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Analysis of Vapor Pressure of Some Molecular Crystals[*1]

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Vapor pressure equations of the form $\log PT^{n/2}=a/T+b$ were derived, using high temperature Thirring expansion, which are applicable to crystals of polyatomic molecules. The exponent n is determined by the type of motion of molecules in the crystal, libration or rotation. If combined with the heat capacity data, the method of analysis may be used to derive such vibrational propoerties as static energy, zero point energy, geometric mean frequency, and molecular libration frequency. Examples of the analysis of existing vapor pressure data are given for solid iodine, iodine monochloride, and high temperature modifications of nitrogen, hydrogen chloride, and methane.

A vapor pressure equation for monatomic crystals was derived by Salter[1] using high temperature expansion for the Gibbs energy of the crystal. He was also able to show that the vapor pressures could 'see' the effect of vacancy formation near the triple point of solid argon. Salter's treatment was later extended to the case of alkali halides by Leadbetter and Newsham.[2]

The present paper is an extention of Salter's equation to molecular crystals in an attempt to extract information about molecular motion in crystalline solids from available vapor pressure data. The result turns out to be rather against our expectation but it will be shown that in certain cases some useful deductions can be made from vapor pressures if combined with other experimental information such as heat capacity and entropy.

Vapor Pressure Equations

What we are interested in is to incorporate the molecular rotational degrees of freedom in solid into Salter's formulation. It will be assumed that the temperature is sufficiently high so that Thirring expansion holds for the free energy of the crystal but not too high so that we can ignore anharmonic terms in the vibrations.

The molar Gibbs energy of a molecular crystal may be written as

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[*1] Presented before the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, March 31, 1966; Abstract of Paper 1S005.

[1] L. Salter, *Trans. Faraday Soc.*, **59**, 657 (1963).

[2] A. J. Leadbetter and D. M. T. Newsham, *ibid.*, **61**, 1646 (1965).

$$G^c = G^c_{\mathrm{trans}} + G^c_{\mathrm{vib}} + G^c_{\mathrm{rot}} + G^c_{\mathrm{exp}} \qquad (1)$$

Here the terms represent contributions from translational, vibrational (intramolecular), and rotational degrees of freedom and from thermal expansion. At high temperatures ($T > \Theta_D/6$), the translational part may be expanded into a series of the form[1]

$$G^c_{\mathrm{trans}} = E_0' + 3\boldsymbol{NkT}\Big[\ln(\boldsymbol{h}\nu_g/\boldsymbol{kT}) + \sum_{n=1}^{\infty}(-1)^{n-1}B_{2n}/2n(2n)! \times \eta_{2n}(\boldsymbol{h}/2\pi\boldsymbol{kT})^{2n}\Big] \qquad (2)$$

where E_0' is the pseudo-static lattice energy, N the Avogado's number, ν_g the geometric mean frequency for the translational lattice modes, B_{2n} the Bernoulli number, and η_{2n} the $2n$th moment of the translational part of the lattice frequency spectrum. The static lattice energy E_0 is related to E_0' by

$$E_0 = E_0' - E_{z,\mathrm{lib}}$$

because '*translationally static*' lattice may still possess the zero-point kinetic energy $E_{z,\mathrm{lib}}$ of molecular libration. For monatomic crystals or crystals in which all molecules are rotating, E'_0 is of course equal to E_0.

The vibrational part of the Gibbs enrgy is given by[3]

$$G^c_{\mathrm{vib}} = \boldsymbol{NkT}\sum_i[\ln(\boldsymbol{h}\nu_i^c/\boldsymbol{kT}) - \boldsymbol{h}\nu_i^c/2\boldsymbol{kT} + 1/24(\boldsymbol{h}\nu_i^c/\boldsymbol{kT})^2 + \cdots] + \sum_i \boldsymbol{Nh}\nu_i^c/2 \qquad (3)$$

where ν_i^c is the frequency for the ith intramolecular vibration mode, the last term being the vibrational zero point energy.

