137.8 Å.[3] (Table II). The corresponding value of $D_E(\theta)$ is then read off of the theoretical D_E *versus* λ_0 curve in Fig. 1.

The rotation about the carbon–carbon bond is hindered not only by $F(\theta)$ but presumably also[10] by a potential energy $U(\theta)$ of the type which exists in gaseous ethane and related compounds. We can approximate $U(\theta)$ by

$$U(\theta) = (U_0/2)(1 + \cos\theta) \qquad (13)$$

The minimum in U is undoubtedly at $\theta = \pi$; hence both $U(\theta)$ and $F(\theta)$ tend to emphasize the "maximum extension" ($\theta = \pi$) configuration. U_0 is not known but we make the calculation for $U_0 = 0$, 1, 2 and 3 kcal./mole.

We calculate ΔpK_m here from[10]

$$\Delta pK_m = \log(\alpha/\beta) \qquad (14)$$

$$\alpha = \int_0^{2\pi} \exp(-U/kT)d\theta \qquad (15)$$

$$\beta = \int_0^{2\pi} \exp[-(U + F)/kT]d\theta \qquad (16)$$

using numerical integration. Experimental and theoretical values are compared in Table III. We include also, for comparison, theoretical values of ΔpK_m calculated in the same way except that only a single configuration (value of R) is considered, using R_{fr}, R_{max} and $\bar{R}$ from Table II (C = 4). In this case Eq. (14) reduces to Eq. (9).

TABLE III

CALCULATION OF ΔpK_m FOR SUCCINIC ACID IN WATER AT 25°

Source	ΔpK_m
Experimental[14]	0.682
$U_0 = 0$	.924
$U_0 = 1$ kcal./mole	.725
$U_0 = 2$ kcal./mole	.624
$U_0 = 3$ kcal./mole	.576
R_{fr} only	1.184
R_{max} only (or $U_0 = \infty$)	.492
$\bar{R}$ only	.728

In Table III, the four values of ΔpK_m allowing for rotation all fall between the R_{fr} and R_{max} values, as expected. It is apparent from the table that the Kirkwood–Westheimer theory, together with a not unreasonable value of U_0, is again in satisfactory agreement with experiment even in this more detailed calculation.

In conclusion, although we are aware of the approximate nature of both the Kirkwood–Westheimer model and of the present calculations, we feel that the analysis given here furnishes additional[13] evidence that the theory does succeed in taking into account the dominant features of the problem.

We are indebted to Professors W. D. Walters and H. E. Gunning for a number of very helpful suggestions.

BETHESDA, MD.

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[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

The Densities of Liquid Tritium, 20.6 to 29°K.[1]

BY E. R. GRILLY

Most of a 70 cc. (S.T.P.) sample of tritium (containing 2.0% HT) was liquefied in a Pyrex bulb of 58 mm.^{3} capacity between two fixed marks. The amount of gas used for this filling gave the difference between liquid and gas density. The results were corrected for gas density and for the presence of HT.

The Tritium Sample.—For this work 70 cc. (S.T.P.) of tritium was used. The source, purification, and storage have been described elsewhere.[2] The gas used in the present work contained 2.0% HT and negligible amounts of other constituents, such as H_2, air, and tritocarbons, all determined mass spectrometrically.

The Apparatus.—This was essentially the same as that used in the vapor pressure measurements.[2] In addition, there were provisions for measuring accurately the amounts of gas and of liquid. For the former, the gas was kept under constant volume, constant temperature and variable pressure, or approximately 255 cc., 25°, and 0 to 230 mm., respectively. The Pyrex liquid bulb consisted of a 17 mm. length of 2 mm. i.d. tubing, above and below which were regions narrowed down to 0.4 mm. i.d. Inked reference marks for the liquid levels, "empty" and "full," were put on the narrow regions. The bulb was observed through a traveling microscope. The bulb volume was calibrated with liquid hydrogen at 19.50°K., the average of six determinations giving a volume of 57.80 mm.^{3} with a mean deviation of ±0.06%. Volume determinations were also made between 14 and 22.8°, but no consistent variation was observed. The liquid hydrogen molar volumes below 20.4° were taken from Scott and Brickwedde,[3] and those above 20.4°, from Woolley, Scott and Brickwedde,[4] who recomputed the results of Mathias, Crommelin and Onnes.[5] At 19.500°K. the value used was 28.021 cc./mole.

