

Lawrence Berkeley National Laboratory

LBL Publications

Title

STUDIES OF THE VAPORIZATION KINETICS OF HYDROGEN BONDED LIQUIDS

Permalink

<https://escholarship.org/uc/item/2298k11z>

Authors

McFeely, F.R.
Somorjai, G.A.

Publication Date

1971-07-01

Submitted to Physical Chemistry

RECEIVED
REFERENCE
RADIATION LABORATORY

LBL-127 c.1
Preprint

AND
DOCUMENTS SECTION

STUDIES OF THE VAPORIZATION KINETICS
OF HYDROGEN BONDED LIQUIDS

F. R. McFeely and G. A. Somorjai

July 1971

AEC Contract No. W-7405-eng-48

For Reference

Not to be taken from this room

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

LBL-127 c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Studies of the Vaporization Kinetics of Hydrogen Bonded Liquids.

F. R. McFeely and G. A. Somorjai

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
and Department of Chemistry, University of California
Berkeley, California 94720

ABSTRACT

The vacuum evaporation rates of glycerol, ethylene glycol and triethylene glycol have been measured in the temperature range 5°-50°C using a microbalance. The activation enthalpies of vaporization of the three liquids were found to be different from their enthalpies of vaporization. The vacuum evaporation rates for glycerol and triethylene glycole were about one-third of the maximum rate that can be calculated from the vapor pressures, and one-twentieth of the maximum rate for diethylene glycol. It appears that breaking one or more hydrogen bonds at the surface is the rate limiting step in the mechanism of vaporization of these largely hydrogen bonded liquids.

Introduction

To date there have been many studies of the vaporization kinetics of single crystal surfaces. These investigations have revealed a variety of vaporization mechanisms.¹ For some of the solids the desorption of loosely-bound surface species was rate limiting (most metals). For other compounds, bond-breaking at well-defined surface sites, surface chemical reactions, association or dissociation were rate limiting. In cases where desorption of molecules at the vaporizing surface was not the rate limiting step, the observed vaporization rate was frequently found to be less than the maximum possible rate that can be calculated from the kinetic theory of gases. The vaporization coefficient $\alpha_v = \frac{J_{\text{obs}}}{J_{\text{max}}}$ has been used to indicate the magnitude of the deviation of the observed rate from the maximum rate.

In contrast, the vaporization kinetics of liquids have not been investigated. Wyllie² has measured the vacuum vaporization rates of several liquids at one temperature and has thus obtained values for the vaporization coefficient α_v . However the lack of information about the activation enthalpy of vaporization, ΔH_v^* , which can only be obtained from studies of the vaporization rates as a function of temperature, preclude any deduction of the vaporization mechanism.

We have studied the vacuum vaporization rates of glycerol ($\text{CH}_2\text{OHCHOHCH}_2\text{OH}$), diethylene glycol ($\text{CH}_2\text{OHCH}_2\text{OCH}_2\text{CH}_2\text{OH}$) and triethylene glycol ($\text{CH}_2\text{OHCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$) in the temperature ranges 18-50°C, 5-30°C and 10-40°C respectively. From the data the vaporization rates and ΔH_v^* for each liquid were obtained. The experimental results indicate that the breaking of a specific number of hydrogen bonds may be the rate limiting step in each case.

Experimental

The vacuum vaporization experiments were carried out using a Cahn microbalance mounted in a vacuum chamber. The weight change of the balance was displayed on a recorder as a function of time so that the weight of the vaporizing sample could be monitored continuously. The balance could measure weight changes of less than 10 μg .

The liquid that was to be vaporized, (spectrograde for glycerol, and reagent grade for the two glycols), was placed in a cylindrical aluminum sample holder and was maintained in a vacuum of $5 - 50 \times 10^3$ torr for a period of up to five hours to remove dissolved gases and other more volatile impurities (water, etc.). The sample was then placed on the balance and the chamber evacuated by means of an oil diffusion pump to an ambient pressure of $\sim 5 \times 10^{-6}$ torr. At this pressure, the flux of vaporized or ambient molecules striking the vaporizing liquid surface is negligible.

