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THERMAL CONDUCTIVITY MEASUREMENTS AND MOLECULAR ASSOCIATION IN ETHANOL VAPOR

by

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ABSTRACT

Thermal conductivity measurements on ethanol vapor are reported as a function of temperature (329-419K) and pressure (100-1800 torr). The thermal conductivity *versus* pressure plots at constant temperature exhibit strong upward curvature at the lower temperatures and nearly linear increases at the higher temperatures. This enhancement in the thermal conductivity is indicative of the presence of a dimeric species and one or more larger clusters in the vapor. Analysis of the data gave best fits for monomer-dimer-tetramer and monomer-dimer-hexamer models. The resulting thermodynamic parameters for the association reactions in the monomer-dimer-tetramer model are: $-\Delta H_2 = 3.70$ kcal mol^{-1}, $-\Delta S_2 = 16.36$ cal mol^{-1} K^{-1}; $-\Delta H_4 = 22.15$ kcal mol^{-1}, $-\Delta S_4 = 74.65$ cal mol^{-1} K^{-1}. Quantum mechanical evidence indicates that the tetramer is the most probable associated species larger than the dimer.

I. INTRODUCTION

There have been a large number of experimental studies of alcohol vapors which indicate that associated hydrogen bonded species exist in the vapor.[1] In a study of methanol vapor from this laboratory[2], the thermal conductivity isotherms exhibited a strong upward curvature as a function of pressure. It was found that the methanol thermal conductivity data could be fit very well assuming the presence of a tetrameric associated species in addition to the monomer.

In this paper we report thermal conductivity measurements on ethanol vapor in the temperature range 329-419 K and at pressures ranging from 100-1800 torr. At the lower temperatures (up to ∿360 K) the isotherms exhibit upward curvature with increasing pressure similar to that of methanol. However, at higher temperatures the ethanol isotherms showed essentially linear increases with pressure. All of the ethanol thermal conductivity isotherms were fit quite well using the Butler-Brokaw theory[3,4] assuming the presence of a dimer and one higher associated species in addition to the monomer. In section II details of the thermal conductivity measurements on ethanol are given. In section III the data is fit to the Butler-Brokaw theory assuming various possible associated species. Finally, in section IV the thermodynamic quantities of the associated species are discussed.

II. EXPERIMENTAL METHOD

The thermal conductivity, λ, of ethanol vapor was measured as a function of pressure at eight temperatures (329, 337, 347, 357, 367, 377, 405 and 419 K). All the measurements were made with a thick hot wire cell using a relative technique in which the cell was calibrated with high purity reference gases (*e.g.* N_2, Ar, Kr). Details of the apparatus, experimental procedure, and reference gas thermal conductivities have been given in other publications.[5,6] The reagent grade ethanol sample (obtained from U.S. Industrial Chemicals Company) was dried and degassed *in vacuo* prior to use. Due to the so-called "temperature-jump" effect,[7] no data were recorded at pressures below 100 torr.

For the cell used in this study, the measured cell voltages, V, at constant input current, were empirically found to be related to the reference gas thermal conductivities by the relation

$$V= A + B/\lambda \tag{1}$$

where A and B are constants dependent only on the temperature. Because of this linear relationship, it was sufficient to calibrate the cell with only two gases (N_2 and Ar) in order to determine A and B. We estimate that the absolute error in the calculated conductivities is less than 1% and the relative error less than 0.5%. The experimental thermal conductivity data for ethanol are listed in Table I and plotted in Fig. 1.

There have been relatively few experimental studies of the thermal conductivity of ethanol vapor. The compilation of Touloukian, Liley, and Saxena,[8] gives recommended values of the thermal conductivity at p = 1 atm. based on the experiments of Shushpanov[9]. These values are consistently 4% lower than our results. A more recent experimental study by Foz, Banda, and Masia[10] report values for ethanol vapor at 384 K which are only ca. 1% lower than values extrapolated from our data.

III. DATA ANALYSIS

The thermal conductivity of an associating gas can be expressed as

$$\lambda = \lambda_f + \lambda_c + \lambda_R \tag{2}$$

where λ_f is the thermal conductivity of a frozen (non-reacting) composition of all the vapor species, λ_c is the enhancement of the thermal conductivity due to "collisional transfer," and λ_R is the contribution to the thermal conductivity from the transport of association enthalpy in a thermal gradient. Generally, λ_f and λ_c are very weakly dependent on pressure, whereas, λ_R is strongly dependent on pressure if there are associated species in the vapor.

