DENSITIES OF ISOPROPYL AND n-BUTYL ALCOHOLS AT LOW TEMPERATURES.

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Densities of isopropyl- and n-butyl alcohols were determined with the pycnometers made of pyrex glass as shown in Fig. 1. The pycnometer has a bulb of about 3.5 c.c. capacity which is connected to a capillary tube, whose inner diameter is 0.2 cm. and whose length 20 cm. Two marks (a and b) were etched on the capillary tube.

The volumes of the pycnometers are calibrated with mercury according to the method proposed by K. Issac and I. Masson.[1] The schematic diagram of the calibration apparatus is shown in Fig. 2. The pycnometer, mounted vertically in a water jacket kept at constant temperature, is connected to a two way capillary stopcock (A), one way of which is connected through a trap (B) to a mercury diffusion pump, by which the pycnometer can be evacuated. When the pycnometer has been completely exhausted, the stopcock (A) is turned 180° and the mercury in the cup (D) is allowed to enter in it by the other way of the stopcock. The cup (D), which is to be taken out and weighed, is placed in a bottle with a rubber stopper (E), so that the cup can be kept free from all dirty substances that may prevent accurate weighing. By means of the glass tube (C) with two stopcocks, one being connected to a pump and the other to atmosphere, the pressure of the bottle is regulated in order that the mercury in the pycnometer is allowed down to an appropriate position, say a. The volume of the bulb is thus determined by the difference of the weight of mercury in D before and after emptying the pycnometer with mercury. The total volume and the volume of the every cm. of the capillary tube between the marks a and b are similarly determined. In all cases the height of the meniscus of mercury and the mark a or b are read by a cathetometer. With the data thus obtained the correction for the capillary at the position l cm. from the mark a is calculated and plotted against l.

Fig. 1.

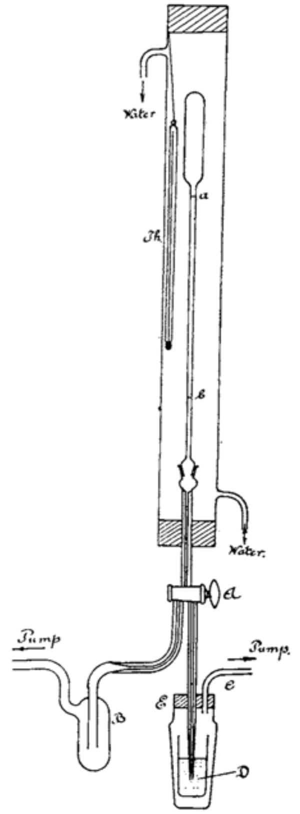

Fig. 2.

After the pycnometer has been allowed to cool several times to the temperature of liquid air, its volume is again determined. It is thus ascertained that the hysteresis of volume change of pycnometer is negligibly small. (The difference of volume before and after is 1 parts in 15000.)

(1) *J. Phys. Chem.*, **28** (1924), 166.

The volume of the sample filled in the pycnometer at the temperature t is calculated as follows.

$$V = V_0(1-3\alpha t)+vl(1-2\alpha t)+\Delta v_I+\Delta v_{II} \quad . \ . \ . \ . \ . \ . \ . \quad (1)$$

where V_0 is the volume of bulb at 0°, v, the mean volume of the capillary tube per cm., l, the distance between a and the meniscus of the liquid filled in the pycnometer, Δv_I, the above mentioned correction of volume of the capillary tube at the position l, Δv_{II}, the correction of volume of the meniscus given in the Int. Nat. Crit. Table, Vol. 1, p. 73., α, the expansion coefficient of the glass.

The expansion coefficient α of the glass is determined, by using ethyl ether as a standard. Ether is filled in the pycnometer as described below and with the aid of formula (1), neglecting the expansion coefficient of the glass, the apparent volumes at several temperatures of ether are calculated. The true volumes of ether at corresponding temperatures are calculated from the data given by Keyes and Felsing.[1] From the differences between the true and apparent volumes of ether, the contraction of the pycnometer is calculated, assuming the contraction to be linear to temperature. The linear expansion coefficient of the glass thus found is 5.1×10^{-7}.

