100 grams H_2O, and weight per cent. At 662° F., the vapor depression for a 6.25-molal sodium hydroxide solution is about three times as great as for a lithium hydroxide solution of the same molal strength. More dilute solutions showed smaller differences. In other words, sodium hydroxide shows a greater lowering of vapor pressure than does lithium hydroxide at the same molal concentrations. In addition, the extent of this difference increases as the concentration of the solution rises. Data for sodium hydroxide, as given in the *International Critical Tables* (*1*), have been confirmed recently by Kiyama and Kitahara (*2*).

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Vapor Pressure of Glycerol

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RECENT INTEREST in the properties of highly polar compounds (*1, 5, 10*) has indicated the lack of reliable information concerning the vapor pressure of glycerol in the range from room temperature to about 100° C. The accepted high temperature values were obtained by Stedman (*9*) from an extrapolation of data on the equilibrium concentrations of glycerol in water solutions at known temperatures and pressures. He plotted partial pressure of glycerol against total pressure and extrapolated to the point where the two were equal. At 70° C., however, only two points were available; at 60° and again at 50° only one point is given. The latter two were at very low glycerol concentration and thus the vapor pressures reported represent only an estimate of the proper values.

Low temperature data available are the single effusion value obtained by Wyllie (*11*) at 18° C. for glycerol of unknown purity and the effusion results obtained by Zil'berman-Granovskaya (*12*), after repeated distillations and thus possibly subject to thermal decomposition. The heat of vaporization calculated from this latter study was only 4.9 kcal./gram-mole, less than one third of the value expected for such a highly polar substance (*1*). Filosofo and co-workers (*4*) measured the pressure of glycerol atmospheres with a fiber vacuum gage at three temperatures below 50° C. and obtained values in reasonable agreement with the extrapolation of Stedman's data.

EXPERIMENTAL

Method Selected. Because of the extremely low volatility of glycerol at room temperature, Knudsen's vapor effusion technique (*6*) was chosen for vapor pressure determination. The Knudsen equation relates the rate of efflux of a vapor through an orifice to the pressure differential, provided the major dimension of the opening is much less than the mean free path of a molecule in the gas phase.

$$-\frac{1\,\mathrm{d}W}{A_o\mathrm{d}\theta} = \left(\frac{M}{2\pi RT}\right)^{1/2}\left(P_v' - P\right) \tag{1}$$

Clausing (*3*) has calculated the probability that molecules entering a cylindrical canal in free molecule flow will reach the exit without being reflected back through the entrance. Such efficiency factors may be evaluated both for the orifice itself and for the body of the cell. Ross has shown (*8*) that for a cell with diameter equal to height the cell body correction is negligible, and the cell pressure may be related to the vapor pressure as in Equation 2

$$P_v = (1 + W_bA_o/\alpha A_s)\ P_v' \tag{2}$$

where α is the evaporation coefficient and the effusion is assumed to be into very high vacuum. A value for α of 0.05 was used in this correction in accord with the most recently reported coefficient for glycerol surfaces (*5*). This calculation (Table I, column 5) is not sensitive to the value of α used.

When the orifice area in Equation 1 is modified by the Clausing factor, these two equations may be combined to yield the final form used to calculate vapor pressures.

$$P_v - P = -\frac{\mathrm{d}W}{\mathrm{d}\theta}\left(\frac{1 + \frac{W_bA_o}{\alpha A_s}}{W_bA_o}\right)\left(\frac{2\pi RT}{M}\right)^{1/2} \tag{3}$$

Apparatus and Procedure. The effusion systems used in this work, similar in design to those of Bradley (*2*), are shown schematically in Figure 1. The basic components of each system were the spring case, quartz spring, effusion cell, liquid nitrogen cold trap, diffusion pump, and mechanical vacuum pump.

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The effusion cell (Figure 1*B*) consisted of a glass bulb 1 to 2 cm. in diameter on which a small disk of 0.001-inch thick platinum foil had been sealed with a needle flame. Prior to sealing, orifices were drilled or punched in the foil and their areas measured with the aid of a projection microscope. After use, the foil was removed, and the areas were remeasured to ensure that fusion to the cell had not altered their dimensions. Several different orifice diameters (Table I, column 3) were employed over the temperature range covered. An initial estimate of the vapor pressure at the temperature in question was based on an equation communicated by Bondi and reported elsewhere (*5*). The selection of orifice size was then made to keep the diameter much less than the mean free path but to permit rapid enough effusion to be easily measureable. After calculation of the measured vapor pressure, the dimensions of the orifice compared to the mean free path were always verified.

To avoid excessive spring lengths, it was necessary for the effusion cell to weigh less than 1 gram. The weight loss was indicated by the change in extension of a fine quartz spring used to suspend the cell. The springs used had capacities of 2 grams at approximately 20 cm. extension. The Hooke's law constants were found to be independent of temperature. Changes in spring extension were read with a precision cathetometer having a scale readable to 0.001 cm.