During the experiments the temperature of the liquid was monitored by a .005" Cu-Constantan thermocouple placed directly in the liquid. While diethylene glycol cooled from 22°C to 5°C and triethylene glycol to 10° due to rapid heat loss by vaporization, the temperature measured by the thermocouple was found to be independent of its position in the crucible. It therefore appears that under the given experimental conditions there was no detectable temperature gradient between the surface and the bulk and that we therefore had an accurate measure of the temperature of the vaporizing surface.

The liquid was heated by radiation from a coil of nichrome resistance wire placed near the sample. The liquid was maintained at a constant temperature within $\pm 0.2^\circ\text{C}$ by means of a variable gain feedback control unit. Reproducible steady state vaporization rates at as many as five different temperatures could be measured before the sample surface receded significantly into the holder. The evaporation rates were measured by both starting at low temperature and increasing the temperature and also by starting at high temperature and decreasing the temperature. The vacuum evaporation rates were reproducible regardless of the thermal history of the sample. Fifty vaporization rates were measured with the various glycerol samples, forty were made using diethylene glycol and thirty-five using triethylene glycol in the indicated temperature ranges.

Results

Figure 1 shows a plot of the logarithm of the evaporation rate ($\text{mg}/\text{cm}^2\text{min}$) as a function of the reciprocal temperature for glycerol. The solid line indicates the experimental vacuum vaporization rate, while the dotted line represents the maximum rate predicted by the kinetic theory of gases using the well-known Langmuir equation³

$$J(\text{mg}/\text{cm}^2\text{min}) = P_{\text{eq}}/(2\pi MRT)^{\frac{1}{2}}$$

using the equilibrium vapor pressure data of Stedman.⁴ Here P_{eq} is the equilibrium vapor pressure, M is the molecular weight of the vapor (assumed to be monomer) and R and T have their usual meaning. The isolated point on the graph represents the vacuum vaporization rate of glycerol as determined at a single temperature by Heideger and Boudart.⁵

Figures 2 and 3 give the vacuum vaporization rates of diethylene and triethylene glycol, along with the maximum rates calculated from the equilibrium vapor pressure data of Gallagher and Hibbert.⁶ The equilibrium heats of vaporization, ΔH_v , and the experimentally determined activation enthalpies, ΔH_v^* for all three liquids are summarized in Table 1, along with $\alpha_v(300^\circ\text{K})$, the ratio of the observed vacuum evaporation rate to maximum rate for each of the liquids at 300°K . It should be noted that α_v is not constant throughout the studied temperature range due to the difference in ΔH_v and ΔH_v^* .

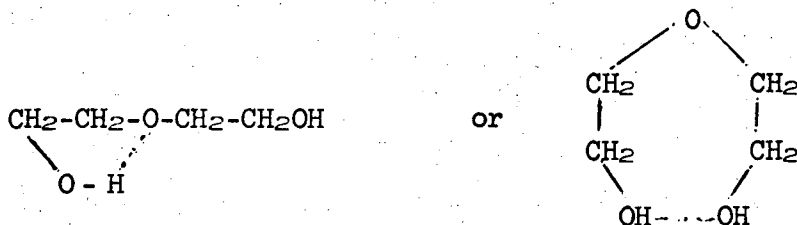
Discussion

In the three organic liquids studied, the energy binding a molecule to its neighbors at the liquid surface is primarily due to hydrogen bonding and attractive interactions through dispersion forces. Bondi and Simkin⁷ have devised a method of separating these two major contributions. The interaction energy due to dispersion forces is estimated by the heat of vaporization of a compound in which methyl groups are substituted for the hydroxyl groups. For example the dispersion force contribution for glycerol is taken to be the ΔH_v of 3-methylpentane. The hydrogen bonding contribution is then accounted for using a semi-empirical parameter $\delta(\text{OH})$, the hydrogen bond energy increment per OH group. For the purposes of our analysis we chose $\delta(\text{OH}) = 4.3$ kcal mole since that is the average reported value of the hydrogen bond energies for alcohols given by Pimentel⁸ and since that value fits the data well.