A general expression for λ_R when there are associated species present in the vapor has been given by Butler and Brokaw[3] and is discussed in detail elsewhere.[4] An approximate equation for λ_R when there are only small amounts of associated species present is given by

$$\lambda_R = \sum_n (pD_{1n}/RT)\ (\Delta H_n^2/RT^2)\ K_n p_1^{n-1} \tag{3}$$

where n is the cluster size, T is the temperature in degrees Kelvin, pD_{1n} is the pressure-binary diffusion coefficient, R is the gas constant, K_n is the equilibrium constant for $nA \rightleftharpoons A_n$, ΔH_n is the association reaction enthalpy change, and p_1 is the partial pressure of the monomer. Equation (3) indicates that the effect on the thermal conductivity of the presence of a small amount of dimer (n=2) in the vapor is a nearly linear increase in the thermal conductivity with pressure at constant temperature (pD_{1n} is pressure independent). Equation (3) also illustrates the p^{n-1} dependence of λ_R which leads to the upward curvature of conductivity *versus* pressure plots when there is a sufficient concentration of higher polymers ($n>2$) present.

The experimental isotherms for ethanol, shown in Fig. 1, change in overall shape with temperature in a very interesting manner. The lower temperature isotherms show strong upward curvature indicative of a polymeric species larger than the dimer. At the higher temperatures, however, the isotherms increase linearly with pressure indicative of a dimeric contribution to λ_R. Thus, in light of the above discussion, it qualitatively appears that there are indeed at least two association reactions occurring simultaneously in ethanol vapor. The temperature dependence of the terms in Eq. (3) apparently cause the dimeric reaction to dominate the thermal conductivity enhancement at high temperatures and the higher polymer to dominate at low temperatures. In order to fit the ethanol vapor thermal conductivity data to Eq. (2), values for $pD_{k\ell}$, λ_c, and λ_f are necessary. We now proceed to explain how equations for these quanitities were obtained.

The pressure binary diffusion coefficient product, $pD_{k\ell}$, can be expressed in terms of the monomer self diffusion coefficient by the semi-empirical relation[2]

$$pD_{k\ell} = pD_{11}\ [(k + \ell)/2k\ell]^{1/2}[2/(k^{1/3} + \ell^{1/3})]^2. \qquad (4)$$

The term pD_{11} is evaluated[2] from the experimental gas viscosity reported by Touloukian, Saxena, and Hestermans[11] and the Lennard-Jones potential parameters[12], $\varepsilon/K = 391$ K and $\sigma = 4.455\mathring{A}$. The resulting equation for pD_{11} is

$$10^5\ pD_{11} = 0.0015828T^2 + 0.039428T\ (\text{cal cm}^{-1}\text{sec}^{-1}) \qquad (5)$$

The λ_f and λ_c terms are somewhat pressure dependent and must be included in the complete data analysis. In calculating these terms for ethanol vapor the assumption is made that the equilibrium composition can be represented in terms of a monomer-dimer mixture only, *i.e.*, the partial pressures of the higher polymers are negligible compared to the monomer or dimer. This assumption will be seen to be justified by the final results.

Using the scheme outlined in Ref. 6 and the experimental heat capacity reported by Touloukian and Makita[13], the resulting equation for λ_f is

$$\lambda_f = \lambda_1 \left[\frac{1}{1+1.57K_2p_1} + \frac{0.92}{1+0.699/K_2p_1}\right] \tag{6}$$

where λ_1 is the value of the thermal conductivity at zero pressure and is taken to be a fitting parameter for each isotherm. At 357 K the λ_f term contributes a 1.1% decrease in the total thermal conductivity over one atmosphere. This is small compared to the ca. 18% increase observed.

The λ_c term, also obtained using the scheme outlined in Ref. 6 (using the Lennard-Jones potential parameters given previously), is given by

$$\lambda_c = 3.25\ \lambda_1\ p/T \tag{7}$$

with p in atmosphere and T in Kelvin. The λ_c team contributes an increase of ca. 0.9% over a pressure range of one atmosphere. This is again small compared to the experimentally observed increase and also nearly cancels the λ_f effect.

Using a least squares fitting procedure described in detail in Ref. 5 the measured thermal conductivity data at all eight temperatures were fit simultaneously to Eq. (2) with λ_R given by the complete Butler-Brokaw expression[3,4], λ_f defined by Eq. (6), and λ_c defined by Eq. (7). In the equation for λ_R the associated species assumed present were the dimer and one higher polymer ($3 \leq n \leq 8$). The variables in the fitting procedure were ΔH_2, K_2, ΔH_n, K_n, and the eight λ_1 values (one for each isotherm).

