a gas with temperature less than T_c incident upon a surface with temperature higher than T_c, the molecules desorb with temperature T_c. For gas temperatures higher than T_c, "normal" accommodation results. It is conceivable that T_c for H_2 on tungsten is near room temperature; this would lead to the results of Smith and Fite[3] as well as cause both k_1 and k_2 to be independent of gas temperature for the range of the present work.

Since the complex for condensation into the precursor is not accommodated to the surface, we have, from the absolute rate theory,

$$\eta=\alpha(h^2/2\pi mkT)(q^*/q_r), \qquad (2)$$

where q^* is the molecular partition function of the activated complex with the contribution from the decomposition mode factored out, q_r is the rotational partition function of the gas molecule, and α is the transmission coefficient required for nonequilibrium situations. For hydrogen, α is of the order of 0.3 and tends to decrease with increasing temperature.[6] Any restrictions on the translational or rotational freedom of the complex will oppose this trend. Since these restrictions are likely to be slight in a physisorption complex, we expect η to be nearly independent of gas temperature. Thus, in the context of this argument, the sticking probability is independent of gas temperature for the range 77° to 273°K.

It was assumed earlier that the whole surface was available for dissociative chemisorption. If $\eta \leq 0.3$ and the entropy of activation for chemisorption from the precursor state is less than that for desorption from the precursor state, any serious restriction on the available area for chemisorption would force the chemisorption sticking probability to be far less than the value 0.1 observed by Hickmott.[2]

* Present address: Department of Mechanical Engineering, Syracuse University, Syracuse, New York.

[1] J. H. deBoer, *The Dynamical Character of Adsorption* (Oxford University Press, London, 1952).
[2] T. W. Hickmott, J. Chem. Phys. **32**, 810 (1960).
[3] J. N. Smith and W. L. Fite, J. Chem. Phys. **37**, 898 (1962).
[4] L. Meyer and R. Gomer, J. Chem. Phys. **28**, 617 (1958).
[5] G. L. dePoorter and A. W. Searcy, J. Chem. Phys. **39**, 925 (1963).
[6] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A156**, 6 (1936).

Assignment of the 71-cm^{-1} Band in Polyethylene

S. KRIMM AND M. I. BANK
Harrison M. Randall Laboratory of Physics, University of Michigan Ann Arbor, Michigan

(Received 28 December 1964)

SEVERAL investigators[1–4] have reported the presence of a band near 71 cm^{-1} in the infrared spectrum of polyethylene. Although thought at first to be due to an impurity,[2] it was soon shown[3,4] that the intensity of this band is correlated with the degree of crystallinity of the polymer. This has led to the suggestion[3] that this band is associated with a vibration of the crystal lattice, and in particular that it originates from one or both of the predicted[5] infrared-active translational modes of the lattice. We wish to present experimental evidence which confirms this assignment, and also to discuss the basis for the observed variation in frequency of this band with temperature.[3]

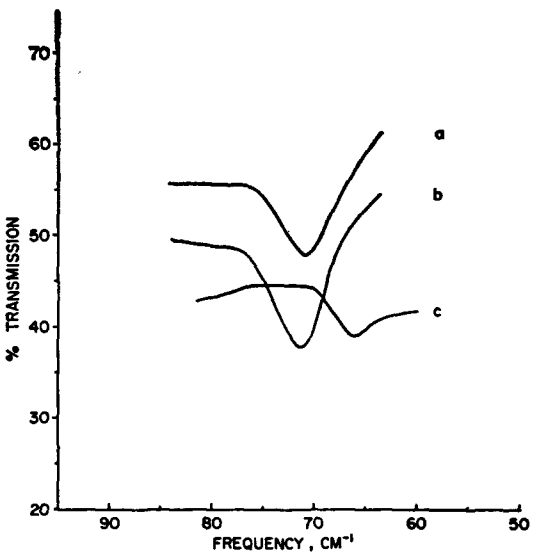

FIG. 1. Infrared spectra of (a), commercial high-density polyethylene (b), an *n*-paraffin, $C_{36}H_{74}$ and (c) a deuteroparaffin, $\sim C_{100}D_{202}$.