Merck reagent grade glycerol was purified by distillation in a drip point column under vacuum such that the maximum temperature never exceeded 150° C. The center cut was collected in glass vials and sealed while still under vacuum. To begin an effusion run, the stem of a sample vial was broken and about 1 ml. of glycerol transferred by means of a hypodermic syringe into the cell. These operations were performed in a dry box supplied with a steady flow of dry nitrogen because of the highly hygroscopic character of glycerol. The cell was then suspended from the spring, the case sealed and evacuated, and the temperature bath regulated to the desired condition. The rate of effusion, as indicated by the decrease in spring length, was recorded until a constant rate was obtained. This was assumed to signify complete removal of traces of water.

In measurements below 45° C., the cold trap around the spring case was filled with a dry ice-acetone mixture to reduce the back pressure. Since the pumps were capable of maintaining a pressure below 10^{-6} mm. Hg with no glycerol in the system and the vapor pressure at the cold trap temperature may be assumed negligible, the pressure outside the orifice was assumed to be effectively zero. For measurements above 45° C., a system without this trap was used. Because of observed condensation on the walls, a back pressure correction was made based on the vapor pressure previously measured at room temperature. For one series of measurements, a thermocouple was inserted into the liquid in the effusion cell. No measureable difference was noted between this temperature and that of the heating bath.

Table I. Summary of Results

T, ° C.	$A_o \times 10^3$, Sq. Cm.	r, Cm.	W_b[a]	$\frac{W_b A_o}{\alpha A_s}$	$-(\mathrm{d}W/\mathrm{d}\theta) \times 10^4$, Gram/Hr.	P_v, μ Hg
High temperature system back pressure correction based on vapor pressure at 25° C. of 0.175 μ Hg						
Spring constant = 9.296 cm./gram						
33.9	2.46	0.0176[b]	0.933	0.023	0.871	0.51
43.0	7.12	0.0476	0.974	0.059	7.41	1.19
44.8	2.46	0.0176	0.933	0.023	3.39	1.51
44.8	2.46	0.0176	0.933	0.023	2.98	1.35
51.1	2.46	0.0176	0.933	0.023	7.23	3.06
53.0	2.46	0.0176	0.933	0.023	7.82	3.30
57.3	2.46	0.0176	0.933	0.023	11.14	4.66
59.4	2.46	0.0176	0.933	0.023	14.7	6.10
67.0	2.46	0.0176	0.933	0.023	31.4	13.0
Low temperature system back pressure from cold trap assumed negligible						
Spring constant = 10.209 cm./gram						
23.7	17.94	0.076	0.983	0.072	3.32	0.17
30.2	17.94	0.076	0.983	0.072	5.92	0.306
35.0	17.94	0.076	0.983	0.072	9.31	0.485
39.6	17.94	0.076	0.983	0.072	19.6	0.892
44.7	3.40	0.03225	0.962	0.037	6.37	1.79
55.2	3.40	0.03225	0.962	0.037	15.95	4.47
60.0	3.40	0.03225	0.962	0.037	23.9	6.85
66.3	3.40	0.03225	0.962	0.037	44.0	12.75

[a] Estimated from $W_b = \frac{1}{1 + 0.5\, t/r}$

[b] Average radius of three orifices in foil.

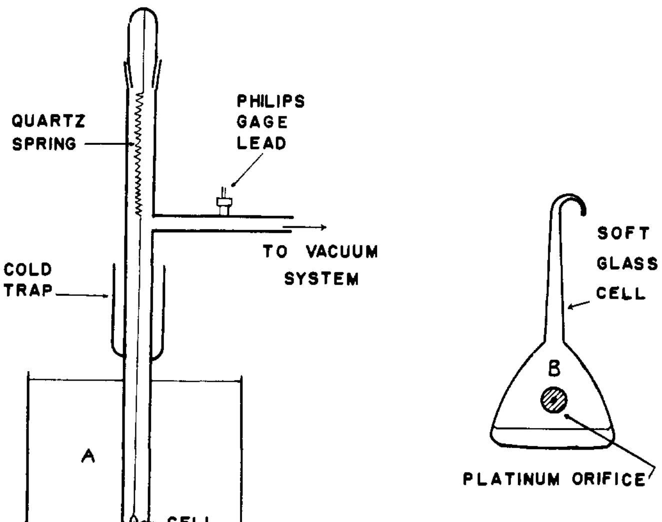

Figure 1. Diagram of apparatus
A Spring case assembly
B Effusion cell

RESULTS AND DISCUSSION

Vapor Pressure and Latent Heat. Measured values of the vapor pressure are listed in Table I and are plotted in Figure 2 along with the correlating equation developed for the range of 20° to 70° C.

$$\log_{10} P_{\text{mm. Hg}} = 11.27423 - 4480.5/\mathrm{T}\,°\mathrm{K}. \qquad (4)$$

It is considered significant to the validity of the results that a single equation was sufficient to describe the data obtained from both the high and the low temperature systems, thus verifying the correction made for pressure outside the orifice. The heat of vaporization calculated from these measurements was 20.5 kcal./gram-mole.

