rather than that of the vibrational pressure.

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# A Study for the Viscous Flow of Sodium Chloride Through a Cuprophane Membrane

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For the study of transport phenomena of an aqueous NaCl solution through a cuprophane membrane, a new apparatus was constructed. The volume flow rate $Q$, the permeability coefficient $U$, and the permeability constant $K$ were measured or determined by using this apparatus. The experimental temperature range was 5 to 35°C, and the applied pressure increments were 10 to 40 psi. By assuming that the cuprophane membrane is composed of $n$ parallel cylindrical capillaries of circular cross-section and that the flow of the solution through the capillaries follows the Poiseulle law, the mean radius $r$ of the capillaries and the number $n$ of the latter in the membrane were evaluated. By using a reasonable assumption concerning the radius $\eta'$ of the species diffusing through the membrane, it was concluded that the contribution of the diffusive flow to the total flow rate $Q$ is less than 10%. Thus, the $Q$ was treated as the rate due to the viscous flow, and the viscosity $\eta_m$ of the solution in the membrane phase was evaluted, and it was found that $\eta_m$ is nearly equal to $\eta_b$, the bulk viscosity of the solution. From this fact, it was concluded that in the capillaries, no change occurs in the physical state of the NaCl solution.The value of $\Delta H_m^{\neq}$(=4.27 kcal/mole) and $\Delta S_m^{\neq}$(4.28 eu) were obtained for the viscous flow. A possible explanation was given.

## Introduction

*Application of the Eyring Viscosity Theory to the Viscous flow of Hydrated Ions Through a Porous Membrane.* In the theory of liquid viscosity, Eyring considered that the molecules displaced relative to one another in the course of viscous flow[1-4] have to overcome the energy barrier between the adjacent equilibrium positions. The theory can be applied to the case that the hydrated ions of dilute electrolytic solutions diffuse through a porous membrane disregarding the electric potential gradient against the external pressure gradient. The rate of this process is determined by factors similar to those acting in chemical reactions, therefore the theory of viscous flow can be treated on the basis of the absolute reaction rate theory.

According to the absolute reaction rate theory[5,6] the net velocity ($U$) of a flow unit under shear stress $f$ is given as follows:

$$U=(k_{mf}-k_{mb})\lambda=\lambda k_m\left\{\exp\left[\frac{f\lambda_2\lambda_3\lambda}{2kT}\right]-\exp\left[-\frac{f\lambda_2\lambda_3\lambda}{2kT}\right]\right\} \quad (1)$$

$$=2U_0\sinh\left(\frac{f\lambda_2\lambda_3\lambda}{2kT}\right) \quad (2)$$

where $U_0$ is the velocity of the flow unit by other driving force such as concentration gradient, and is defined by

$$U_0=\lambda k_m=\lambda\frac{kT}{h}\exp\left(-\frac{\Delta G_0^{\neq}}{RT}\right) \quad (3)$$

In the above equations, $\lambda$ and $\lambda_2\lambda_3$ are the jumping distance