The predicted enthalpies of vaporization with varying hydrogen bonding contributions (assuming the additivity of hydrogen bond energies) are shown in Table 2 along with the experimental enthalpies and activation enthalpies of vaporization. The homologous compounds used to estimate the dispersion force contribution to ΔH_v were, for glycerol, 3-methylpentane, for diethylene glycol, dipropyl ether, and for triethylene glycol, dipropoxyethane. The heats of vaporization of 3-methylpentane and dipropyl ether are given by Jordan.⁹ Unfortunately we could find no reliable data for dipropoxyethane, but judging by the variations in heats of vaporization of similar compounds we can be reasonably confident that its heat of vaporization is greater than that of dipropoxyethane by no more than 1-2 kcal/mole.

Inspection of Table 2 reveals that the three liquids studied have vaporization energy requirements that are distinctly different. For glycerol, which exhibits the strongest total hydrogen bonding, $\Delta H_v^* < \Delta H_v$. Thus the activation enthalpy of vaporization is less than the total enthalpy of vaporization. It is apparent from Table 2 that the enthalpy of vaporization reflects the breaking of three hydrogen bonds. It is also apparent that the activation enthalpy corresponds to the breaking of only two hydrogen bonds. It is assumed that the molecules vaporize as monomers.

For the vaporization of diethylene glycol $\Delta H_v^* > \Delta H_v$. There is strong experimental evidence that this molecule exists in a ringlike form caused by internal hydrogen bonding.



Its enthalpy of vaporization $\Delta H_v = 12.5$ kcal/mole is appreciably smaller than that for ethylene glycol (17.0 kcal/mole).⁶ Similarly the entropy of vaporization at the boiling point indicates weaker association in liquid diethylene glycol ($\Delta S_v \approx 24.14$ e.u.)⁶ than in liquid ethylene glycol ($\Delta S_v \approx 29.0$ e.u.)⁶ or triethylene glycol ($\Delta S_v \approx 30.9$ e.u.)⁶. Thus vaporization near equilibrium is likely to require the breaking of only one hydrogen bond per molecule, in addition to overcoming the attractive dispersion forces between the molecules in the liquid.

The activation enthalpy of vaporization however, indicates a much greater energy requirement (16.8 kcal/mole) for breaking the molecule away at the vaporizing surface. This larger energy requirement would indicate that two hydrogen bonds must be broken before the molecule could vaporize into vacuum.

For triethylene glycol ($\text{CH}_2\text{OHCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$) the activation enthalpy of vaporization is only slightly larger (18.4 kcal/mole) than the heat of vaporization (> 17.0 kcal/mole).⁶ Also this liquid has a large evaporation coefficient. The breaking of two hydrogen bonds is clearly necessary for vaporization to occur, both in equilibrium and in vacuum. The less than unity evaporation coefficient indicates that

although the energetics of vaporization far from equilibrium are not much different from the equilibrium case, the surface concentration of molecules that may vaporize is less than their surface concentration at equilibrium. Since the presence of minute impurities at the vaporizing surface that could block the vaporization cannot be ruled out, a more detailed analysis of this effect would not be useful.

Studies of the vaporization of ice single crystals¹⁰ have revealed that the breaking of one hydrogen bond can be a rate limiting step in the sequence of reaction steps leading to the vaporization of water molecules. At low temperatures ($\leq -80^\circ\text{C}$), $\Delta H_v^* \approx \Delta H_v - 12.2$ kcal/mole and $\alpha_v = 1$. This value reflects the energy necessary to break two hydrogen bonds. However, above -45°C ΔH_v^* approaches the values of $\frac{1}{2}\Delta H_v$ and $\alpha_v \ll 1$, reflecting the breaking of only one hydrogen bond. A typical log rate vs. $1/T$ curve for the vacuum vaporization of ice is shown in Fig. 4. It appears that ice at equilibrium with the vapor has a surface population of a highly mobile species, thought to be water molecules hydrogen bonded to only one nearest neighbor. These molecules are the source of vapor flux leaving the surface. At sufficiently low temperatures the vacuum vaporization rate is low enough so as not to significantly alter the equilibrium surface population. However, sublimation at high temperatures depletes this population and the rate limiting step in the vaporization changes from the desorption of the mobile water molecules at low temperatures, to their formation at high temperatures.

