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Vapor pressure measurements, by the Knudsen effusion method, have been obtained for n-hexadecane and n-dodecylcyclohexane within the temperature range 299–324°K. From these the following vapor pressure equations have been derived:

$$C_{16}H_{34}; \quad \log_{10} p \text{ (in mm)} = 11.2822 - 4212/T,$$
$$C_{18}H_{36}; \quad \log_{10} p \text{ (in mm)} = 12.4190 - 4880/T.$$

Thence, values at 298.16°K have been calculated for (a) the changes in enthalpy and free energy in the standard-state vaporization of these hydrocarbons and (b) the corresponding enthalpies and free energies of formation in the gaseous state.

INTRODUCTION

THIS investigation was carried out in 1940 in order to provide some vapor pressure data for n-hexadecane and n-dodecylcyclohexane in the neighborhood of room temperature. Since these two substances are rather typical hydrocarbons of high molecular weight, the results are naturally of considerable interest in themselves. Moreover, the vapor pressure values also provide a basis for computing important enthalpy and free energy data pertaining to the hydrocarbons in the gaseous state.

In the present study the effusion method, used previously by Knudsen[1] and others, was employed. It consists essentially in measuring the rate of flow of the gaseous substance through a hole in a thin plate, the diameter of which is small compared with the mean free path of the gas molecules. When the pressure on one side of such a plate is that of the gas saturated by contact with the liquid phase and a high vacuum is maintained on the other side, the vapor pressure of the liquid is given by the relation

$$p = (w/at)(2\pi RT/M)^{\frac{1}{2}}, \tag{1}$$

where w is the mass of gas effused in the time t, a is the cross section of the hole in the plate, R is the gas constant per mole, T is the absolute temperature, and M is the molecular weight of the substance under study.

APPARATUS

The apparatus, which we devised for the application of Eq. (1), consisted essentially of a small vaporizer suspended on a sensitive silica spring within an evacuated, thermostatic space.

This vaporizer was a thin-walled, glass bulb, weighing about 0.07 g and with a volume of about 1.5 cc. Its top was closed by a disk, made out of platinum foil 0.07 mm thick, which was fused tightly onto the glass surface. Prior to installation, a small hole, ranging in diameter from 0.15 to about 1.0 mm in different sets of measurements, was drilled through such a disk and the platinum was then carefully thinned around the hole by hammering, so that the edge of the orifice would be sharp. After each set of measurements, the cross-sectional area of the hole was determined by taking photo-micrographs beside a Zeiss standard scale. Enlargements were then made and the areas of the hole could thus be evaluated by a planimeter with an absolute error of less than 2 percent. Prior to measurements, the glass vaporizer bulbs were filled with a suitable amount of hydrocarbon by means of a small hypodermic needle inserted through a capillary side tube, which was subsequently sealed off in a minute flame.

In the course of the measurements the vaporizer rested in a light basket of copper wire, with the platinum disk uppermost, and the basket in turn was suspended

TABLE I. Vapor pressure data.

	n-hexadecane			n-dodecylcyclohexane	
Hole No.	Temp., °K	$p \times 10^3$ mm of Hg	Hole No.	Temp., °K	$p \times 10^3$ mm of Hg
1	309.3	4.92	3	304.4	0.245
1	323.1	17.6	3	309.2	0.457
2	299.8	2.30	3	323.4	2.14
2	310.1	6.34	4	301.9	0.180
2	323.3	22.9	4	309.6	0.458
3	299.1	1.65	Calc.	298.16	0.113
3	300.4	1.72			
3	304.2	2.66			
3	309.4	4.41			
Calc.	298.16	1.43			

TABLE II. Enthalpy and free energy data at 298.16°K (in calories per mole of hydrocarbon).

	$C_{16}H_{34}$	$C_{18}H_{36}$
$\Delta H°$ of vaporization	19,270 ($\pm$360)	22,330 ($\pm$300)
$\Delta F°$ of vaporization	7810 ($\pm$30)	9320 ($\pm$30)
$\Delta H_f°$ of liquid	−108,720 ($\pm$600)	−112,010 ($\pm$800)
$\Delta F_f°$ of liquid	11,300 ($\pm$800)	18,940 ($\pm$1000)
$\Delta H_f°$ of gas	−89,450 ($\pm$700)	−89,680 ($\pm$850)
$\Delta F_f°$ of gas	19,110 ($\pm$800)	28,260 ($\pm$1000)

