

Letters to the Editor

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Centrifugal Distortion Effects in Methyl Chloride

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THE centrifugal distortion constants of the methyl halides were calculated some time ago by Slawsky and Dennison.¹ Using the values of the potential constants which were available at that time they obtained for CH₃Cl the following figures for the coefficients, respectively, of the $-(J^2+J)^2$ and $-(J^2+J)K^2$ terms: $D_{JJ}=+3$ kc/sec and $D_{JK}=-293$ kc/sec. More recently² these constants have been determined experimentally from the microwave spectrum of methyl chloride and have been found to be $D_{JJ}=+26.4$ kc/sec, $D_{JK}=+189$ kc/sec for CH₃Cl³⁶ and $D_{JJ}=+27.0$ kc/sec, $D_{JK}=+184$ kc/sec for CH₃Cl³⁷. The agreement between theory and experiment is obviously very poor.

Since the work of Slawsky and Dennison, new experimental data have been found which make possible a much more accurate evaluation of the molecular potential constants, and consequently a recalculation of the centrifugal constants has been undertaken. The data now comprise the following items: (1) the six fundamental frequencies³ of CH₃Cl, (2) the six fundamental frequencies³ of CD₃Cl, (3) the three ζ of the perpendicular⁴ bands of CH₃Cl, and (4) two of the ζ of the perpendicular bands of CD₃Cl. Since the parallel and perpendicular bands of the light and heavy methyl chloride are related through the product rule and since the sum of the ζ is a function only of the moments of inertia, the above items constitute 14 independent data which are available for the calculation of the 12 general potential constants describing the molecule.

The following procedure was employed. The product rules were used to estimate the normal frequencies of both CH₃Cl and CD₃Cl using the methods developed by Hansen and Dennison.⁵ It is believed that the normal frequencies so determined are probably accurate to around 0.5 percent. A set of 12 potential constants were found which (1) reproduced the 12 normal frequencies of the light and heavy methyl chloride within 0.5 percent, (2) reproduced the 5 experimental spacings of the fine structure of the perpendicular bands (dependent upon the ζ -values) with an accuracy of better than 8 percent (average error = 4 percent), and (3) described a potential which is essentially of the valence type. This last property means that if the potential is expressed by means of valence coordinates, (i.e., the CCl and CH distances and the H-C-Cl and H-C-H angles) the coefficients of the cross-product terms are small in comparison with those of the diagonal terms. It may be remarked that the most significant cross-product term was found to be the one connecting the CCl distance and the H-C-Cl angles.

Using the new potential constants the centrifugal distortion was calculated and led to the values $D_{JJ}=+18.4$ kc/sec, $D_{JK}=+189$ kc/sec for CH₃Cl³⁶ and $D_{JJ}=+17.8$ kc/sec, $D_{JK}=+186$ kc/sec for CH₃Cl³⁷. It will be noted that D_{JK} agrees very well indeed with the corresponding experimental values, but that D_{JJ} differs by a factor of about 1.5.

The discrepancy between the theoretical and observed values of D_{JJ} was examined carefully. Theoretically, the situation appears to be very straightforward. This particular term in the energy arises from the centrifugal distortion of the molecule when it rotates end over end (i.e., when $K=0$). The distortion is caused in large measure by the change in length of CCl distance, and hence it depends directly upon the lowest parallel vibration frequency which lies at 732 cm⁻¹. Indeed a simple calculation in which the methyl chloride molecule is represented as a diatomic molecule with atoms of mass 35 and 15 and with the single frequency 732 cm⁻¹ yields the result $D_{JJ}=+19$ kc/sec. It therefore appears that no reasonable change in the potential constants can resolve the discrepancy.

On the side of experiment, however, the evidence is much less conclusive. The determination of D_{JK} depends upon differences in frequency between adjacent microwave lines and an examination of the self-consistency of these lines leads to the estimate that D_{JK} is probably correct to around 1 percent. D_{JJ} , on the other hand, is found by combining lines in quite different regions of the microwave spectrum, e.g., the lines at 26585.77 and 79754.85 mc/sec for CH₃Cl³⁶. If the first of these should be decreased by 0.17 and the second increased by 0.17 mc/sec, the resulting experimental D_{JJ} would equal +18.4 kc/sec in exact agreement with the theoretical value.

The details of the calculation together with the values of the potential constants of methyl chloride will be published shortly.

¹ Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. 7, 509 (1939).

² J. W. Simmons and W. E. Anderson, Phys. Rev. 80, 338 (1950).

³ G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 315.

⁴ See reference 3, p. 438.

⁵ G. E. Hansen and D. M. Dennison, J. Chem. Phys. 20, 313 (1952).