The results for the monomer - dimer - n-mer fits are listed in Table II. The standard deviations indicate that the best fits were obtained by the monomer-dimer-tetramer and the monomer-dimer-hexamer models. Both of these fits are essentially indistinguishable and are represented by the solid lines in Fig. 1. These fits do a good job in reproducing the data at both high and low temperatures. The 1-2-5, 1-2-7, and 1-2-8 fits are very similar to the 1-2-4 and 1-2-6 fits, but with slightly larger standard deviations. The 1-2-3 model gives the poorest fit with too much curvature at high temperatures and too little curvature at low temperatures. Addition of a second higher polymer ($n>2$) to the models did not produce a significantly better fit than that found from the 1-2-4 or 1-2-6 models.

IV. DISCUSSION

The thermodynamic quantities obtained for the various polymerization reactions are given in Table II. Note the relative constancy of the dimerization thermodynamic parameters ΔH_2 and ΔS_2 from the 1-2-n fits, $n > 3$. The reason for this is that the fitting procedure extracts the dimerization thermodynamic data mainly from the high temperature data where there is little contribution from the higher polymer association reactions.

Due to the essential equivalence in quality of the various 1-2-n fits for $n>3$, we cannot definitively conclude that only one particular n-mer is responsible for the thermal conductivity enhancement. Certainly the actual physical picture is one in which many different polymers exist in the vapor and one cannot separate their contributions to the thermal conductivity in the data analysis. However, the results in Table II allow us to set definitive upper limits to the concentration of the associated species, n = 3,4,5,6,7,8. In other words, the best fit values of K_n at any temperature in the experimental range represent the largest possible values consistent with the thermal conductivity data. Table III lists the maximum mole fractions of these species at 100°C and 1 atm. pressure.

Our thermodynamic results for the ethanol tetramer are similar to those obtained in the study of the thermal conductivity of methanol vapor[2] where the best fit was obtained assuming the presence of a tetramer. The thermodynamic parameters for the methanol and ethanol tetramer are similar. Since no thermal conductivity data for methanol were measured at high temperatures (where the dimer dominates the features of the isotherms), no thermodynamic values were obtained for the methanol dimer.

Our thermodynamic quantities for the ethanol dimer and tetramer are close to those obtained from analyses of second virial coefficient data of ethanol vapor. Analysis of the heat capacity data of ethanol by Barrow[14] gave $-\Delta H_2 = 3.40$ kcal mol^{-1}, $-\Delta S_2 = 16.57$ cal mol^{-1}K^{-1}, $-\Delta H_4 = 24.8$ kcal mol^{-1}, $-\Delta S_4 = 81.45$ cal mol^{-1}K^{-1}. Similar results were obtained in a PVT study by Kretschmer and Wiebe.[15]

Theoretical *ab initio* molecular orbital calculations by Curtiss[16] indicate that for a series of methanol polymers, the largest increase in binding energy occurred in the tetrameric species. This apparently occurs due to favorable hydrogen bonding geometry in the cyclic tetrameric structure. Since ethanol is very similar to methanol (theoretical calculations by Curtiss[17] on the ethanol dimer resulted in a binding energy essentially equal to the methanol dimer), one might expect a similar trend in the case of clusters of ethanol molecules. These theoretical results lend to support the presence of a tetramer in ethanol vapor.

V. CONCLUSIONS

The following conclusions can be drawn from this study of association in ethanol vapor.

(1) The enhancement of the ethanol vapor thermal conductivity due to vapor phase association is similar to methanol vapor. Both show steep upward curvature in the lower temperature isotherms.

(2) Because of the linearity of the pressure dependence at higher temperatures, thermodynamic data for the ethanol dimerization reaction could be deduced. These are $-\Delta H_2 = 3.70$ kcal mol^{-1}, $-\Delta S_2 = 16.36$ cal mol^{-1}K^{-1} (from the 1-2-4 fit).

(3) Data analysis indicates that one or more associated species larger than the dimer exist in ethanol vapor. Although we are not able to determine exactly which of these species exist, upper limits to the actual amounts present are reported. Quantum mechanical calculations on methanol lead us to conclude that the tetramer is the most likely species. Our measurements lead to a value of $-\Delta H_4 = 22.15$ kcal mol^{-1} and $-\Delta S_4 = 74.65$ cal mol^{-1}K.