The rotational part of the free energy can not be treated in a general way since the Schrödinger equation for three-dimensional rotation of a molecule in a general periodic potential field can not be solved. We shall therefore be content with two extreme cases, *viz.* either librational motion or free rotation.

In the harmonic librational case, G^c_{rot} assumes exactly the same form as Eq. (3). In the case of free rotation it is given by[3]

$$G^c_{\mathrm{rot}} = -\boldsymbol{NkT}\sum_j \ln[(1/n_j)(8\pi^2 I_j \boldsymbol{kT}/\boldsymbol{h}^2)^{1/2}] \qquad (4)$$

where I_j is the moment of inertia and n_j is the symmetry number of the rotational potential. Finally, the expansion part contributes

$$G^c_{\mathrm{exp}} = Npv_c \qquad (5)$$

to the total Gibbs energy, p and v_c being the pressure and the volume per molecule.

The corresponding Gibbs energy of a mole of vapor is

$$G^v = G^v_{\mathrm{trans}} + G^v_{\mathrm{vib}} + G^v_{\mathrm{rot}} + G^v_{\mathrm{exp}} \qquad (6)$$

and terms on the right-hand side are given in a standard textbook[3]:

$$G^v_{\mathrm{trans}} = -\boldsymbol{NkT}[\ln(2\pi m\boldsymbol{kT}/\boldsymbol{h}^2)^{3/2} + \ln v_v - B(T)/v_v + 1] \qquad (7)$$

$$G^v_{\mathrm{vib}} = \boldsymbol{NkT}\sum_i[\ln(\boldsymbol{h}\nu_i^v/\boldsymbol{kT}) - \boldsymbol{h}\nu_i^v/2\boldsymbol{kT} + (1/24)(\boldsymbol{h}\nu_i^v/\boldsymbol{kT})^2 + \cdots] + \sum_i \boldsymbol{Nh}\nu_i^v/2 \qquad (8)$$

$$G^v_{\mathrm{rot}} = -\boldsymbol{NkT}[\sum_j \ln(8\pi^2 I_j\boldsymbol{kT}/\boldsymbol{h}^2)^{1/2} - \ln(\sigma/\pi^{1/2})] \qquad (9)$$

$$G^v_{\mathrm{exp}} = Npv_v \qquad (10)$$

where m is the mass of a molecule, $B(T)$ is the second virial coefficient, and v_v is the volume per molecule. v_v may be approximated by

$$v_v = \boldsymbol{kT}/p. \qquad (11)$$

For a linear molecule, the symmetry number σ of the molecule in Eq. (9) is to be replaced by $\sqrt{\pi}\sigma'$, where σ' is 2 or 1 according as the molecule has the center of symmetry or not.

From the condition for vapor-solid equilibrium, we obtain the equation of the form

$$\ln P(T^{1/2})^n = a/T + b \qquad (12)$$

The exponent n is determined by whether the molecule executes libration or rotation and a is given by

$$a = E'_0/N\boldsymbol{k}, \qquad (13)$$

and therefore a linear plot of $\ln(PT^{n/2})$ against $1/T$ gives the static lattice energy from its slope, and its intercept b should give the geometric mean frequency ν_g. Values of n and expressions of b are given in Table 1 for typical cases. Other cases can be evaluated easily. It is evident that Eq. (12) reduces to Salter's equation for monatomic case.[1] In deriving b, it has been assumed that

$$\boldsymbol{h}\nu_i/\boldsymbol{kT} < 1, \quad \boldsymbol{h}\eta_{2n}^{1/2n}/2\pi\boldsymbol{kT} \ll 1, \quad B(T)/v_v \ll 1. \qquad (14)$$

The first of these assumptions may be justified only in the case of the low frequency librational modes in the solid state. While it may not be valid for intramolecular vibrations, the terms containing ν_i enter only as a difference between the gaseous and the crys-

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[3] J. E. Mayer and M. G. Mayer, "Statistical Mechanics," John Wiley, New York (1940); G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, 2nd Ed., McGraw-Hill, New York (1961).