Solutions of Fluorocarbons and Hydrocarbons; the Energy of Mixing

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RECENT articles on solutions of fluorocarbons and hydrocarbons¹⁻³ show that large discrepancies exist between the energies of mixing and those calculated from the approximate equation:

$$\bar{E}_1 - E_1^0 = \left(\frac{X_2 V_2}{X_1 V_1 + X_2 V_2} \right)^2 V_1 \left[\left(\frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} - \left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 \quad (1)$$

developed by Hildebrand and Wood⁴ and by Scatchard,⁵ Simons and Dunlap¹ using the procedure of Hildebrand and Wood, but using $V = X_1 \bar{V}_1 + X_2 \bar{V}_2$ instead of $V = X_1 V_1 + X_2 V_2$, derived the following equation:

$$\bar{E}_1 - \frac{V_1}{\bar{V}_1} E_1^0 = \left(\frac{X_2 \bar{V}_2}{X_1 \bar{V}_1 + X_2 \bar{V}_2} \right)^2 \bar{V}_1 \left[\left(\frac{V_1 \Delta E_1}{\bar{V}_1^2} \right)^{\frac{1}{2}} - \left(\frac{V_2 \Delta E_2}{\bar{V}_2^2} \right)^{\frac{1}{2}} \right]^2 \quad (2)$$

from which $\bar{E}_1 - \bar{E}_0$ can be calculated. This gives a considerable increase in the energy of mixing, which is primarily due to expansion (about 3 percent in these mixtures), but it was pointed out that this alone was not enough to account for the large energy attending the mixing of *n*-pentane with *n*-pentafluorane. The discrepancy was ascribed to properties of the hydrocarbon, and the concept of interpenetration was invented as an adjustment to the existing theory. Simons and Mausteller studied the system *n*-butane-*n*-butfluorane² and found the same discrepancy from the simple theory as was found with the five carbon system. Hildebrand discussed discrepancies from the simple theory⁶ in the case of hydrocarbons and designated their behavior as "anomalous." For practical purposes he adjusted the solubility parameter $(\Delta E/V)^{\frac{1}{2}}$ of the hydrocarbons by calculating an empirical value for this quantity from the solubility data.

In the articles^{1,2} the partial molal heats and free energies of mixing calculated from liquid vapor equilibrium data are plotted

TABLE I. System $n\text{-C}_5\text{H}_{12} - n\text{-C}_5\text{F}_{12}$.

Partial molal heats and energies for C_5F_{12}				Partial molal heats and energies for C_5H_{12}			
Mole fraction of $n\text{-C}_5\text{F}_{12}$	$\bar{E}_1 - E_1^0$ Eq. (1) (calc)	$\bar{E}_1 - E_1^0$ Eq. (3) (calc)	$\bar{H}_1 - \bar{H}_1^0$ exp. (calc)	Mole fraction of $n\text{-C}_5\text{H}_{12}$	$\bar{E}_2 - E_2^0$ Eq. (1) (calc)	$\bar{E}_2 - E_2^0$ Eq. (3) (calc)	$\bar{H}_2 - \bar{H}_2^0$ exp. (calc)
0.0		1798		0.0		1168	
0.1	220	1428	1425	0.1	170	989	985
0.2	155	1019	925	0.2	145	824	870
0.3	110	711	655	0.3	120	672	735
0.4	80	476	490	0.4	95	536	535
0.5	45	296	320	0.5	75	410	415
0.6	30	158	250	0.6	50	297	355
0.7	15	56	150	0.7	30	196	275
0.8	6	1	0	0.8	15	111	205
0.9	1	0	0	0.9	4	50	140
1.0		0	0	1.0		0	0

against the quantity $(X_2V_2/X_1V_1 + X_2V_2)^2V_1$. The free energy plot is essentially a straight line, while the points for the heats of mixing fall on a sinuous curve which is characteristic of both the four and five carbon systems. Neither the concept of interpenetration as it is presently used, nor an adjustment to the solubility parameters will give a wavy line. One might argue that the geometric mean assumption might not hold in these systems. The energy of mixing calculated from simple theory can be increased to the desired magnitude in these systems by assuming the geometric mean to be off by 5 percent. However, this spreads the curves for the two components farther apart on the volume-fraction plot and does not impart the characteristic wavy behavior.

Implicit in the derivations of Eqs. (1) and (2) is the concept that the product of energy and volume for each component is a constant and remains so during the mixing process. Thus Eq. (2) gives the partial molal energy of mixing for component 1 when both liquids are expanded to their partial molal volumes. The quantities $[(V_1/\bar{V}_1^2)E_1]^{\ddagger}$ and $[(V_2/\bar{V}_2^2)E_2]^{\ddagger}$ are the solubility parameters for each of the components at their partial molal volumes, and $(V_1/\bar{V}_1)E_1^0$ is the point on the energy curve to which component 1 must be changed before it is mixed. If we designate this point as E_1' , we see that $V_1E_1^0 = \bar{V}_1E_1'$.

