

The Phase Transition and the Piezoelectric Effect of KH_2PO_4

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Citation: *J. Chem. Phys.* **17**, 102 (1949); doi: 10.1063/1.1747039

View online: <http://dx.doi.org/10.1063/1.1747039>

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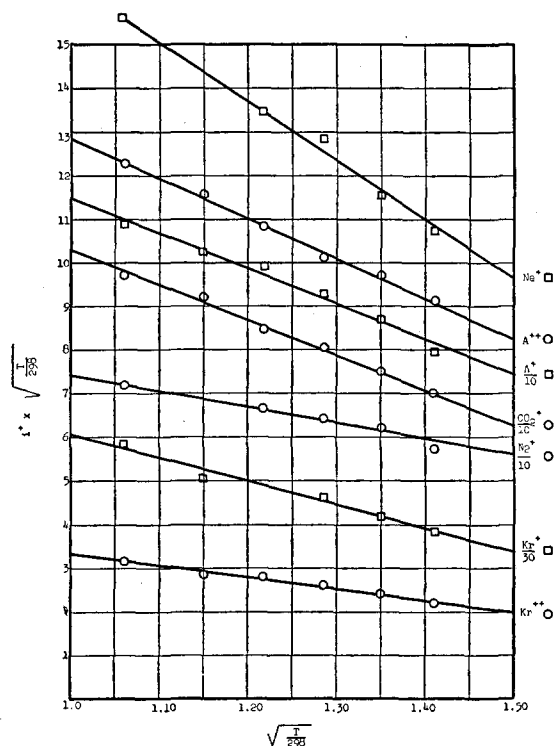


FIG. 1. The variation of specific ion currents (i^*) with absolute temperature (T) for various simple ions (Westinghouse type LV mass spectrometer, 75-volt ionizing electrons). Although the specific current units are arbitrary, the same units have been used for all substances and thus are consistent with the relative sensitivities of the various substances. The temperatures have been normalized to "room temperature" (25°C) to provide a more convenient scale.

nounced for complex than for simple molecules. The largest effects have been found in the mass spectra of branched chain paraffins.

Both 1 and 2 have their origin in the increase in energy of the molecules associated with the increase in temperature. The increase in kinetic energy ($\frac{3}{2}kT$) is the source of effect 1, while the increase in internal (vibrational) energy brings about effect 2.

The increase in kinetic energy of the molecules results in a decrease in the average number of molecules in the ionization chamber since the flow of gas through the mass spectrometer tube is effusive. This results in the ion current being proportional to $T^{-1/2}$. The increase of kinetic energy further results in the ions being formed with greater initial kinetic energy and since the discrimination losses in the ion source increase as $T^{1/2}$, the observed ion current decreases as $(1 - \alpha T^{1/2})$, where α is a function of the ion source geometry, the ion accelerating fields, and the magnetic fields across the ionization chamber.² Thus the decrease of ion current with temperature is expressed as

$$i(T) = i_0 T^{-1/2} [1 - \alpha T^{1/2}]. \quad (\text{A})$$

Equation A has been found to represent the temperature variation of the ion currents in the mass spectra of neon, argon, krypton, nitrogen, and carbon dioxide over, $335 \leq T \leq 593^\circ\text{K}$. This may be seen from Fig. 1, where

$i \times (T/298)^{1/2}$ is plotted against $(T/298)^{1/2}$ for selected ions. It will be noted that for the rare gases (argon and krypton), the formula for the temperature variance of specific ion current fits singly and double charged ions equally well.