TABLE 1. THE VALUES OF n AND THE EXPRESSIONS OF b TO BE USED IN EQ. (12). APPROPRIATE FOR DIFFERENT MODELS OF MOLECULAR MOTION

Model	n	b
Linear molecule; librations about two axes	3	$\ln[8\pi^2(2\pi m/k)^{3/2}\cdot 1/\sigma'\cdot I_v\nu_g^3\cdot\nu_l^2\nu_c^{\mathrm{intra}}/\nu_v^{\mathrm{intra}}]$
Linear molecule; libration + rotation	2	$\ln[(8\pi^2)^{1/2}(2\pi m)^{3/2}\cdot 1/k\cdot n_c/\sigma'\cdot I_v/I_c^{1/2}\cdot\nu_g^3\nu_l\cdot\nu_c^{\mathrm{intra}}/\nu_v^{\mathrm{intra}}]$
Linear molecule; rotations about two axes	1	$\ln[(2\pi m)^{3/2}\cdot 1/k^{1/2}\cdot n_1 n_2/\sigma'\cdot I_v/(I_{c1}I_{c2})^{1/2}\cdot\nu_g^3\cdot\nu_c^{\mathrm{intra}}/\nu_v^{\mathrm{intra}}]$
Non-linear molecule; librations about three axes	4	$\ln[8\pi^5 m^{3/2}\cdot 1/k\cdot 1/\sigma(I_{v1}I_{v2}I_{v3})^{1/2}\cdot\nu_g^3\cdot\nu_{l1}\cdot\nu_{l2}\cdot\nu_{l3}\cdot\prod_i(\nu_{ci}/\nu_{vi})]$
Non-linear molecule; rotations about three axes	1	$\ln[(8\pi)^{1/2}m^{3/2}\cdot 1/k^{1/2}\cdot n_1 n_2 n_3/\sigma\cdot(I_{v1}I_{v2}I_{v3}/I_{c1}I_{c2}I_{c3})^{1/2}\cdot\prod_i(\nu_{ci}/\nu_{vi})]$

talline states and therefore the higher order terms of $h\nu_i^v/kT$ and $h\nu_i^c/kT$ would give only trivial effects on the results derived here.

We have ignored the effect of vacancy formation or any other type of defects but these can be taken into account if the energy and the combinatory factor associated with the defect formation can be evaluated. If the molecules in the vapor associate to form dimers or higher polymers, the effect has also to be and can be taken into accout provided that the molecular structures and concentrations of the associated species are known. Equation (12) is also applicable to such a case of NH_4Cl that dissociation is accompanied with vaporization.

Analysis of Experimental Vapor Pressures

All that one may anticipate to deduce from the application of Eq. (12) to experiment are, besides E_0 and ν_g, whether the molecules are librating at a certain frequency or rotating almost freely. Yet the application is not straightforward since the appropriate value of n is not known in advance. One obvious way is to decide n by trial-and-error procedure and see which value gives the best fit to Eq. (12). This is possible only when extremely accurate vapor pressure data are available over a reasonably wide temperature range. Usual situation is, as illustrated by the three equally well fitted straight lines in Fig. 3, that the exponent n can not be determined unambiguously. If the primary pressure and temperature values were sufficiently accurate, one should, in principle, be able to discriminate between different values of n. However in order for this to be practical, it appears that the accuracy of measurements will have to be improved by a factor of 10 or to within ±0.005 Torr. Under these circumstaces, the analysis by use of Eq. (12) must be assisted by other information. Figure 1 is the diagram of cycles devised for this purpose. What is aimed at here is to use a and b of Eq. (12) for deriving other vibrational properties and at the same time examining the internal consistency of the calculation. It is noted that the derived properties all refer to a volume at some mean tem-