From these studies it appears that the breaking of one or more hydrogen bonds can be a rate determining step in the vaporization of

hydrogen bonded liquids. This effect is likely to be more pronounced for smaller molecules where the proportion of hydrogen-bonding groups is large (ice, glycerol, diethylene glycol). For longer carbon chain organic molecules (e.g., triethylene glycol) the activation enthalpy of vaporization may not be markedly different from the enthalpy of vaporization, as these experimental data suggest. Their evaporation rates may be reasonably approximated by the Langmuir equation assuming an evaporation coefficient near unity.

Acknowledgement

This work was performed under the auspices of the U.S. Atomic Energy Commission.

Table 1

The heat of vaporization, ΔH_V , the activation enthalpy of vaporization, ΔH_V^* and the evaporation coefficient, $\alpha_V(300^\circ\text{K})$ for glycerol, diethylene glycol and triethylene glycol.

	$\Delta H_V(\text{kcal/mole})$	$\Delta H_V^*(\text{kcal/mole})$	$\alpha_V(300^\circ\text{K})$
Glycerol	21.0	17.1	0.34
Diethylene Glycol	12.5	16.8	0.05
Triethylene Glycol	17.0	18.4	0.46

Table 2

Comparison of the enthalpies and activation enthalpies of vaporization with the enthalpies of vaporization calculated by adding different hydrogen bond contributions to the enthalpy of vaporization of the homologous molecules ΔH_H .

	ΔH_H	$\Delta H_H + \delta(\text{OH})$	$\Delta H_H + 2\delta(\text{OH})$	$\Delta H_H + 3\delta(\text{OH})$	ΔH_V	ΔH_V^*
Glycerol	8.0	12.3	16.6	20.9	21.0	17.1
Diethylene Glycol	8.7	13.0	17.3	-	12.5	16.8
Triethylene Glycol	>8.7	>13.0	>17.3	-	17.0	18.4

Figure Captions

Figure 1 ——— vacuum vaporization rate of glycerol
 - - - maximum rate⁴
 determination by Heideger and Boudart