Procedure.—The Toepler pump was used to transfer low-pressure gas into the condensing tube so that the liquid level just came to the bottom mark. The amount of gas left on the other side of the pump was measured by noting the pressure. More gas was liquefied until the upper mark was reached. Bulb immersion in the bath was kept 1 cm. above the mark by raising the dewar. Again the amount of gas left was measured. The amount of gas (in moles) used to fill the liquid bulb divided by the bulb volume (between the marks) gives the difference between liquid and gas densities. The gas densities were calculated as previously[2] and amounted to a maximum correction of 3.6%. To make a slight (0.3%) correction for the 2.0% HT, linearity between mole fraction and molar volume was assumed, and the molar volume of HT was taken equal to that of D_2.

Results.—As a check, the density of deuterium at 19.48°K. was determined (after correcting for 0.72% HD) to be 42.89 mole/liter, 0.2%

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[1] This paper is based on work performed under University of California contract with the Atomic Energy Commission.

[2] E. R. Grilly, THIS JOURNAL, **73**, 843 (1951).

[3] R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **19**, 237 (1937).

[4] H. W. Woolley, R. B. Scott and F. G. Brickwedde, *ibid.*, **41**, 379 (1948).

[5] E. Mathias, C. A. Crommelin and H. Kamerlingh Onnes, *Comm. Leiden*, **154b** (1921).

higher than the result of Clusius and Bartholomé.[6]

Table I gives the tritium results as follows: the direct measurements on liquid density minus gas density; the calculated gas densities; the liquid densities after correcting for 2.0% HT; the deviations of the final densities from a smooth curve. Table II gives smoothed tritium densities at several temperatures, from the triple point to 29°K.

Accuracy.—Error analysis shows the following possible contributions to $\rho_{\text{liq}} - \rho_{\text{gas}}$ values (first as direct units, then as error per cent.): (a) missing a liquid level mark, 0.2 mm. = 0.04%; (b) temperature of the bath, 0.003° = 0.005%; (c) temperature of the liquid tritium being above the bath temperature due to radioactive heat, 0.006° = 0.01%; (d) temperature in the gas measuring system, 0.1° = 0.03%; (e) pressure of the gas, 0.1 mm. = 0.04%; (f) volume of the gas, 0.05 cc. = 0.02%. These give a maximum error of ±0.18% if additive or a "probable" error of ±0.08% if random. The gas densities should be accurate to 0.1% in the best case (lowest temperature) and to 1% in the worst, contributing 0.000% and 0.04% errors, respectively. Finally, the HT correction should be reliable to 3%, contributing 0.01% error. Summarizing, the liquid density maximum error should be 0.23% for the worst case.

TABLE I

MOLAR DENSITIES OF LIQUID TRITIUM

T, °K.	$\rho_{\text{liq}} - \rho_{\text{gas}}$,[a] mole/liter	ρ_{gas}	ρ_{liq}[b]	Dev. from curve
20.61	45.17	0.13	45.39	0.04
22.50	43.97	.16	44.21	−.01
22.99	43.51	.29	43.88	−.04
23.59	43.11	.35	43.55	.00
24.41	42.49	.44	43.01	−.01
24.72	42.24	.48	42.81	−.02
25.66	41.53	.62	42.25	.03
26.36	40.91	.73	41.74	.00
27.09	40.17	.87	41.14	−.05
28.32	39.06	1.14	40.31	.07
29.13	38.02	1.37	39.49	−.06

[a] With 2.0% HT present. [b] Corrected to 0.0% HT.