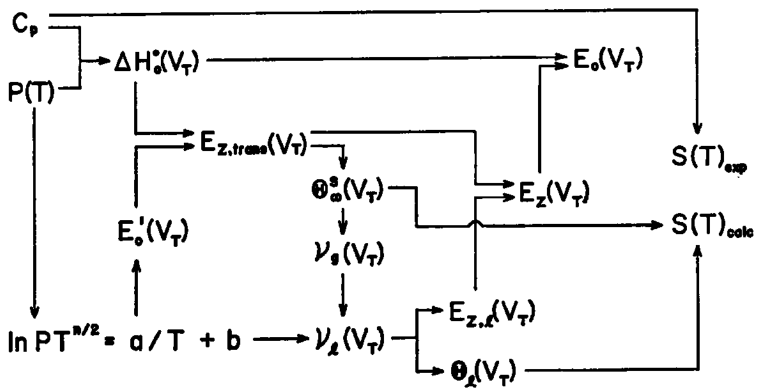

Fig. 1. Correlation diagram.

perature of the vapor pressure measurements.

Thus $\Delta H_0^0(V_T)$ is the heat of sublimation as 0°K corresponding to the crystal volume at temperature T; it is calculated from the relation

$$\Delta G^\circ/T = \boldsymbol{R}\ln(760/P) = \Delta(G^\circ - H^0)/T + \Delta H_0^0/T \qquad (15)$$

ΔG° is the standard Gibbs energy of sublimation at temperature T and $\Delta(G^\circ - H_0^0)$ may be obtained from heat capacity values. The translational zero point energy $E_{z,\mathrm{trans}}(V_T)$, obtained by

$$E_{z,\mathrm{trans}}(V_T) = -E_0'(V_T) - \Delta H_0^0(V_T),$$

is related to the limiting Debye temperature (from entropy) Θ_∞^s and the geometric mean frequency ν_g through[2,4]

$$E_{z,\mathrm{trans}} = \frac{9}{8}\boldsymbol{Nk}\Theta_\infty^s \fallingdotseq \frac{9}{8}\mathrm{e}^{1/3}\boldsymbol{Nh}\nu_g$$

n the quasi-harmonic approximation. $\nu_l(V_T)$ is the molecular libration frequency and may be obtained as an average over the degrees of freedom (two or three) by inserting appropriate figures to the expression of b. The solid-state shift of the intramolecular frequencies is usually small so that it may be ignored if spectral frequencies in solid are not available. Knowledge of $\nu_l(V_T)$ may be directly compared with Raman or far-infrared spectral data on what is called '*lattice modes*' or with ν_l derived from temperature dependence of nuclear quadrupole resonance frequency. It also leads to the harmonic librational zero point energy $E_{z,\mathrm{lib}}(V_T)$ and Einstein temperature $\Theta_l(V_T)$; the former gives, together with $E_{z,\mathrm{trans}}(V_T)$, the total zero point energy $E_z(V_T)$ and the static lattice energy $E_0(V_T)$.

An overall check for internal consistency may be done by the help of entropy $S(T)$. Thus two characteristic temperatures Θ_∞ and Θ_l give an entropy for translational and librational modes to which intramolecular contributions are added. This $S(T)_{\mathrm{calc}}$ is then compared with the calorimetric entropy. Entropy may look a rather insensitive quantity for the purpose of consistency check. However the value of b is very sensitive to the choice of the exponent n in Eq. (12) and this outweighs the insensitivity of the entropy.

Results of Calculation

Results of calculations are displayed in Tables 2 and 3.