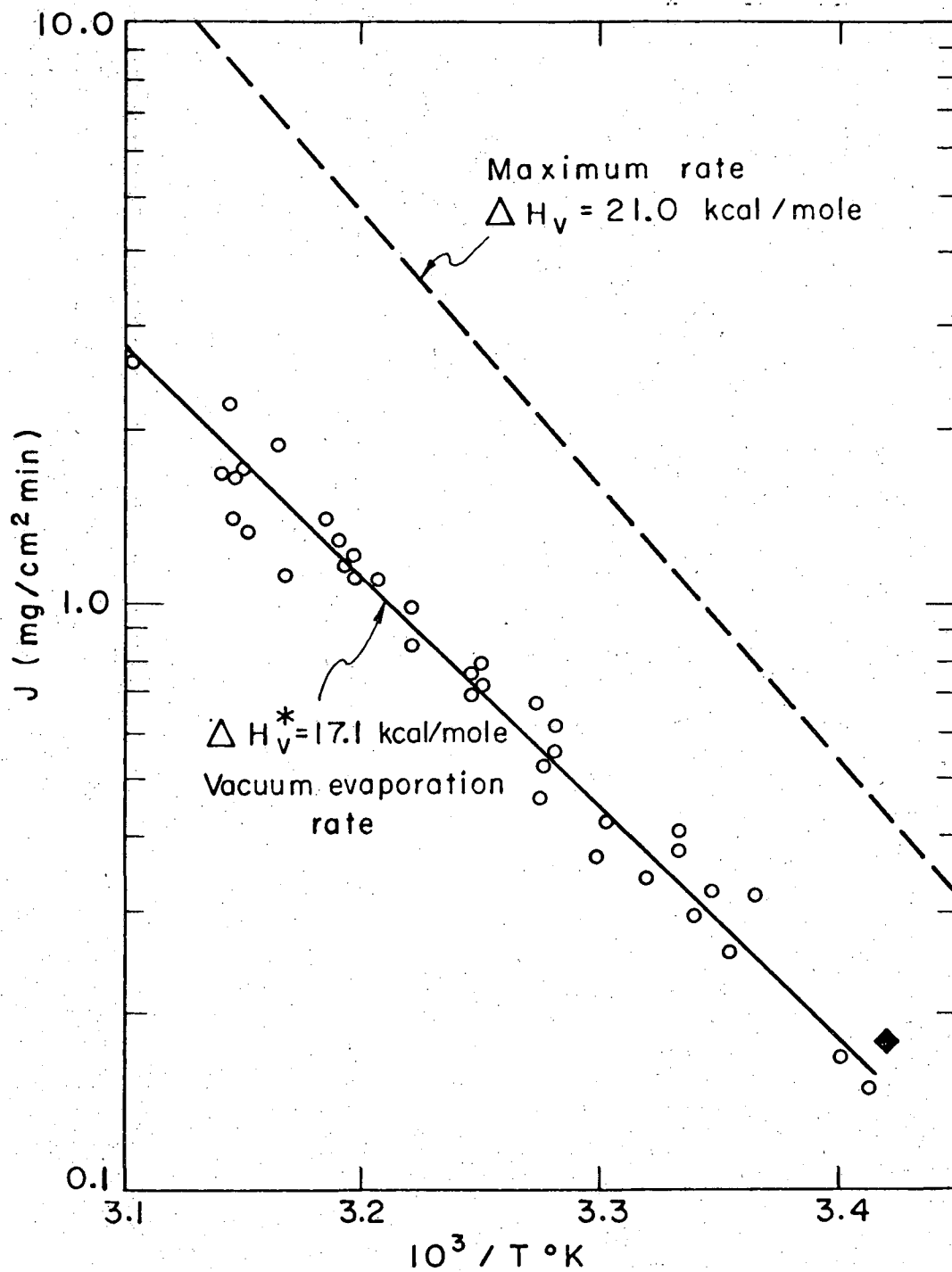
Figure 2 ——— vacuum vaporization rate of diethylene glycol
 - - - maximum rate⁶

Figure 3 ——— vacuum vaporization rate of triethylene glycol
 - - - maximum rate⁶

Figure 4 Vacuum vaporization rate and maximum vaporization rate of ice.