The increase in internal energy that accompanies increasing temperature results in an increased fraction of the molecules of a substance being in configurations which permit excitation to energy levels above dissociation limits of the states of the molecule-ion. This results in a larger fraction of the molecule-ions produced by electron impact dissociating, and thus the parent ion forms a smaller fraction of the total ion current. This effect, (2), is related to the greater probability of the breaking of C-H bonds than of C-D bonds in deuterio-hydrocarbons.³

In Table I there are given the ratios, $i_p^+/\sum i_n^+$, where i_p^+ = specific intensity of parent ion, i_n^+ = specific intensity of any ion, and the summation is over all ions, including i_p^+ , in the mass spectra of a number of hydrocarbons for $T = 340, 440$, and 540°K . This ratio equals the fraction of

TABLE I. Effect of temperature on the fraction of the mass spectra due to parent ions.

Substance	p^a	75-volt ionizing electrons		
		$T = 340$	440	540°K
Methane	16	0.572	0.555	0.542
Acetylene	26	0.796	0.792	0.788*
Acetylene- d_2	28	0.829	0.821	0.820*
Ethane	30	0.164	0.152	0.135
Propane	44	0.154	0.132	0.108
<i>n</i> -Butane	58	0.095	0.071	0.048
<i>i</i> -Butane	58	0.0295	0.0204	0.0117

^a p = molecular weight of parent ion.

* $T = 575^\circ\text{K}$.

ions formed which do not dissociate. These data were obtained with a Westinghouse type LV mass spectrometer, i.e., the same type used by Fox and Hipple.¹ The spectra were recorded by varying the magnetic field, and the ion intensities were not corrected for ion source discrimination. As would be expected, the less rigid the molecule the greater is the effect of temperature on the probability of dissociation of the molecule ion, i.e., the smaller the fraction of ions which do not dissociate.

¹ R. E. Fox and J. A. Hipple, *J. Chem. Phys.* 15, 208 (1947).

² For discussions of ion source discrimination, see Norman D. Coggeshall, *J. Chem. Phys.* 12, 19 (1944); H. W. Washburn and C. E. Berry, *Phys. Rev.* 70, 559 (1946).

³ The differences in the mass spectra of such isotopic molecules arise in part from the greater amplitude of the zero-point vibrations of the -H bonds than of the -D bonds. See Evans, Bauer, and Beach, *J. Chem. Phys.* 14, 701 (1946); N. Bauer and J. Y. Beach, *J. Chem. Phys.* 15, 150 (1947); David P. Stevenson, *J. Chem. Phys.* 15, 409 (1947).

The Phase Transition and the Piezoelectric Effect of KH_2PO_4

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November 1, 1948

A NOMALOUS behaviors of the dielectric constants^{1,2} and the phase transition³ at 122°K of KH_2PO_4 were treated by the methods of statistical mechanics by Slater⁴ and others.^{5,6} In this crystal, PO_4 groups are linked by hydrogen bonds which are directed nearly parallel to the

axis a or b . In Slater's model it is assumed that two hydrogen atoms (or protons) out of the four hydrogen bonds linking each PO_4 group to its neighbors lie nearer to it, and the resulting $(\text{H}_2\text{PO}_4)^-$ group has a dipole moment directed to one of the crystalline axes. Further, it is assumed that the energy of the crystal in the absence of external electric field is given by the number of those dipoles which are perpendicular to the c axis multiplied by a constant ϵ . The number of configurations with the same energy and the same polarization was calculated by an approximate method, and a unique type of transition was predicted. His theory does not, however, account for the anomaly of the piezoelectric effect which was also observed^{2,7} and was found to be very similar to the anomaly of the dielectric constants, although he considers it to be the primary cause of the λ -type broadening of the transition temperature. We must expect a close relationship between them.