Spectra of a commercial high-density polythylene, of an *n*-paraffin ($C_{36}H_{74}$), and a deuteroparaffin (approximate composition $C_{100}D_{202}$) were obtained at room temperature on a Perkin–Elmer 301 spectrophotometer, and are shown in Fig. 1. The absorption maxima were found at 71.0, 71.5, and 66.5 cm^{-1}, respectively. The presence of the 71-cm^{-1} band in the spectrum of the *n*-paraffin shows that this frequency is associated with the vibrations of the two planar zigzag carbon chains in the orthorhombic unit cell,[6] and rules out any possibility that this band might in some way originate from the fold regions of folded-chain crystals[7] (since the *n*-paraffin contains no such folds). The shift in frequency to 66.5 cm^{-1} in the deuteroparaffin is consistent with an assignment of the 71-cm^{-1} band to an infrared-active translatory mode of the lattice.[5] Such a mode would be predicted, on the basis of a harmonic model, to shift on deuteration to $71.0/(m_{CD_2}/m_{CH_2})^{\frac{1}{2}} = 71.0/1.07 = 66.4$ cm^{-1}, in excellent agreement with its observed position. Normal vibration analyses[8,9] also indicate that such a translatory mode is to be expected in the region near 71 cm^{-1}, further supporting the proposed assignment. Finally, the spectrum of *n*-$C_{20}H_{42}$

showed no absorption band near 71 cm^{-1}, which would be predicted on the basis of the above assignment since in the triclinic structure of this *n*-paraffin there is only one chain per unit cell.[10,11]

From measurements made at 300°, 190°, and 100°K it was found[3] that the frequency of the above polyethylene band decreases with increasing temperature, shifting 6.5 cm^{-1} between 100° and 300°K. No detailed explanation was offered for this behavior. We wish to point out that this phenomenon can be understood on the basis of the decrease in "effective" force constant, $(\partial^2 V/\partial q^2)_{\text{eff}}$, with increasing chain separation at higher temperatures. Furthermore, the linear change of frequency with temperature can be predicted (the data[3] fit exceptionally well the formula $\bar{\nu}(cm^{-1}) = 80.7 - 0.0323\ T$, where T is in Kelvin degrees, and the first term has been chosen so as to give a value of 71.0 cm^{-1} at 300°K).

The calculation for a translatory vibration along the *a* axis, the B_{2u} mode,[5] was made assuming a Lennard-Jones 6–12 potential between chains and a dissociation energy of 300 cal/mole.[8,12] The frequency was calculated as that of an equivalent diatomic molecule, i.e., $\bar{\nu} = (\frac{1}{2}\pi c)(k/\mu)^{\frac{1}{2}}$ where $k = \partial^2 V/\partial q^2$ and μ is the reduced mass. The separation between chains was assumed to be governed by an average linear-expansion coefficient α. Since αT is small compared to 1, suitable approximations were possible, and an equation of the form $\bar{\nu} = 73.6 - 583\ \alpha T$ was then obtained. Depending on the averaged value of a α chosen,[13,14] the coefficient of T varied from about 0.027 to 0.058. In view of the simplified model treated, the numerical agreement must be considered satisfactory, and the assignment of the 71-cm^{-1} band to the B_{2u} mode as probable. (A similar calculation for the B_{1u} mode indicates that it would occur near 50 cm^{-1} and with a temperature coefficient about one-fourth that for the B_{2u} mode.) That an equation of the observed form can be derived with coefficients of the correct order of magnitude is an indication that the underlying physical assumption for the variation of frequency with temperature is probably correct.

This research was supported by a grant from the National Science Foundation.