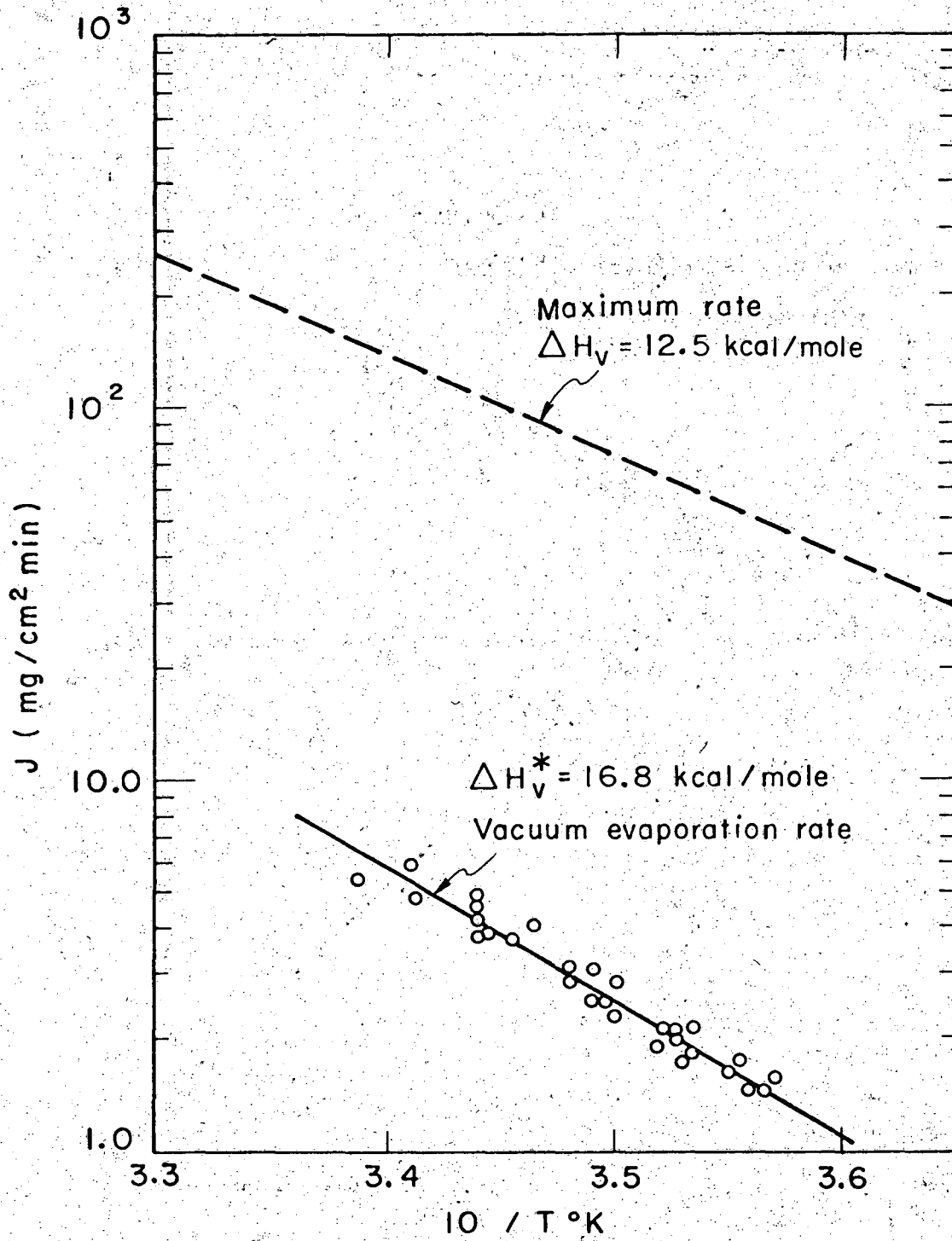
References

1. G. A. Somorjai and J. E. Lester, *Progress in Solid State Chemistry*, Vol. 4, 1967.
2. G. Wyllie, *Proc. Roy. Soc. A* 197, 383-95, (1949).
3. I. Langmuir, *J. Am. Chem. Soc.* 35, 931 (1913).
4. D. F. Stedman, *Trans. Faraday Soc.* 24, 289-98
5. W. J. Heideger and M. Boudart, *Chem. Eng. Sci.* 17, 1-10 (1962).
6. A. F. Gallaughier and J. Hibbert, *J. Am. Chem. Soc.* 59, 2523 (1937).
7. A. Bondi and P. J. Simkin, *A.I.Ch.E. Journal* 3(4), 473-79 (1957).
8. G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman and Co., San Francisco, 1960.
9. T. E. Jordan, *Vapor Pressures of Organic Compounds*, Interscience, New York, 1954.
10. J. G. Davy and G. A. Somorjai, *J. Chem. Phys.*, to be published. 1970