Instead of assuming the energy of the $(\text{H}_2\text{PO}_4)^-$ dipoles directed to $+c$ and that of the dipoles directed to $-c$ as being equal, we took them in the form

$$\epsilon_+ = -\epsilon_0 - \beta x_y, \quad \text{and} \quad \epsilon_- = -\epsilon_0 + \beta x_y, \quad (1)$$

respectively, where ϵ_0 and β are constants and ϵ_0 stands for Slater's ϵ . x_y is the strain of the crystal. The assumption (1) is consistent with the point group symmetry of the crystal, V_d . Denoting the dipole moment associated with a $(\text{H}_2\text{PO}_4)^-$ group by μ , the external electric field by E , and the normal elastic constant corresponding to x_y by $N\alpha$, where N is the number of molecules of the crystal of unit volume, we can write the energy of the crystal as

$$U = N_+\epsilon_+ + N_-\epsilon_- - (N_+ - N_-)\mu E + \frac{1}{2}N\alpha x_y^2, \quad (2)$$

N_+ and N_- being the numbers of $(\text{H}_2\text{PO}_4)^-$ dipoles which are parallel to $+c$ and $-c$, respectively. To (2) we further added the term which is due to the induced polarization, and the term which represents the normal piezoelectric effect, namely,

$$-\frac{1}{2}\chi_1 E^2 - \xi_1 x_y E, \quad (3)$$

χ_1 and ξ_1 being constants. The writers believe that the problem of the local field is cared for by the inclusion of the terms (3) and that the inclusion of the local field factor a in the form $\chi = a\chi_0 + \chi_1$ for the susceptibility, as was done by Slater, is not correct.

Combining the energy given above with the entropy formula derived by Slater, and minimizing the free energy with respect to N_+ and N_- , the equations for describing the equilibrium state can be obtained. Further, the polarization p in the direction of the c axis and the stress component X_y are derived from the free energy A through the equations

$$P = -\partial A / \partial E = N\mu z + \chi_1 E + \xi_1 x_y, \quad (4)$$

$$X_y = -\partial A / \partial x_y = -N\alpha x_y + N\beta z + \xi_1 E, \quad (5)$$

where $z = (N_+ - N_-) / N$.

The nature of the phase transition is practically the same as that predicted by Slater's theory in that the transition is accompanied by a latent heat and that the crystal is abruptly and spontaneously polarized below the transition

temperature. However, our theory predicts a further fact that the crystal is spontaneously deformed with a constant shearing strain $x_y = \beta / \alpha$ below the transition temperature. In fact, the relation

$$x_y / z = \beta / \alpha \quad (6)$$

always follows from (5) when there is no stress and no external electric field.

From the condition of the minimum of the free energy we have

$$z = \frac{\sinh[(\beta x_y + \mu E) / kT]}{2 \exp[-\epsilon_0 / kT] - \cosh[(\beta x_y + \mu E) / kT]}. \quad (7)$$

If we substitute this into (4) and (5) and assume x_y and E to be small, we can derive the following equations:

$$P = \chi E - d_{36} X_y \quad \text{and} \quad x_y = d_{36} E - s_{66} X_y, \quad (8)$$

with

$$\begin{aligned} \chi &= N\mu'^2 / (D - 2\delta) + \chi_1 + \xi_1^2 / N\alpha, \\ d_{36} &= (\beta\mu' / \alpha) / (D - 2\delta) + \xi_1 / N\alpha, \\ s_{66} &= (\beta^2 / N\alpha^2) / (D - 2\delta) + 1 / N\alpha; \end{aligned} \quad (9)$$

$$D = kT(2e^{-\epsilon_0/kT} - 1), \quad 2\delta = \beta^2 / \alpha, \quad \mu' = \mu + \beta\xi_1 / N\alpha. \quad (10)$$

The three quantities of the Eqs. (9) can be written approximately in the form $A / (T - T_c) + B$ for the temperature range above the transition temperature which is of practical interest. The following numerical values explain all the results of Mason's² measurements:

$$\begin{aligned} \beta / \alpha &= 6.8 \times 10^{-3} = 23' \text{ in angle,} \\ N\alpha &= 7.04 \times 10^{10} [1 - (T - T_c) \times 6.7 \times 10^{-4}] \text{ dyne/cm}^2, \\ \epsilon_0 &= 1.22 \times 10^{-14} \text{ erg,} \\ \mu' &= 1.55 \times 10^{-18} \text{ c.g.s.e.s.u.} \end{aligned}$$