All the materials used for the present experiments are Kahlbaum extra pure chemicals. After dehydrating by anhydrous calcium oxide, they have the following boiling point: isopropyl alcohol, 81.9°–82.4°/768.6 mm., corr. and red. b.p.=81.9°C; n-butyl alcohol, 116.7°–117.0°/757.0 mm., corr. and red. b.p.=117.0.

The loading apparatus of the sample is shown in Fig. 3. It is made of ordinary glass except the portion below D, which is made of pyrex glass and they are sealed together at D with pyrex-ordinary glass graded sealing. The sample loads first in A, removes any gases dissolved by evacuation, distills twice at ordinary temperature under vaccum using liquid air as cooking reagent for condenser. Each time first and last one fourth of distillate are rejected. When the proper quantities of the sample have condensed in the pycnometers, they are sealed off at a. The pycnometers with sample are then immersed vertically in the cryostat.

The cryostat is constructed according to R. Hara and H. Shinozaki[2] and its temperature is kept constant within 0.05°. Its temperature is determined by a platinum-resistance thermometer from Leeds and Northrup Co., which has been calibrated at the normal boiling point of oxygen (–182.97°), the normal sublimation point of carbon dioxide (–78.5), the ice point and

(1) *J. Am. Chem. Soc.*, **41** (1919), 589.
(2) *J. Soc. Chem. Ind. of Japan*, **29** (1926), 269.

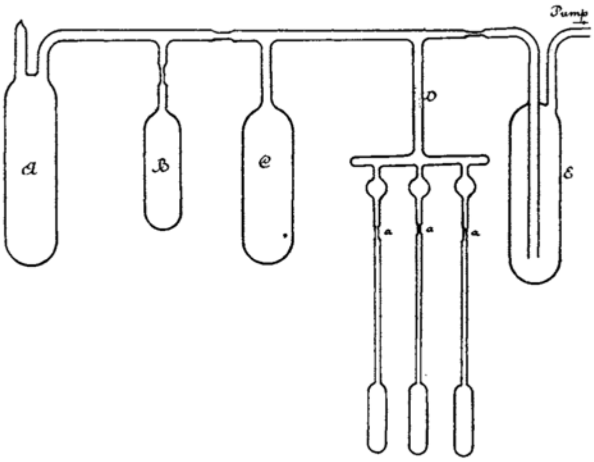

Fig. 3.

boiling point of water. It has the resistance of 2.5089 (r_0) at 0° and the resistance (r) at any temperature t is calculated by the following formula.

$$r/r_0=1+3.97186\cdot10^{-3}\,t+6.148\cdot10^{-7}\,t^2+5.08\cdot10^{-12}\,t^4\;.\;.\;.\quad(2)$$

Cylindrical Dewar vessel of the cryostat is silvered except the spaces of about 1 cm. wide along the mother line of the vessel, through which the meniscus of the pycnometer is observed from outside by a cathetometer, so as to calculate the volume of the sample in the pycnometer by the formula (1).

The densities at each temperature can be expressed by

$$D=w/V\;.\quad(3)$$

where w is the weight of the sample in the pycnometer which is determined by emptying the pycnometer after the observations. The results given in the following tables and in Fig. 4 are the mean values of several independent results with different pycnometers.

D (calc.) in the third columns of Tables 1 and 2 are calculated by the following formulae, which have been obtained from the observed data with the aid of the method of least square.

For isopropyl-alcohol,

$$D=0.80430-0.0008201\,t-0.000001405\,t^2$$

Table 1. Densities of Isopropyl-alcohol.