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Table I: Experimental Thermal Conductivities (cal $cm^{-1}s^{-1}K^{-1}$) of Ethanol Vapor.

T = 328.71 K		T = 337.43 K		T = 347.07 K		T = 357.07 K		T = 366.65 K		T = 377.42 K		T = 405.27 K		T = 418.69 K	
p,torr	$10^5\lambda$	p,torr	$10^5\lambda$	p,torr	$10^5\lambda$	p,torr	$10^5\lambda$	p,torr	$10^5\lambda$	p,torr	$10^5\lambda$	p,torr	$10^5\lambda$	p,torr	$10^5\lambda$
103	4.251	116	4.443	107	4.651	130	4,842	102	5.061	115	5.362	103	5.915	109	6.373
105	4.256	132	4.459	117	4.644	171	4,877	142	5.086	150	5.352	116	5.938	202	6.413
115	4.265	154	4.478	155	4.680	207	4.916	179	5.111	174	5.392	159	6.950	216	6.420
118	4.271	173	4.509	163	4.676	237	4.903	252	5.162	223	5.402	213	5.985	361	6.473
131	4.287	192	4.533	203	4.714	276	4.943	277	5.166	309	5.438	296	6.009	362	6.473
132	4.300	210	4.553	223	4.743	317	4.962	315	5.191	442	5.495	396	6.051	501	6.514
140	4.315	235	4.594	246	4.760	349	5.007	390	5.219	490	5.548	412	6.045	503	6.521
147	4.310	265	4.652	257	4.768	381	5.008	463	5.288	535	5.542	485	6.081	657	6.542
149	4.329	297	4.728	295	4.807	415	5.053	542	5.360	601	5.591	505	6.081	668	6.570
158	4.352	314	4.776	315	4.834	443	5.064	543	5.327	657	5.612	594	6.118	800	6.598
166	4.347	333	4.830	342	4.864	467	5.091	608	5.373	723	5.656	648	6.105	816	6.619
168	4.375	352	4.862	363	4.891	494	5.116	681	5.435	800	5.701	723	6.161	927	6.641
179	4.409			382	4.923	525	5.158	713	5.482	851	5.741	794	6.155	998	6.684
187	4.440			402	4.964	557	5.180	723	5.466	886	5.753	880	6.199	1079	6.669
190	4.436			426	5.006	590	5.253	774	5.535	968	5.834	971	6.205	1122	6.713
203	4.472			447	5.053	636	5.333	822	5.574	1084	5.894	1059	6.250	1240	6.749
208	4.460			473	5.102	668	5.351	874	5.640	1104	5.918	1073	6.237	1281	6.749
				503	5.181	695	5.402	876	5.654	1212	6.004	1279	6.335	1368	6.794
				525	5.227	717	5.463	928	5.712	1284	6.055	1305	6.302	1411	6.779
				532	5,252	759	5.530	931	5.708	1286	6.068	1410	6.361	1506	6,832
						764	5.546	986	5.802			1441	6.354	1555	6.832
						802	5.615	988	5.790			1587	6.401	1659	6.885
						806	5.620	1045	5,868					1713	6,885
								1051	5,900						

TABLE II: Results of Monomer - Dimer - n-mer Fits to the Ethanol Thermal Conductivity Data.

n	Standard Deviation	$-\Delta H_2$ [a]	$-\Delta S_2$ [b]	$-\Delta H_n$ [a]	$-\Delta S_n$ [b]
3	.0242	3.20	16.09	12.99	46.62
4[c]	.0174	3.70	16.36	22.15	74.65
5	.0186	3.92	16.88	27.14	89.43
6	.0173	3.86	16.43	35.87	114.72
7	.0181	3.88	16.31	48.11	149.93
8	.0210	3.90	16.33	55.09	169.82

[a] kcal mol^{-1}

[b] cal $mol^{-1}K^{-1}$

[c] λ_1 values for this fit are 4.11, 4.31, 4.54, 4.73, 5.00, 5.29, 5.91, and 6.39 in order of increasing temperature. Units are 10^{-5} cal $cm^{-1}sec^{-1}K^{-1}$.