XBL716-3712

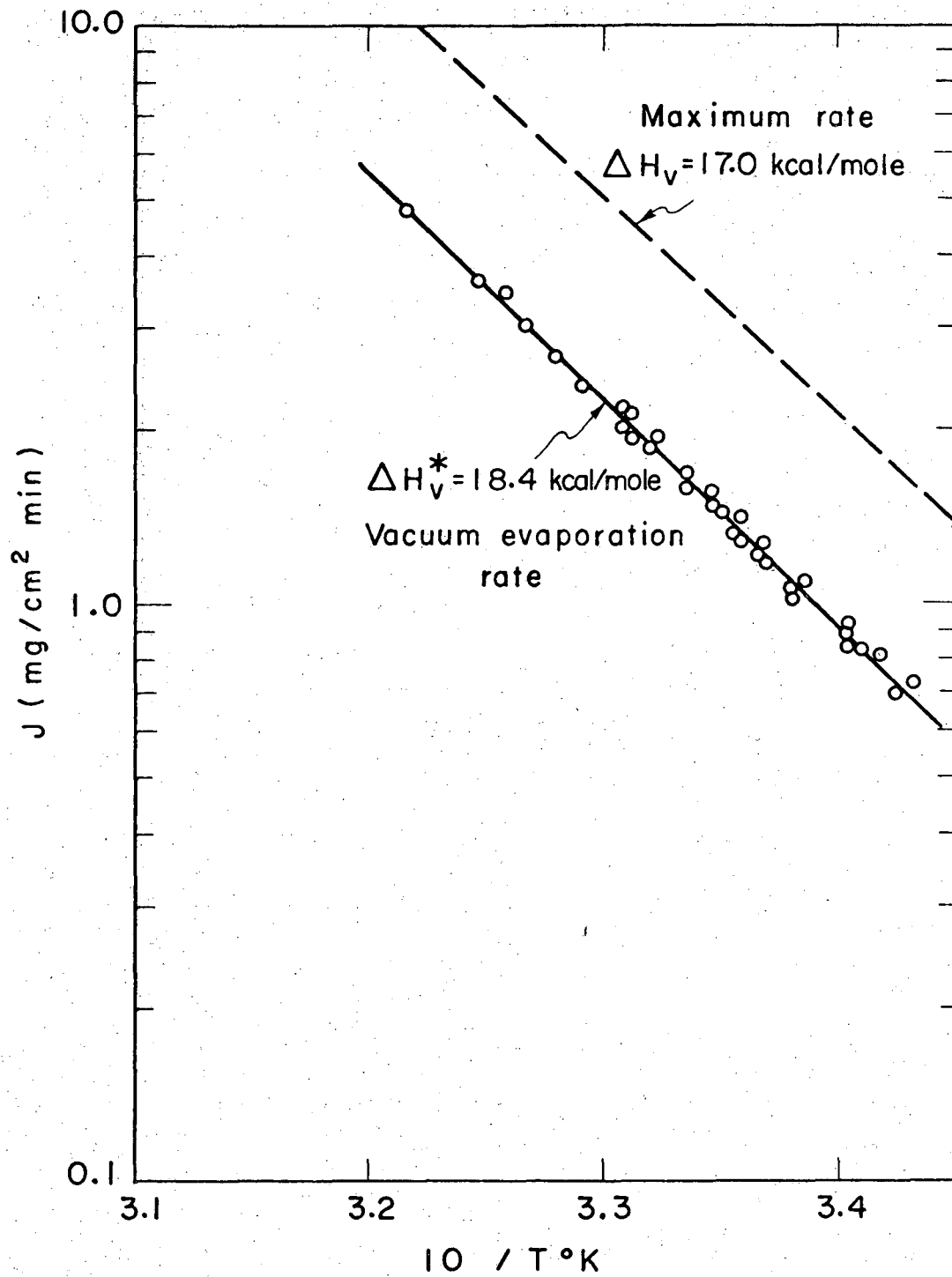
Fig. 1



XBL716-3713

Fig. 2

-15-



XBL716-3711

Fig. 3

T, °C