I_2 and ICl

The case of solid iodine probably serves best to illustrate how our analysis works. Molecules in solid iodine are undergoing librational motion (though perhaps not isotropic) in the orthorhombic crystal. Figure 2 shows the plot of $\log(PT^{3/2})$ *vs.* $1/T$, from which

TABLE 2. THE RESULT OF THE ANALYSIS OF THE VAPOR PRESSURE DATA

Substance	Model	T_M[a]	ΔH_0^0[b]	E_z	$-E_0'$	$-E_0$	Θ^s	ν_g	Θ_l	ν_l	Reference
		(°K)	(cal/mol)				(°K)	(10^{12}sec^{-1})	(°K)	(cm^{-1})	for $P(T)$
I_2	libration	321	15658	312	15800	15970	63.5	1.01	85.7	59.5	g)
ICl	libration	268	13273	428	13476	13701	89.5	1.43	113	78.6	h)
N_2	libration	59	1653	233	1823	1886	76.1	1.21	31.5	21.9	i)
N_2	rotation[c]	59	1653	153	1765	1806	50.1	0.80	41.4	28.8	i)
CH_4	libration	78	2237	521	2615	2758	169	2.69	47.8	33.2	j)
CH_4	rotation[d]	78	2237	150	2387	2387	67.1	1.07	——	——	j)
HCl	libration	146	4452	716	5059	5168	272	4.32	27.4	19.0	k)
HCl	rotation[e]	146	4452	571	4915	5023	207	3.30	54.4	37.8	k)
HCl	rotation[f]	146	4452	319	4771	4771	143	2.27	——	——	k)

a) Mean temperatures of vapor pressure measurement.

b) Computed from literature values for thermodynamic quantities (Landolt-Börnstein, "Zahlenwerte und Funktionen," II Band, 4 Teil, Springer, Berlin (1961).

c) Rotation about one axis; $n_c=6$ assumed.

d) Rotation about three axes; $n_1=n_2=n_3=4$ assumed.

e) Rotation about one axis; $n_c=1$ assumed. f) Rotation about two axes; $n_1=n_2=1$ assumed.

g) G.P. Haxter, C.H. Hickey and W.C. Holmes, *J. Am Chem. Soc.*, **29**, 127 (1907).

h) G.V. Calder and W.F. Giauque, *J. Phys. Chem.*, **69**, 2443 (1965).

i) W.F. Giauque and J.O. Clayton, *J. Am. Chem. Soc.*, **55**, 4875 (1933).

j) D.R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

k) W.F. Giauque and R. Wiebe, *J. Am. Chem. Soc.*, **50**, 101 (1928).

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[4] C. Domb and L. Salter, *Phil. Mag.*, **43**, 1083 (1952).

TABLE 3. CALCULATED AND OBSERVED ENTROPIES OF SOME MOLECULAR CRYSTALS

Substance	T (°K)	S_{exp} (e. u.)	S_{calc} (e. u.)	$\Delta S/S$ (%)	Reference for S_{exp}
I_2	298	27.76	28.20	1.6	a)
ICl	268	22.1	23.0	4.1	b)
N_2(lib.)	60	13.08	13.28	1.5	c)
N_2(rot.)	60	13.08	13.12	0.31	c)
CH_4(lib.)	80	12.26	13.29	8.4	c)
CH_4(rot.)	80	12.26	13.40	9.3	c)
HCl(lib.)	140	14.07	14.99	6.5	c)
HCl(lib. +rot.)	140	14.07	14.14	0.5	c)
HCl(rot.)	140	14.07	12.49	11.2	c)

a) D. A. Shirley and W. F. Giauque, *J. Am. Chem. Soc.*, **81**, 4778 (1959).
b) G. V. Calder and W. F. Giauque, *J. Phys. Chem.*, **69**, 2443 (1965).
c) Landolt-Börnstein, "Zahlenwerte und Funktionen," II Band, 2 Teil, Springer, Berlin (1960).