An equation similar to (2) can be derived using the more general energy-volume relationship $E = k/V^n$. We now have $V_1^nE_1^0 = \bar{V}_1^nE_1'$, and $V_2^mE_2^0 = \bar{V}_2^mE_2'$, and the equation for the partial molal energy of mixing after rearranging and setting $E_1^0 = -\Delta E$ is:

$$\bar{E}_1 - E_1^0 = \left(\frac{X_2\bar{V}_2}{X_1\bar{V}_1 + X_2\bar{V}_2} \right) \bar{V}_1 \left[\left(\frac{V_1^n \Delta E_1}{\bar{V}_1^{n+1}} \right)^{\ddagger} - \left(\frac{V_2^m \Delta E_2}{\bar{V}_2^{m+1}} \right)^{\ddagger} \right] - \left(\frac{V_1^n - \bar{V}_1^n}{\bar{V}_1^n} \right) \Delta E_1. \quad (3)$$

This equation reduces to Eq. (1) when there is no volume change on mixing. The first term gives the partial molal energy of mixing at \bar{V}_1 and \bar{V}_2 , and the second term is the energy required to change component 1 from V_1 to \bar{V}_1 .

In applying this equation to the n -pentane- n -pentofrane system and to the n -butane- n -butofrane system, let subscript 1 designate

TABLE II. System $n\text{-C}_4\text{H}_{10} - n\text{-C}_4\text{F}_{10}$.

Partial molal heats and energies for $n\text{-C}_4\text{F}_{10}$				Partial molal heats and energies for $n\text{-C}_4\text{H}_{10}$			
Mole fraction of $n\text{-C}_4\text{F}_{10}$	$\bar{E}_1 - E_1^0$ Eq. (1) (calc)	$\bar{E}_1 - E_1^0$ Eq. (3) (calc)	$\bar{H}_1 - \bar{H}_1^0$ exp. (calc)	Mole fraction of $n\text{-C}_4\text{H}_{10}$	$\bar{E}_2 - E_2^0$ Eq. (1) (calc)	$\bar{E}_2 - E_2^0$ Eq. (3) (calc)	$\bar{H}_2 - \bar{H}_2^0$ exp. (calc)
0.0				0.0			
0.1	171	1444	1455	0.1	133	845	1185
0.2	123	999	1062	0.2	114	746	992
0.3	86	689	786	0.3	94	692	696
0.4	57	359	638	0.4	75	639	574
0.5	37	265	513	0.5	56	477	495
0.6	21	115	386	0.6	39	367	403
0.7	11	42	138	0.7	24	225	222
0.8	5	40	0	0.8	12	144	69
0.9	1	0	0	0.9	3	58	49
1.0				1.0			

the fluorocarbon. The exponent n for the fluorocarbon can be evaluated from the experimental data when $V_2 = \bar{V}_2$, that is, at a high concentration of hydrocarbon. The exponent m for the hydrocarbon can be evaluated at $V_1 = \bar{V}_1$ or at a high fluorocarbon concentration.

For n -pentane m was found to be 1.28 and for n -pentofrane n was found to be 1.85. These exponents were used to calculate the partial molal energy of mixing at each composition for the five carbon and four carbon systems, and these values are compared with the partial molal heats of mixing in Tables I and II. The shape of the energy-volume fraction curves are reproduced rather well. A small discrepancy in the volume change attending mixing would result in a large error in the calculated energy. Calculations of this type certainly show the need for careful measurements on the volume change attending mixing, and may provide a method for determining energy-volume relationships for the expansion of liquids at constant temperature.

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Linear Film Growth in Tarnishing Reactions

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ACCORDING to the Cabrera-Mott theory of tarnishing reactions,¹ in the early stages of film growth electrons pass through the tarnishing film either by tunnel effect or thermionic emission to form negative ions at the outer surface. The field of these ions, which is inversely proportional to film thickness, then pulls positive metal ions through the film. This should give rise to an initial logarithmic growth rate, followed by a parabolic one.

Experiments of Perry and Winkler of this University,² indicate for growth of AgCl on silver in triphenylmethyl chloride (at temperatures slightly above the critical temperature for film growth), a transition from an initial logarithmic rate of growth to a linear one at greater thickness. In attempting to interpret these results, we were led to investigate critically the mechanism proposed by Cabrera and Mott.

Using a one-dimensional square-well model for crystalline AgCl, and adjusting the constants in such a way as to have the top of the valence band at -7.5 eV and the bottom of the conduction band at -3.4 eV³ as given by L. P. Smith, we first calculated the probability of quantum-mechanical tunnelling of electrons through the film as a function of thickness assuming certainty of capture in ionic levels at the outer film surface. We found that the supply of electrons for forming Cl^- was adequate for sustaining the Mott-Cabrera mechanism up to a film thickness of about 80Å, which coincides approximately with the point at which the logarithmic growth law goes over (a) at 65.4°C, to a parabolic one, and (b) at 44.9°C to a linear one. It was thus evident that some other process had to supply the electrons past this point.

We then calculated the flow of electrons due to thermionic emission from the Fermi surface of the metal into the conduction band of AgCl. At all temperatures used in the Perry-Winkler experiments, it was found that the number of electrons getting through the film by this process was inadequate to sustain the reaction, by a large factor. This was due to the large work function (1.3 eV).

Since the existence of a linear growth law clearly suggests that the rate-controlling mechanism does not depend on the thickness of the film, it would seem that in such a case this limiting mechanism is *not* the diffusion of Ag^+ ions, as assumed by Mott and Cabrera, but the formation of Cl^- ions at the film-reagent inter-