was inserted. This time was doubtless needed to bring the catalyst to the temperature of the furnace. Since chlorine was not produced before the sulfuric acid began to come off, it is needless to assume that copper sulfate acted as catalyst even at the very start of the action; because as soon as a very small amount of copper sulfate was converted into chloride, the latter could function as the catalyst.

Summary

1. At 450°, sulfuric acid is quantitatively displaced from copper sulfate by the action of dry hydrogen chloride gas alone, or admixed with oxygen. We may assume that the residual salt is entirely in the form of copper chloride or oxychloride.

2. Hence the mechanism of the Deacon Process when copper sulfate is used as the initial form of the catalyst is no more complicated than it is when cupric chloride is used initially.

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VAPOR PRESSURE DATA FOR ISOPROPYL ALCOHOL AND TERTIARY BUTYL ALCOHOL

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The literature apparently contains no data for the vapor pressures of *iso*propyl alcohol and tertiary butyl alcohol over a range of temperatures. In view of the increasing importance of these substances, the present investigation was undertaken to remedy the deficiency.

Experimental Part

Two methods for measuring the vapor pressures of the liquids were employed. From 20 to 90° the static method of Smith and Menzies[1] was utilized. The isoteniscope was of the U type and was immersed in a small hand-regulated thermostat. The temperatures were measured to 0.01° by a thermometer which had been calibrated against a similar thermometer standardized by the United States Bureau of Standards. The manometer was U-shaped, with the evacuated side permanently connected to a high-vacuum pump consisting of a bulb of activated charcoal immersed in liquid air.

A second static method, developed in this Laboratory, was employed in measurements on *iso*propyl alcohol from 0 to 30° and on undercooled *tert.*-butyl alcohol at 20 and 25°. In this case our apparatus was essentially similar in principle to that described by Johnston,[2] although at the

[1] Smith and Menzies, This Journal, **32**, 1419 (1910).

[2] Johnston, *Z. physik. Chem.*, **62**, 333 (1908).

time of its development we were unaware of anything similar in the literature. However, we dispensed with the large manometer employed by Johnston, as none of our pressure readings by this method were above 70 mm. For a pump we again used a tube of activated charcoal in liquid air. Manometer readings were made by a brass cathetometer reading to 0.05 mm.

The *iso*propyl alcohol was prepared from "refined" material supplied by the Eastman Kodak Co. This was subjected to four treatments and distillations with lime in the ordinary manner and then to two very careful fractionations. The middle 50% was used for the measurements. It had a density of 0.78091 at 25°/4°, corresponding to a purity of 99.97% on the basis of the criteria[3] previously employed.

The *tert.*-butyl alcohol was a refined material (m. p. 12°) given to us by the Petroleum Chemical Corporation. It was first subjected to ten fractional crystallizations. The resulting product was treated with lime and distilled, then treated with a small amount of metallic sodium and redistilled. The distillate thereby obtained was next subjected to fifteen additional fractional crystallizations. The final product had a freezing point of 25.50°.

Three or more sets of determinations were carried out upon each alcohol by the two different methods, the measurements being made over the temperature ranges previously indicated at intervals of approximately 5°. The results obtained were in general very concordant. The vapor pressure values for each alcohol were plotted against the corresponding temperatures; a smooth curve was then drawn and from this the vapor pressures were read at exactly five degree intervals. These are the results appearing in Table I. In the case of the *iso*propyl alcohol they are probably accurate to within 0.2 mm. at the lower temperatures and to within 0.8 mm. at the highest temperatures; for the *tert.*-butyl alcohol the errors may be 50% greater than these, owing to more difficulty in the purification

TABLE I

VAPOR PRESSURE DATA

Temp., °C.	Vapor pressure of		Temp., °C	Vapor pressure of	
	C_3H_7OH	C_4H_9OH		C_3H_7OH	C_4H_9OH
0.00	8.9	...	50.00	176.8	174.3
5.00	12.1	...	55.00	227.4	224.2
10.00	17.0	...	60.00	288.5	285.2
15.00	23.8	...	65.00	363.1	358.2
20.00	32.4	30.6	70.00	454.8	447.3
25.00	44.0	42.0	75.00	561.4	553.2
30.00	59.1	56.9	80.00	691.8	679.4
35.00	78.9	76.3	85.00	845.6	826.3
40.00	105.6	102.3	90.00	1020.7	996.2
45.00	136.8	133.8			

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[3] Parks and Kelley, THIS JOURNAL, **47,** 2090 (1925).

of the sample. In all cases the pressures are expressed in terms of millimeters of mercury at 0°.

Derived Data

If we neglect the volume of the liquid in the well-known Clausius-Clapeyron relationship and assume the perfect gas equation for the vapor, we obtain the approximation, $\frac{-R \, \mathrm{d} \ln p}{\mathrm{d}(1/T)} = \Delta H$, where ΔH is the heat of vaporization per mole. In the present case the values for $-R \ln p$ were plotted against the reciprocals of the absolute temperatures for both alcohols and the slopes of the two curves were measured at points corresponding to 25 and 50° and the respective boiling points. The values thus obtained for 50° and for the boiling point were then decreased by 1.0 and 4.0%,[4] respectively. The resulting heats of vaporization in calories per mole appear in Table II; they are probably accurate to within 150 calories for the *iso*propyl alcohol and to within 200 calories for the *tert.*-butyl alcohol. The values at the boiling points compare favorably with the scanty calorimetric data in the literature.[5]

Following Hildebrand,[6] we have also calculated the molal entropy of vaporization (Table II, Col. 5) at the temperature at which the concentration of vapor is 0.00507 mole per liter. As 27.4 cal. per degree is the mean value obtained by Hildebrand for normal liquids, our higher results indicate that these two alcohols are decidedly "polar."

TABLE II

THERMAL VALUES DERIVED FROM THE VAPOR PRESSURE DATA

Alcohol	Heat of vaporization (cal. per mole) At 25°	50°	B. p.	Molal entropy of vaporization (cal. per degree)
*iso*Propyl	10,620	10,490	9,600 (at 82.28°)	33.8 (at 38.7°)
tert.-Butyl	10,890	10,680	9,480 (at 82.86°)	34.4 (at 39.4°)

Summary

1. Vapor pressure measurements have been made on *iso*propyl alcohol from 0 to 90° and on *tert.*-butyl alcohol from 20 to 90°, inclusive.

2. From these experimental results the heats of vaporization of the two liquids have been estimated for several temperatures. The molal entropies of vaporization indicate that these alcohols are polar liquids.

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[4] These corrections were decided upon after a careful survey of the deviations from the perfect gas law found by Young, *Proc. Roy. Soc.* (*Dublin*), **12,** 376 (1910), for the vapors of alcohols, esters, etc., at corresponding temperatures. The error involved in their use is probably less than 0.5%.

[5] Mathews, THIS JOURNAL, **48,** 572 (1926); Landolt-Börnstein-Roth-Scheel, "Tabellen," 1923, p. 1483.

[6] Hildebrand, "Solubility," Chemical Catalog Co., New York, 1924, p. 94.