Also included in Figure 2 for purposes of comparison are Zil'berman-Granovskaya's correlation, Filosofo and coworkers' three measurements, and Wyllie's single value. The present correlation, when extrapolated to high temperatures, agrees well with Stedman's data obtained by an entirely different technique.

Comparison with Previous Work. On first examination, it is difficult to imagine how Zil'berman-Granovskaya could have obtained results so far removed from those of the present investigation. A close study of this apparently very careful piece of work indicates the use of an effusion orifice large by comparison to the mean free path, as well as exposure of the glycerol to possible absorption of water

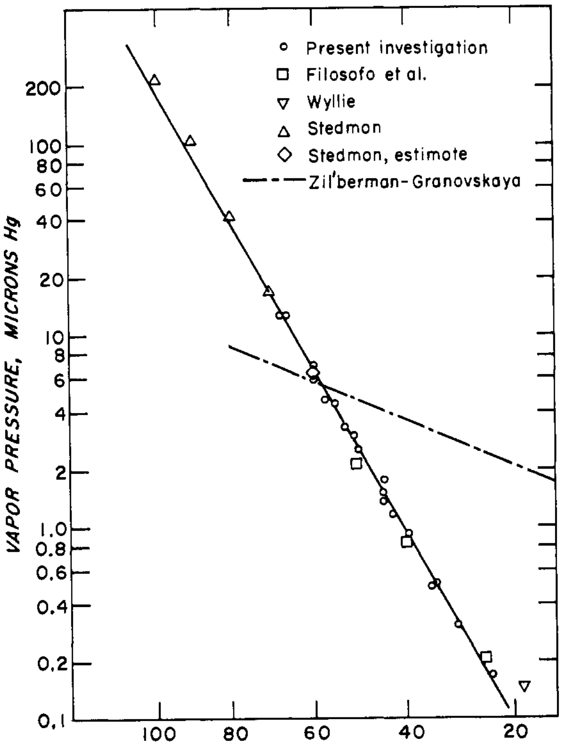

Figure 2. Vapor pressure of glycerol

during weighing intervals. There is the additional possibility of decomposition of the glycerol during the ten successive distillations used for preparation. These probably were simple distillations at atmospheric pressure (b.p. 290° C.) and, since polymerization and decomposition are reported to begin at little over 200° C. (*7*), the purity of the glycerol studied remains in doubt.

To test the effect of minute quantities of water present in the glycerol, an opened sample vial was left in a desiccator for several months and then used for a vapor pressure measurement. The water absorbed, even in this very dry atmosphere, was sufficient to increase the apparent vapor pressure by a factor of five. Thus, it is possible that thorough drying of Wyllie's glycerol could have lowered the measured vapor pressure to coincide with the present study. A prime advantage of the present method thus becomes its ability to obtain weight measurements without exposure of the glycerol to the atmosphere during the weighing process.

NOMENCLATURE

A_o = orifice area, sq. cm.
A_s = surface area of evaporating liquid, sq. cm.
M = molecular weight, grams/gram-mole
P = pressure, dyne/sq. cm.
P_v = vapor pressure, dyne/sq. cm.
P'_v = steady state cell pressure, dyne/sq. cm.
r = radius of effusion canal (orifice), cm.
R = gas content, 8.31×10^7 dyne cm./gram-mole ° K.
t = length of effusion canal (foil thickness), cm.
T = temperature, ° K.
W_b = Clausing factor for orifice, dimensionless
$dW/d\theta$ = rate of weight loss, grams/hour
α = evaporation coefficient, dimensionless

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Compressibility Factors of 2,2-Dimethylpropane (Neopentane)

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A STANDARD Burnett apparatus was modified and used to determine the compressibility isotherms of gaseous 2,2-dimethylpropane (neopentane) between 1 atm. and the vapor pressure at 30°, 50°, 75°, 100°, 125°, and 150° C., and between 1 and 70 atm. at 161.5°, 175°, and 200° C. The critical temperature of 2,2-dimethylpropane is 160.60° C. (*1*).

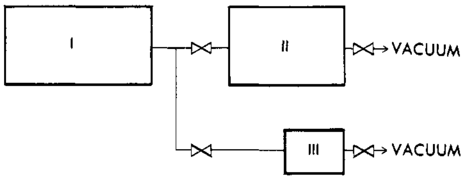

Figure 1. Modified Burnett apparatus

APPARATUS

The Burnett method (*3*) employs two thermostated chambers connected by a valve (Figure 1). The gas under investigation is introduced into V_{I} while V_{II} is evacuated. The pressure in V_{I} is measured, whereupon the gas is expanded into V_{II} and the pressure is again measured. The

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