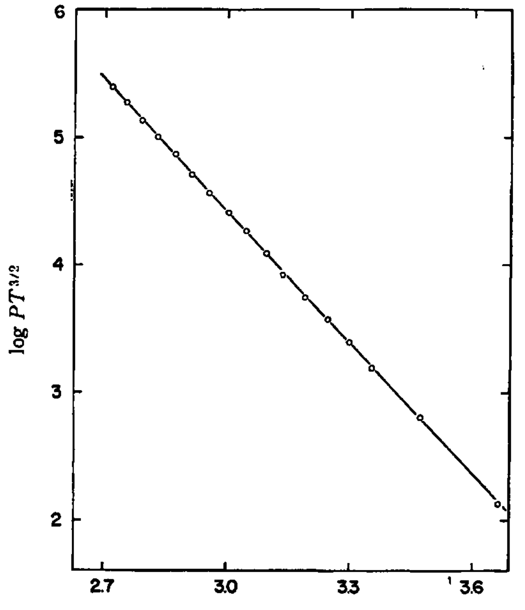

Fig. 2. The plot of $\ln PT^{3/2}$ against T^{-1} for solid iodine.

the static lattice energy 15970 cal/mol and the average libration frequency $\nu_l=59.5$ cm^{-1} were obtained. These two values, combined with the heat of sublimation at 0°K obtained by the calorimetric method, give the librational zero point energy 170 cal/mol (2 degrees of freedom) and the translational zero point energy 142 cal/mol. The libration frequency of 59.5 cm^{-1} compares favorably with 69.5 cm^{-1} obtained from analysis of low temperature heat capacities⁵⁾ if one considers that the former corresponds to a larger volume of the crystal. Far infrared spectrum of solid iodine shows two translational lattice frequencies at 41 cm^{-1} and 65 cm^{-1} at 77°K.⁶⁾ An average of these two gives a Debye temperature of 74°K as compared with $\Theta_{\infty}^{S}=63.5$°K given in Table 2. Also a Mössbauer study around 150°K led to $\Theta=60$°K.⁷⁾ The entropy deviation is only 1.6%. Thus we believe that we have a fairly nice picture for solid iodine. The situation with respect to solid iodine monochloride is similar. The various quantities derived take values of reasonable magnitude in comparison with those of iodine although no other independent informations are available.

N_2

The high temperature phase of nitrogen was examined in two alternative models; *i.e.* the molecule undergoes libration about two axes ($n=3$) or rotates about one axis while doing libration about the other axis ($n=2$). Entropy consideration favors the one-axis rotation model slightly over the two-axes libration. The total zero point energy is then 153 cal/mol, of which 112 cal/mol comes from translational motion. Kohin estimated $E_{z,\mathrm{trans}}$ theoretically to be 213 cal/mol.⁸⁾ Her estimate is based on the low temperature phase and therefore we see that the high temperature structure has a smaller zero point energy. Recent X-ray diffraction study suggested that the molecules precess about the c-axis of the high temperature hexagonal crystal.⁹⁾ They will of course be undergoing nutation also. This type of motion is consist-

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5) H. Chihara and T. Shinoda, *J. Phys. Soc. Japan*, **17**, 1395 (1962).

6) S. H. Walmsley and A. Anderson, *Mol. Phys.*, **7**, 411 (1964).

7) M. Pasternak, A. Simopoulos and Y. Hazony, *Phys. Rev.*, **140**, A1892 (1965).

8) B. C. Kohin, *J. Chem. Phys.*, **33**, 882 (1960).

9) W. E. Streib, T. H. Jordan and W. N. Lipscomb, *ibid.*, **37**, 2962 (1962).

ent with nuclear quadrupole resonance results: We have made a rough estimate, using Scott's unpublished data,[10] that the molecular axis makes an angle of 54°17′ with the precession axis at a precession frequency greater than 4. 10^6 Hz. We also calculated the low temperature libration frequency as 31. 5 cm^{-1} at 35. 6°K from the nuclear quadrupole frequencies[10] by the method described elsewhere.[11] This ν_l is to be compared with 28. 8 cm^{-1} in Table 2.