TABLE III. Maximum Concentrations of Ethanol Polymers at 373 K and One Atmosphere Pressure.

n	Maximum $(CH_3CH_2OH)_n$ Mole Fraction
3	2.5×10^{-3}
4	4.0×10^{-4}
5	1.9×10^{-4}
6	6.8×10^{-5}
7	1.9×10^{-5}
8	1.0×10^{-5}

Fig. 1: The thermal conductivity of ethanol vapor *versus* the total pressure at (a) the four lowest temperatures and (b) the four highest temperatures. The solid lines represent the results of a least squares fit to the data at all eight temperatures assuming either a monomer-dimer-tetramer model or a monomer-dimer-hexamer model.

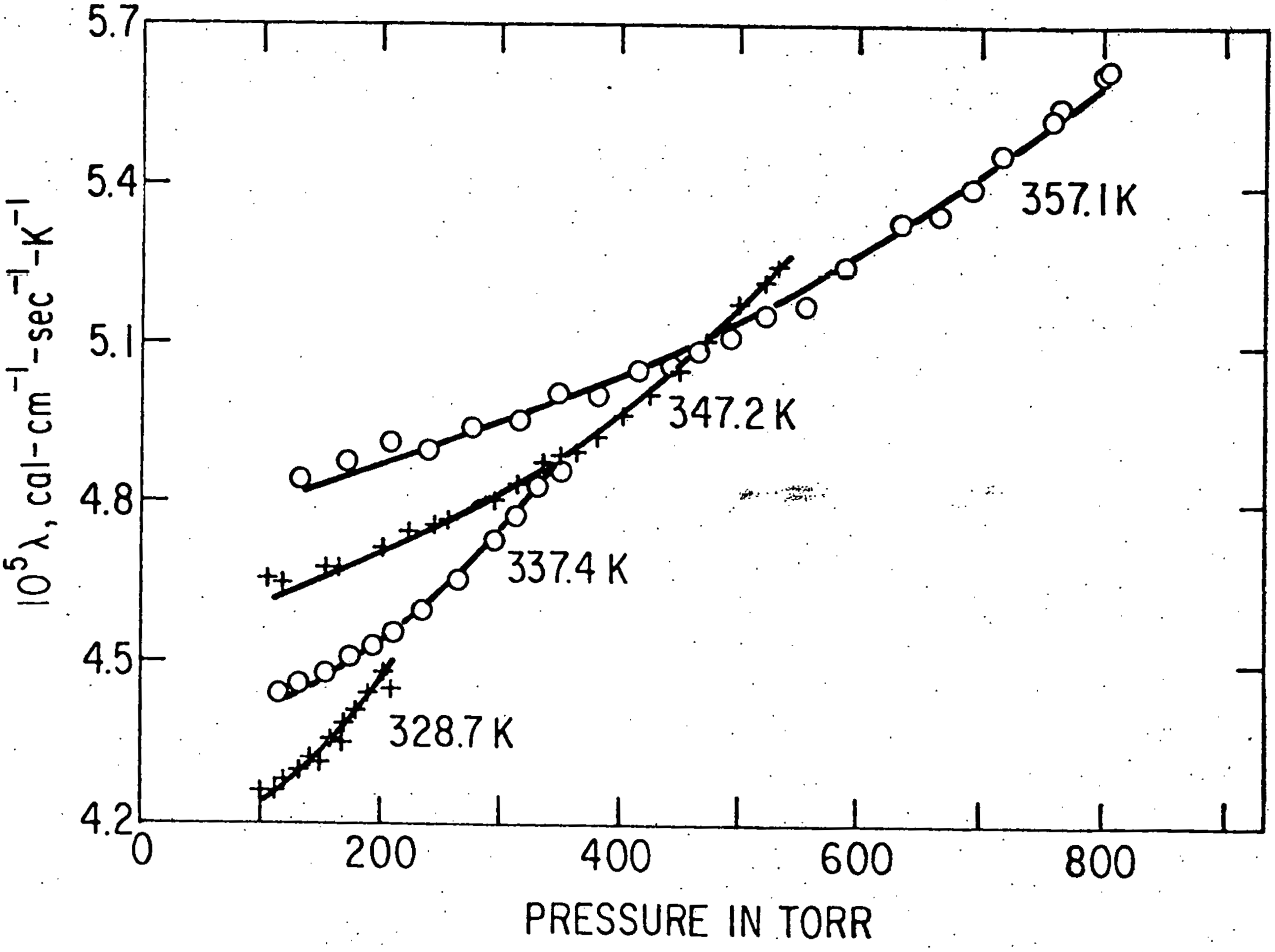
5.7
5.4
5.1
4.8
4.5
4.2
0
200
400
600
800
$10^5\lambda$, cal-cm^{-1}-sec^{-1}-K^{-1}
PRESSURE IN TORR
357.1K
347.2 K
337.4 K
328.7 K