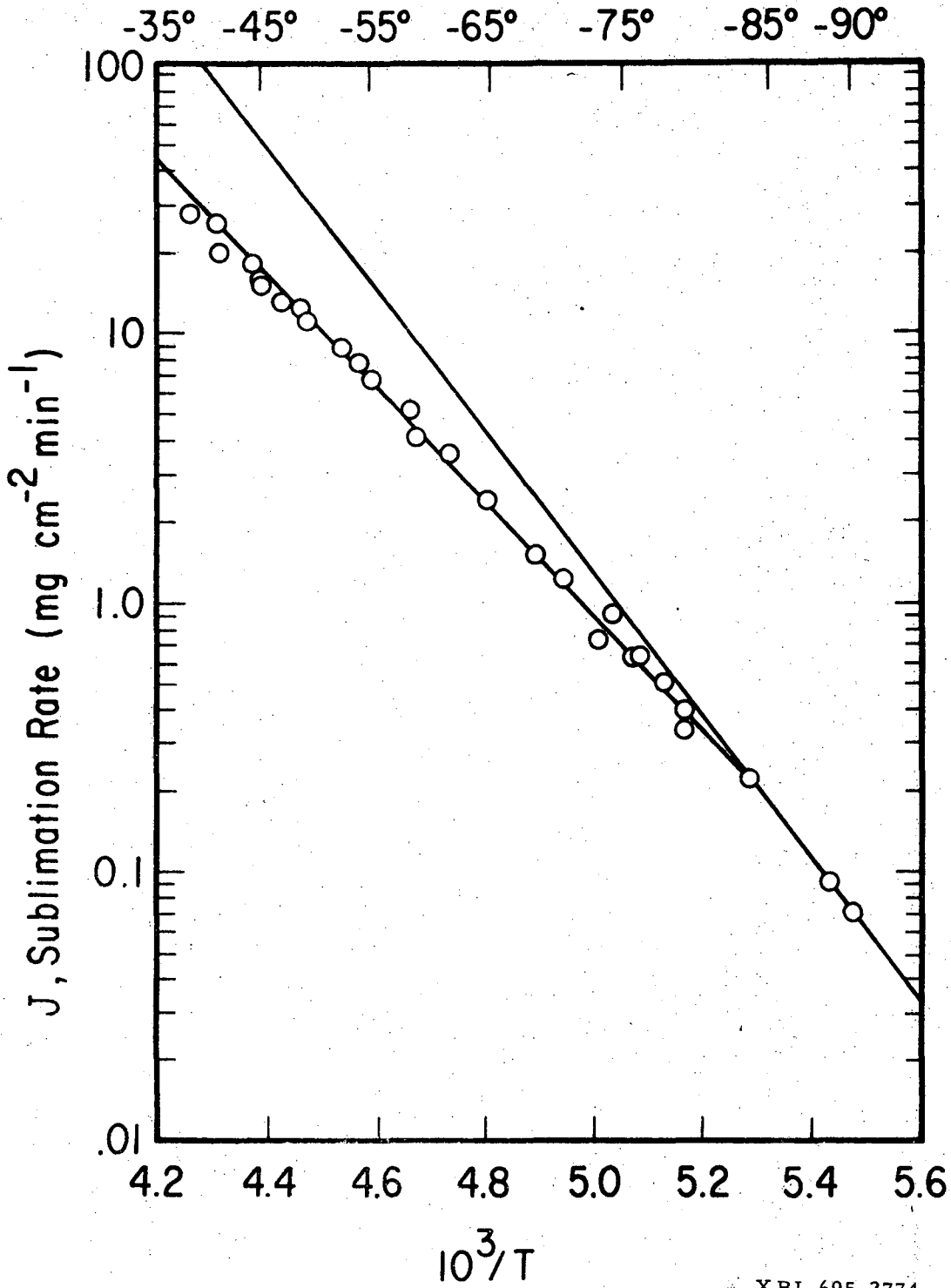


Fig. 4

XBL 695-2774

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720