Figure 1 shows the computed and the measured elastic constant, the dotted curve corresponding to the constant value of $N\alpha$ (the term proportional to $T - T_c$ given above being omitted), and the full curve corresponding to $N\alpha$ given above. The Curie point of the clamped (i.e., strain-free) crystal is lowered by 3.5° as compared with that of the stress-free crystal, in agreement with Mason's result. A somewhat greater value of the dipole moment μ' , which

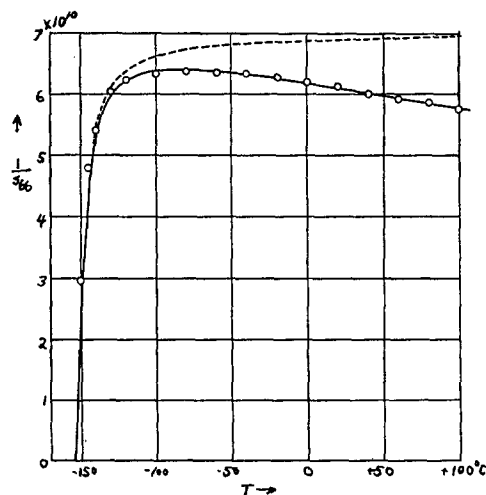


FIG. 1.

is practically equal to μ , compared with that which can be derived from the Busch¹ measured spontaneous polarization, namely, 1.25×10^{-18} , is to be interpreted as due to that not all the domains are parallel to the field in his experiment, or otherwise, as due to the experimental errors.

A detailed account will be published in Journal of the Physical Society of Japan or in Progress of Theoretical Physics.

¹ G. Busch, *Helv. Phys. Acta* 11, 296 (1938).

² W. P. Mason, *Phys. Rev.* 69, 173 (1946).

³ J. C. Stephenson and J. G. Hooley, *Phys. Rev.* 56, 121 (1939); *J. Am. Chem. Soc.* 66, 1397 (1944).

⁴ J. C. Slater, *J. Chem. Phys.* 9, 16 (1941).

⁵ H. Takahashi, *Proc. Phys.-Math. Soc. Japan* 23, 1069 (1941).

⁶ Y. Takagi, Sūbutu Kaisi (the Japanese journal of the Phys.-Math. Soc. of Japan) 17, 280 (1942). This paper treats the theory of the dielectric constant in the direction of the σ axis.

⁷ W. Lüdy, *Zeits. f. Physik* 113, 302 (1939).

Fundamental Vibrational Frequencies and Thermodynamic Functions for Vinylacetylene, Revised Thermodynamic Functions for Hydrogen Cyanide, and Thermodynamics of Two Reactions Involved in the Synthesis of Acrylonitrile

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November 12, 1948

THE Raman^{1,2} and infra-red³ spectra of vinylacetylene (Fig. 1) have been reported in the literature, but no consistent assignment of the vibrational frequencies has been given. Using the recently published assignment for a

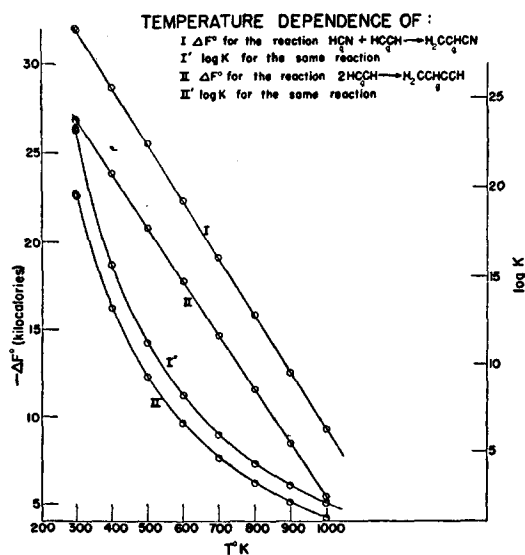


FIG. 1.