[1] M. Knudsen, Ann. d. Physik **28**, 999 and **29**, 179 (1909); T. H. Swan and E. Mack, Jr., J. Am. Chem. Soc. **47**, 2112 (1925); W. H. Rodebush and T. DeVries, J. Am. Chem. Soc. **47**, 2488 (1925); A. R. Ubbelohde, Trans. Faraday Soc. **34**, 282 (1938).
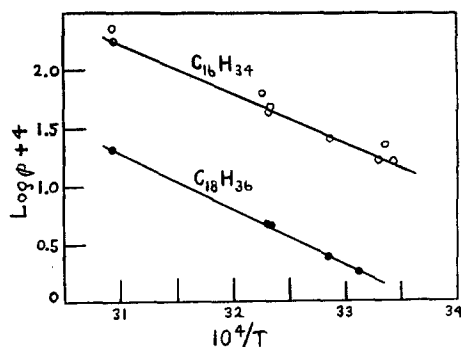
FIG. 1. Plot of $\log_{10}$ of the measured vapor pressures against the reciprocals of the absolute temperatures and the lines representing Eqs. (2) and (3).

on a fused silica, spring balance of the McBain-Bakr[2] type. Extensions of this spring were measured from time to time by a reading telescope and interpreted through a previous calibration with known weights. The vaporizer and balance were contained within a glass chamber, which for the vapor pressure measurements was evacuated to about 10^{-6} mm of mercury by means of a pumping arrangement, consisting consecutively of a Megavac oil pump, a mercury vapor diffusion pump, and finally a tube of activated charcoal immersed in liquid air. Pressures for this system were measured by a suitable McLeod gauge.

This entire vapor pressure apparatus was maintained in a specially constructed air thermostat, the temperatures of which were measured by a two-element, copper-constantan thermocouple in conjunction with a White potentiometer. Computations based on the characteristics of our apparatus indicated that the hydrocarbon sample might require as much as twenty-five minutes to attain thermal equilibrium after a change of setting of this thermostat temperature but that subsequently to such a period it would never differ significantly in temperature from the thermostat.

In the actual determinations, decreases in the weight of the liquid hydrocarbon varied from 0.00257 to 0.02330 g and the time intervals for such evaporations ranged from 17,000 to 138,000 seconds.

MATERIALS

The n-hexadecane employed in this study was a part of Sample 2, used and described previously by Richardson and Parks[3] in their measurements of heats of combustion. Likewise, the n-dodecylcyclohexane was from the same material used by Moore, Renquist, and Parks.[4]

The main impurities in these hydrocarbon samples were undoubtedly closely related isomers and should not produce more than one percent error in the vapor pressure values as experimentally measured.

[2] J. W. McBain and A. M. Bakr, J. Am. Chem. Soc. 48, 690 (1926).
[3] J. W. Richardson and G. S. Parks, J. Am. Chem. Soc. 61, 3543 (1939).
[4] Moore, Renquist, and Parks, J. Am. Chem. Soc. 62, 1505 (1940).

EXPERIMENTAL RESULTS AND DERIVED DATA

Three sets of measurements, with holes of different sizes, were carried out on the n-hexadecane and two sets on the n-dodecylcyclohexane. The results are summarized in Table I and are also represented graphically in Fig. 1, where the $\log_{10}p$ values have been plotted against the reciprocals of the absolute temperatures. Over the limited temperature range involved, the numerical data (except for Hole 2 with the hexadecane) are represented quite satisfactorily by the straight lines

$$C_{16}H_{34}; \quad \log_{10}p \text{ (in mm)} = 11.2822 - 4212/T, \quad (2)$$

$$C_{18}H_{36}; \quad \log_{10}p \text{ (in mm)} = 12.4190 - 4880/T. \quad (3)$$

From the character of the experimental measurements we estimate that vapor pressures computed by such equations may involve uncertainties of about 5 percent in absolute values, although they are probably reliable to within 2 percent for relative purposes.

The three determinations on n-hexadecane with Hole 2 yielded values about 30 percent above those of Eq. (2) and corresponded to a straight line with an almost identical slope. As it was found after these particular measurements that the platinum disk was not completely sealed to its glass bulb, such higher results can be readily explained on the basis that some molecules of the hydrocarbon vapor were also escaping through a crack in the glass-to-platinum seal.

By Eqs. (2) and (3) values for the vapor pressure of these two hydrocarbons were calculated for the standard temperature of 298.16°K (i.e., 25°C) and these are also recorded in Table I.

The vapor pressure results have been used in turn as a basis for deriving the enthalpy and free energy data pertaining to the gaseous state, which are recorded in Table II. Here the molal heats of vaporization were obtained from the slopes of the vapor pressure equations by the Clausius-Clapeyron relationship. The corresponding values for the free energy change for the hypothetical vaporization of liquid hydrocarbon to yield a vapor at 1 atmos. fugacity were computed from the respective vapor pressures by the equation

$$\Delta F° = RT \ln(760/p). \quad (4)$$

In a paper presenting extensive thermal data for hydrocarbons, which is to be published in the near future, Parks and his collaborators have calculated values for the $\Delta H°_{298}$ and $\Delta F°_{298}$ of formation of n-hexadecane and n-dodecylcyclohexane in the liquid state. These are here reproduced in the third and fourth lines of this table. Combination of such values with the present ones for the standard-state vaporization process thus yields our tabulated data for the enthalpy and free energy of formation from the elements (H_2 and β-graphite) of these two hydrocarbons as hypothetical gases at 298.16°K and 1 atmos. fugacity.