CH_4

It has been shown that methane is in effectively free rotation in the highest temperature solid phase.[12] Our analysis of vapor pressure does not provide a clear-cut interpretation but leads to very large discrepancy of the entropies. This is probably due to in sufficient accuracy in the pressure determinations.

HCl

The structure and molecular motion in solid HCl have been extensively discussed elsewhere.[13] In short, neutron diffraction study on DCl favors a disordered orientation model above the transition point,[14] whereas nuclear magnetic and quadrupole studies point to a hindered rotation model.[13] The vapor pressure plots of Fig. 3 alone do not allow to differentiate one from the other possibilities in Table 2. The entropy considerations (Table 3) seem to clearly indicate that a combination of one-axis rotation and one-axis libration is by far appropriate than other models. This may be reconciled to nuclear resonance results if we consider that our treatment of vapor pressures here developed corresponds only to extreme cases of free molecular rotation or harmonic libration. What is actually happening is probably an intermediate, *i.e.* hindered rotation about two axes.

Attempts were also made to examine vapor pressures of solid chlorine, bromine, and the low temperature phases of hydrogen chloride and nitrogen. But these led either to very small E_z or to very large $\Delta S/S$. The failure is perphaps due partly to poor accuracy in the vapor pressure determinations and partly to the breakdown of the high temperature approximation.

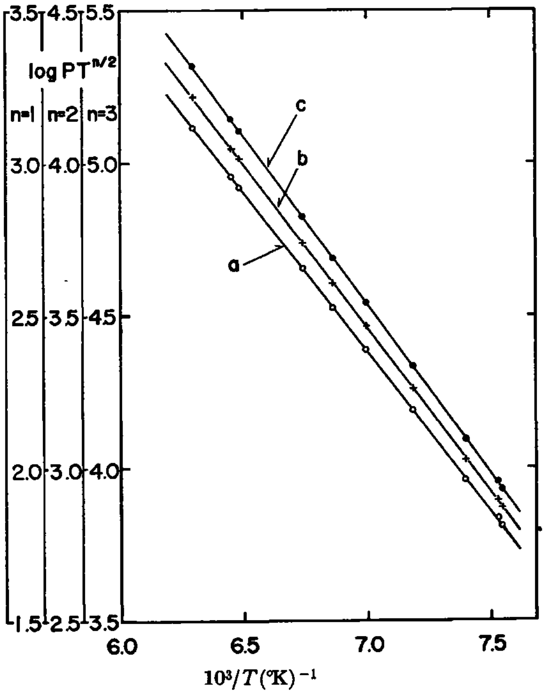

Fig. 3. The plot of ln $PT^{n/2}$ against T^{-1} for the high temperature phase of solid hydrogen chloride. (a: $n=1$; b: $n=2$; c: $n=3$)

Conclusion

It has been demonstrated that accurate vapor pressure values of molecular crystals serve to provide useful informations about the lattice vibrational properties such as the static energy, the geometric mean frequency, the molecular libration frequency, and the zero point energy, in combination with heat capacity data. When the accuracy of the pressure allows, it is possible to detect molecular rotational states in solids. However, most of the presently available data are not accurate enough to deduce the information on higher order effect and the effect of vacancy formation.

The authors are grateful to Professor T. A. Scott of University of Florida for sending us his recent unpublished results on the nuclear quadrupole resonance of solid nitrogen.

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[10] T. A. Scott, private communication.

[11] N. Nakamura and H. Chihara, *J. Phys. Soc. Japan*, **22**, 201 (1967).

[12] H. Chihara and T. Shinoda, This Bulletin, **37**, 125 (1964).

[13] H. Ōkuma, N. Nakamura and H. Chihara, *J. Phys. Soc. Japan*, **24**, 452 (1968).

[14] E. Sándor and R. F. C. Farrow, *Nature*, **215**, 1265 (1967).