[1] H. A. Willis, R. G. J. Miller, D. M. Adams, and H. A. Gebbie, Spectrochim. Acta **19**, 1457 (1963).
[2] R. V. McKnight and K. D. Möller, J. Opt. Soc. Am. **54**, 132 (1964).
[3] J. E. Bertie and E. Whalley, J. Chem. Phys. **41**, 575 (1964).
[4] A. O. Frenzel and J. P. Butler, J. Opt. Soc. Am. **54**, 1059 (1964).
[5] S. Krimm, C. Y. Liang, and G. B. B. M. Sutherland, J. Chem. Phys. **25**, 549 (1956).
[6] C. W. Bunn, Trans. Faraday Soc. **35**, 482 (1939).
[7] P. H. Geil, *Polymer Single Crystals* (Interscience Publishers, Inc., New York, 1963).
[8] S. Enomoto and M. Asahina, Kolloid Z. **196**, 36 (1964).
[9] M. Tasumi, Ph.D. thesis, University of Tokyo, 1964.
[10] A. Müller and K. Lonsdale, Acta Cryst. **1**, 129 (1948).
[11] A. E. Smith, J. Chem. Phys. **21**, 2229 (1953).
[12] W. Brandt, J. Chem. Phys. **26**, 262 (1957).
[13] E. A. Cole and D. R. Holmes, J. Polymer Sci. **46**, 245 (1960).
[14] P. R. Swan, J. Polymer Sci. **56**, 403 (1962).

Volume Correction for the Indirect Moving-Boundary Method and the Transference Numbers of Concentrated Aqueous Sodium Chloride Solutions

M. Spiro
Department of Chemistry, Imperial College of Science and Technology
London, S.W.7, England
(Received 4 December 1964)

It has been proved by Kohlrausch[1] and others[2] that, for a two-electrolyte moving boundary such as KCl←NaCl, the normality (C) of the following or indicator electrolyte (NaCl) adjusts itself behind the boundary according to

$$C_{\text{NaCl}}/C_{\text{KCl}} = T_{\text{Na}^+}/T_{\text{K}^+}, \qquad (1)$$

where T is the transference number of the subscripted ion constituent. More recently, both Bearman[3] and Haase[4] have shown by very detailed arguments that

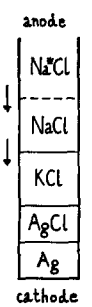

FIG. 1. Schematic diagram of moving-boundary experiment.

the Kohlrausch equation (1) is subject to a previously unsuspected volume correction. In this note the correction is derived more simply and along the same lines as other moving-boundary formulas,[2] and the resulting equation is then applied to the KCl←NaCl data obtained by Currie and Gordon.[5]

Suppose that the KCl←NaCl boundary in Fig. 1 has moved sufficiently far to form an appreciable length of adjusted NaCl solution, and then imagine that the upper part of the tube is rapidly irradiated to produce trace amounts of Na*. The NaCl←Na*Cl boundary so formed will move with the same velocity, V_F liter/faraday, as the KCl←NaCl boundary since the space between them contains only the uniform adjusted NaCl solution. The uncorrected transference numbers are therefore given by the respective moving-boundary equations $T_{\text{K}^+} = C_{\text{KCl}} V_F$, $T_{\text{Na}^+} = C_{\text{NaCl}} V_F$, which on combination reproduce Eq. (1). The volume corrections depend upon the volume increases ΔV occurring between the closed Ag/AgCl electrode and points in the KCl or NaCl solution, respectively, which the corresponding boundaries do not pass.[6] Thus,[7]

$$\Delta V_{\text{KCl}} = V_{\text{Ag}} - V_{\text{AgCl}} + T_{\text{K}^+} \bar{V}_{\text{KCl}},$$

$$\Delta V_{\text{NaCl}} = V_{\text{Ag}} - V_{\text{AgCl}} + T_{\text{Na}^+} \bar{V}_{\text{NaCl}},$$