In this connection it is interesting to note that the

work of American Petroleum Institute Research Project 44,[5] largely dependent on statistical calculations and extrapolations from the lower members of the respective

[5] F. D. Rossini and co-workers, *Selected Values of Properties of Hydrocarbons* (United States Government Printing Office, Washington, D. C., 1947), pp. 362 and 365.

homologous series, has yielded $\Delta F_f{}^\circ = 20{,}520$ cal. for *n*-hexadecane and $\Delta F_f{}^0 = 29{,}930$ cal. for *n*-dodecylcyclohexane as hypothetical gases under these same conditions, with estimated uncertainties of the order of 1000 cal. The agreement with our present results is reasonably good.

The Structure and Growth of Evaporation LiF and NaCl Films on Amorphous Substrates

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Thin films of LiF and NaCl were prepared by evaporation in a vacuum and studied by means of electron diffraction, electron microscopy, x-ray diffraction, and optical methods. It was found that on amorphous substrates the films possessed a crystal orientation which varied with the film thickness. For both LiF and NaCl deposits thinner than a hundred angstroms showed almost completely random structure but with a small amount of [100] preferred orientation. As the thickness was increased there was a change, first to completely random, and then to a very definite and strong preferred orientation which was [111] for LiF and [110] for NaCl. The extent of these orientations both on the surface and in the interior of the film was studied in relation to crystal growth. The films are composed of loosely packed crystals set together so as to give the characteristic orientation and with appreciable spaces where the crystals do not make contact. A less extensive study of five other substances showed the following orientations: CaF₂, [111]; KCl, [110]; MgF₂, [302]; NaBr and KBr, random or a vague [211]. MgF₂ was amorphous for deposits under 1000A but became crystalline for greater thicknesses. Detailed consideration is given to the comparison and interpretation of results obtained by different experimental methods.

INTRODUCTION

THIN films formed by evaporation and deposition of solids in a vacuum have been of scientific interest for some time. More recently they have become of commercial importance, in particular in the optics and vacuum tube industries. These films are in general too thin to be examined by standard x-ray methods and are best studied by electron diffraction. The study of metals using this technique has been extensive and summaries of the work are available.[1-3] Little attention, however, has been given to films of non-metals. The present work was therefore undertaken to examine films of a few well-known alkali halides giving special emphasis to those currently used for optical purposes.

In the formation of thin films three relations are of interest: (1) that of the substrate to the structure of the initial deposit; (2) the changes in orientation with increasing thickness, and (3) the changes in structure produced by variations in the evaporating conditions. All three relations were studied, most effort being given to (1) and (2). Concurrent with this investigation of evaporated films a study of electron diffraction itself was also made. It is unfortunate that the application of

electron diffraction is often seriously limited by the lack of trustworthy interpretations for many of even the most typical patterns. In the experiments to be described an effort was made to eliminate some of the uncertainty by comparing data secured by different methods. In addition, attempts were made to correlate various types of diffraction data with those given by optical methods.

For small thicknesses the results are naturally divided into two groups, one group for amorphous substrates, and the other for polycrystalline substrates. In this paper only the first group will be considered.[4]

EXPERIMENTAL PROCEDURE FOR ELECTRON DIFFRACTION

The electron diffraction experiments were done with a modified electron microscope which has been described in detail elsewhere.[5] To secure approximately uniform radial exposure a sector disk was inserted immediately above the plane of the photographic plate.[6] This disk was run at 1000 r.p.m. and had an opening proportional to the square of the radius. Nearly all the samples were prepared within the vacuum of the diffraction apparatus, evaporation taking place from a small source

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[1] F. Kirchner, Ergeb. d. exskt. Naturwiss. **11**, 64 (1932).

[2] G. I. Finch and H. Wilman, Ergeb. d. exskt. Naturwiss. **16**, 353 (1937).

[3] G. P. Thomson and W. Cochrane, *Theory and Practice of Electron Diffraction* (MacMillan Company, Ltd., London, 1939).

[4] Some of the results have been reported earlier: L. G. Schulz, Phys. Rev. **75**, 345 (1949); Phys. Rev. **75**, 1284 (1949); J. Opt. Soc. Am. **38**, 440 (1948).

[5] A. F. Prebus, *Colloid Chemistry*, (Reinhold Publishing Corporation, New York, 1944) edited by Alexander, Vol. 5, p. 152.

[6] The author wishes to thank Professor Bauer of Cornell University for pointing out the advantages of using a sector disk, and also for suggesting some of the mechanical details.