TABLE II

SMOOTHED MOLAR DENSITIES OF LIQUID TRITIUM

T, °K.	20.62	21	22	23	24
ρ, mole/liter	45.35	45.12	44.52	43.91	43.29
T, °K.	25	26	27	28	29
ρ, mole/liter	42.65	41.98	41.26	40.48	39.66

LOS ALAMOS, NEW MEXICO RECEIVED MAY 28, 1951

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(6) K. Clusius and E. Bartholomé, *Z. physik. Chem.*, **B30**, 237 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

The Gaseous Species of the Al–Al_2O_3 System[1,2,3]

BY LEO BREWER AND ALAN W. SEARCY

The vapor pressures of aluminum and of aluminum oxide have both been measured by the Knudsen effusion method. The results of these vapor pressure determinations and results from heatings of Al–Al_2O_3 mixtures have been used in deciding the identity of the important gaseous species of the Al–Al_2O_3 system. There are two important gaseous oxides of aluminum. Al_2O gas is evolved when Al_2O_3 is heated with aluminum or another reducing metal. AlO appears to be the principal aluminum species when Al_2O_3 is volatilized alone. No gaseous sub-hydroxides of aluminum were found. ΔH^0_{298} for sublimation of aluminum is 77.4 ± 1.4 kcal.; ΔH^0_{298} for $Al_2O_3(s) = 2AlO(g) + O(g)$ is 456 ± 10 kcal. For volatilization of liquid Al_2O_3 by decomposition to AlO and O gases $\Delta F^0 = 443{,}000 + 12T \ln T - 212T$. For the formation of AlO(g) and Al_2O(g) from the gaseous atoms, $\Delta H^0_{298} = -138$ and $\Delta H^0_{298} = -248$ kcal., respectively. The boiling point of aluminum is 2750 ± 50°K. The boiling point of Al_2O_3 is 3800 ± 200°K.

Introduction

The existence of gaseous AlO has long been known from spectroscopic investigations,[4] but until recently nothing was known about what oxide species are principally obtained when Al_2O_3, alone or Al_2O_3 with aluminum is volatilized. Zintl, Krings and Brauning[5] described a process for recovering aluminum from aluminum alloys by volatilization of a suboxide which they identified as AlO; however, by analysis of sublimates from Al_2O_3–Si mixtures Grube, Schneider, Esch and Flad[6] claimed that the oxide species of Al present in the vapor under reducing conditions is Al_2O rather than AlO.

The most satisfactory means of determining the species of the Al–Al_2O_3 gaseous system might be to obtain density and electron diffraction data for the vapor above Al_2O_3 and data for the variation in volatility of Al_2O_3 with aluminum gas pressure at constant temperature. Such data have so far not been obtained because of the obstacles arising from the extremely high temperatures at which volatilization becomes appreciable in this system. Fortunately, by critical analysis of the thermodynamic data obtained for the vaporization of Al and Al_2O_3, both independently and when mixed, we can definitely limit the number of species which can be of importance in the gaseous system and identify the actual species almost unequivocally.

We will present first our determination of the vapor pressures and heats of vaporization of aluminum and of Al_2O_3 and then, using these data and data for volatilization of Al–Al_2O_3 mixtures, present the thermodynamic arguments which

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(1) Based on a thesis submitted by A. W. Searcy in partial fulfillment of requirements for the Ph.D. degree at the University of California.

(2) This research was performed under Contract No. W-7405-eng 48B for the Atomic Energy Commission.

(3) Presented at the 116th National Meeting of the American Chemical Society in Atlantic City, N. J., September, 1949.

(4) See for example G. Herzberg, "Molecular Spectra and Molecular Structure," Prentice-Hall, Inc., New York, N. Y., 1939.

(5) E. Zintl, W. Krings and W. Brauning, German Patent 742,330, Oct. 14, 1943 [*C. A.*, **39**, 2481^9 (1945)].

(6) G. Grube, A. Schneider, U. Esch and M. Flad, *Z. anorg. Chem.*, **260**, 120 (1949).