Temp.	Density (obs.)	D (calc.)	Pycnometer
− 0.00	0.80430		5, 6 and 8
− 7.02	0.81083	0.81005	6
− 10.02	0.81234	0.81243	6
− 10.26	0.81293	0.81256	1
− 10.57	0.81376	0.81295	6
− 17.17	0.81884	0.81834	1 and 6
− 20.77	0.82167	0.82127	6
− 28.09	0.82742	0.82723	2 and 5
− 41.85	0.83855	0.83840	6
− 43.75	0.83938	0.83991	2 and 5
− 44.25	0.84037	0.84031	1 and 6
− 54.17	0.84810	0.84831	2 and 5
− 54.95	0.84869	0.84894	1 and 6
− 65.80	0.85723	0.85762	5
− 76.80	0.86603	0.86645	5
− 90.82	0.87725	0.87762	1 and 6
−106.03	0.89030	0.89967	6

Table 2. Densities of n-Butyl-alcohol.

Temp.	Density	D (calc.)	Pycnometer
0.00	0.82380		2, 2, 5 and 8
−11.28	0.83264	0.83259	2, 5 and 6
−18.14	0.83852	0.83831	5 and 6
−23.30	0.84197	0.84193	2 and 6
−32.87	0.84936	0.84934	2 and 6
−37.70	0.85305	0.85307	2 and 6
−38.36	0.85349	0.85358	2 and 6
−39.45	0.85448	0.85442	2 and 6
−45.70	0.85932	0.85923	2 and 6
−55.33	0.86654	0.86662	2 and 6
−55.44	0.86676	0.86671	2 and 6
−69.06	0.87729	0.87701	2 and 6
−75.58	0.88241	0.88211	2 and 6
−80.80	0.88607	0.88607	2 and 6

and for n-butyl-alcohol,

$$D=0.82380-0.0007819\,t-0.000000129\,t^2$$

Table 3 contains the calculated densities from the above formulae at temperature of round numbers.

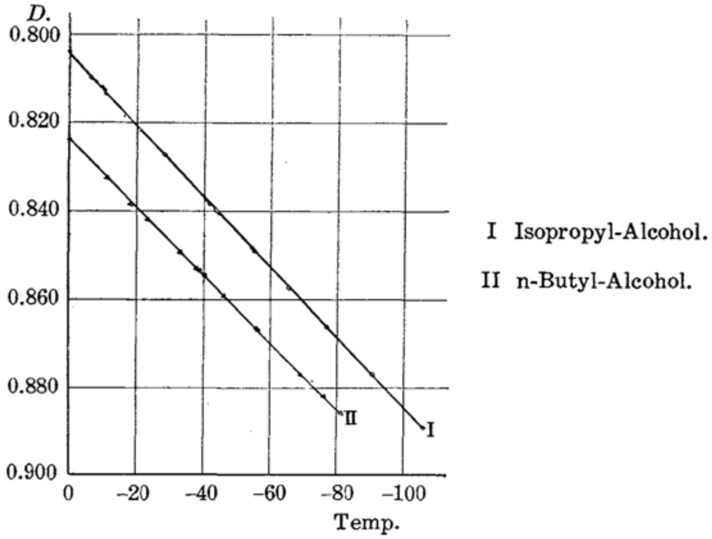

Fig. 4.

Table 3. Densities of Isopropyl-and n-Butyl-alcohol.

Temp.	Isopropyl-alcohol	n-Butyl-alcohol	Temp.	Isopropyl-alcohol	n-Butyl-alcohol
0.00	0.80430	0.82380	− 50.00	0.84179	0.86258
− 5.00	0.80836	0.82771	− 55.00	0.84516	0.86642
− 10.00	0.81236	0.83161	− 60.00	0.84845	0.87025
− 15.00	0.81628	0.83550	− 65.00	0.85167	0.87407
− 20.00	0.82014	0.83939	− 70.00	0.85482	0.87790
− 25.00	0.82392	0.84327	− 75.00	0.85790	0.88171
− 30.00	0.82764	0.84714	− 80.00	0.86091	0.88552
− 35.00	0.83128	0.85101	− 85.00	0.86389	
− 40.00	0.83486	0.85487	− 90.00	0.86672	
− 45.00	0.83837	0.85873	− 95.00	0.86953	
			−100.00	0.87226	
			−105.00	0.87401	

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