Fig. 1a

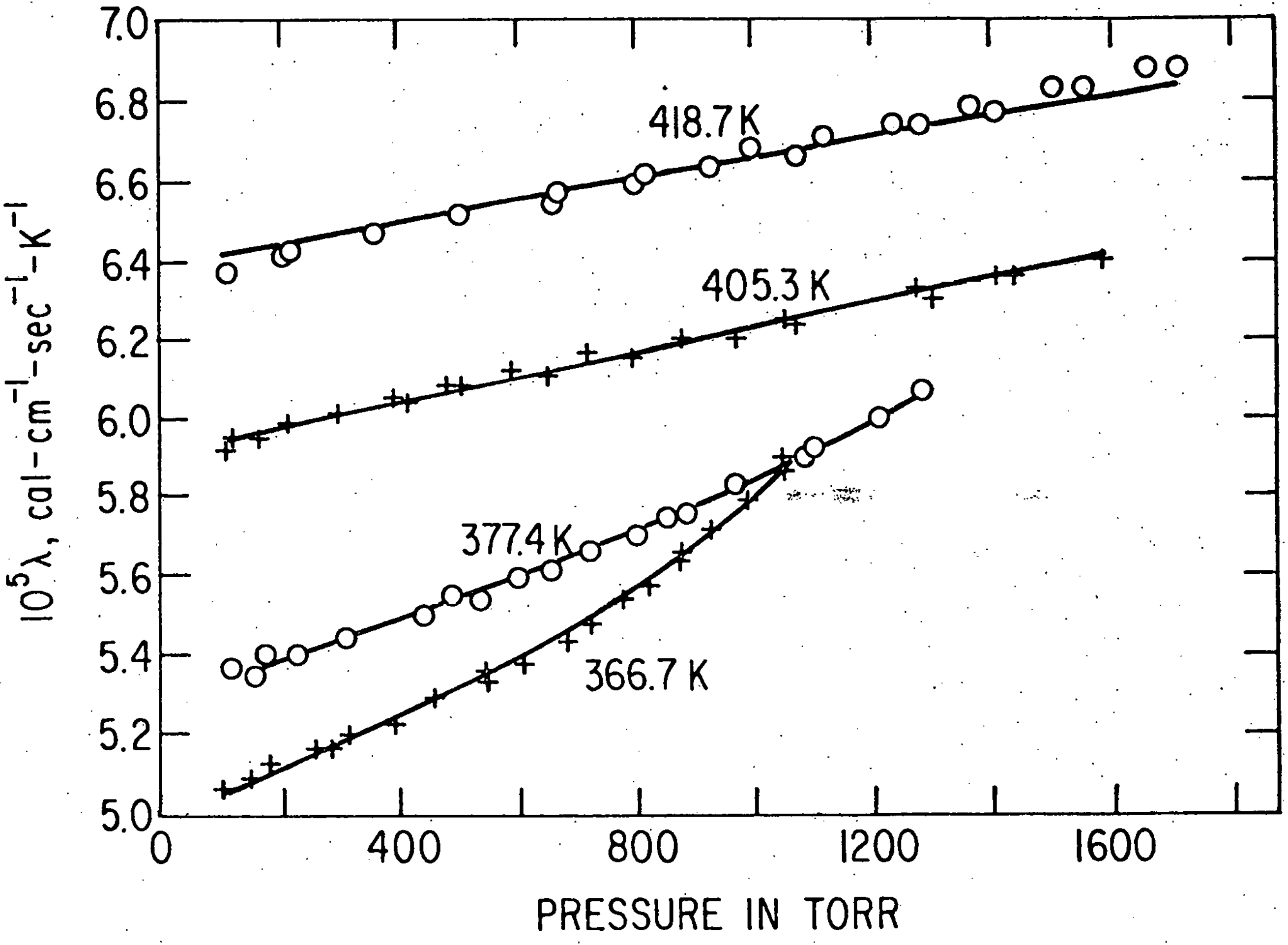
418.7 K
405.3 K
377.4 K
366.7 K
$10^5\lambda$, cal-cm^{-1}-sec^{-1}-K^{-1}
PRESSURE IN TORR
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
0
400
800
1200
1600

Fig. 1b