TABLE I. Fundamental vibration frequencies for vinylacetylene.

Description	Planar	Frequency
ν_1	$\equiv C-H$ stretch	3305*
ν_2	$\left. \begin{array}{l} \equiv C-H \text{ stretch} \\ \equiv C-H \text{ stretch} \\ C \equiv C \text{ stretch} \end{array} \right\}$	3102*
ν_3		(3080)**
ν_4		3012*
ν_5	$C \equiv C$ stretch	2099*
ν_6	$C=C$ stretch	1600**
ν_7	$=CH_2$ deformation	1410**
	H	
ν_8	$=C-H$ rock	1288*
ν_9	$=CH_2$ rock	1090**
ν_{12}	$C-C$ stretch	875*
ν_{14a}	$C \equiv C-H$ bend	615**
ν_{15}	$C=C-H$ bend	535**
ν_{17}	$C-C \equiv C$ bend	219*
	Non-planar	
	H	
ν_{10}	$C \equiv C-H$ wag	950**
ν_{13}	$C=C$ torsion	678*
ν_{11}	$C=CH_2$ wag	935**
ν_{14b}	$C=C-H$ bend	615**
ν_{16}	$C-C \equiv C$ bend	309*

* Reference 1.

** Reference 3.

*** Estimated.

structurally similar molecule, acrylonitrile,⁴ as a basis, a reasonable choice for the fundamental vibrational frequencies of vinylacetylene can be made. This choice of frequencies, together with an approximate description of the vibrational modes, is given in Table I. The planar and non-planar bending vibrations of the $C \equiv C-H$ group have been assumed degenerate, with the frequency 615 cm^{-1} .

Using these frequencies and assuming the structural parameters given in Fig. 1, the thermodynamic functions calculated by the rigid rotator⁵-harmonic oscillator⁶ approximation for vinylacetylene in the ideal gas state under one atmosphere pressure are given in Table II.

Values of the functions $(H^\circ - H_0^\circ)/T$, $(F^\circ - H_0^\circ)/T$, and S° for HCN calculated by the rigid rotator⁵-harmonic oscillator⁶ approximation, and by making corrections for anharmonicity, interactions, stretching, and integration error according to the method of Wagman *et al.*,⁷ are given in Table III. Spectroscopic values given by Herzberg⁸ were used ($\nu_1 = 2089.0$, $\nu_2 = 712.1$, $\nu_3 = 3312.0$ cm^{-1} ; $d_1 = 1$, $d_2 = 2$, $d_3 = 1$; $\alpha_1 = 9.3 \times 10^{-3}$, $\alpha_2 = -7 \times 10^{-4}$, $\alpha_3 = 10.8 \times 10^3$; $B_{(0)} = 1.4784$ cm^{-1} , $D = +3.3 \times 10^{-6}$, $X_{11} = -52.0$, $X_{12} = 4.2$, $X_{13} = 14.4$, $X_{22} = 2.85$, $X_{23} = 19.53$, $X_{33} = 55.48$). A com-

TABLE II. Thermodynamic functions for vinylacetylene (cal./mole/deg.).

Absolute temperature	C_p°	$H^\circ - H_0^\circ/T$	$-(F^\circ - H_0^\circ)/T$	S°
298.16	17.49	11.67	55.11	66.77
300	17.57	11.70	55.18	66.88
400	21.26	13.65	58.82	72.47
500	24.25	15.48	62.06	77.54
600	26.67	17.09	65.03	82.12
700	28.68	18.67	67.79	86.46
800	30.40	20.02	70.37	90.38
900	31.87	21.16	72.82	93.97
1000	33.16	22.39	75.10	97.48
1500	37.52	26.78	85.07	111.85