97. *Equilibrium and Thermodynamic Relation in the Vapour-phase Catalytic Dehydration of Ethyl Alcohol to Ethyl Ether.*

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Equilibrium relations in the gas-phase dehydration of ethyl alcohol to ethyl ether have been studied. The thermo-dynamic functions for both the reaction and the substance ether have been derived. The values found for the heat content for ether are at variance with those previously accepted. Heat capacities calculated from spectroscopic functions agree with those derived from the experimental results.

IN investigations on the formation of ether from alcohol it became necessary to find the requisite equilibrium and thermodynamic relations. For this we required suitable catalysts, a method of analysis for the reaction products, and a suitable apparatus for determination of the equilibrium constant.

Three groups of catalysts are known for the dehydration of alcohol to ether : aluminium oxide; aluminium sulphate; and sulphuric and phosphoric acids. A considerable number of alumina catalysts were investigated, but all were only slightly active at $<250°$, while at and

above that temperature they formed ethylene as well as ether and were thus unsuitable for equilibrium determinations. An alum catalyst prepared according to Jatkar and Watson (*J. Soc. Chem. Ind.*, 1926, **45**, 168T) was found to lead to ether exclusively and in good yield at 200—240°. For equilibrium determinations at lower temperatures a new catalyst was developed consisting of sulphuric acid, promoted with copper sulphate, on a silica-gel carrier. This catalysed the formation of ether from alcohol exclusively, at 120—170°.

The product of the dehydration reaction was analysed by a method based on the fluoroboric-acid-catalysed reaction with acetic anhydride (Valentin, *J. S. African Chem. Inst.*, 1949, **2**, 59).

<p align="center">EXPERIMENTAL.</p>

Preparation of the Sulphuric Acid–Copper Sulphate Catalyst.—Commercial silica gel was washed in a stream of water for 12 hours, then dried, and heated at 350° for 4 hours in a slow current of air. The gel (125 g.) was then soaked for 2 hours in a solution of sulphuric acid (12 c.c.) and copper sulphate (4·5 g.) in water (388 c.c.). The solution was decanted and the gel dried in an oven at 105° for 8 hours. The soaking and drying were repeated 4 times, all the solution being then taken up by the gel. The final drying was for 16 hours.

Apparatus for Equilibrium Determinations.—This consisted of a jacketed 4-l. steel autoclave containing the catalyst spread on two porcelain basins one above the other. Electric heating of the bottom kept a liquid boiling under reflux in the jacket at an accurately controlled low pressure. This ensured precise temperature control by virtue of the high heat transfer coefficient from a condensing vapour to a metal surface. Tetralin, used up to 170°, and " Dowtherm," used at higher temperatures, satisfactorily maintain their vapour pressure–temperature relations. The lid of the autoclave was heated electrically. The whole apparatus was well lagged and the temperature was the same (within $\frac{1}{2}$°) at the bottom, centre, and top.

<p align="center">*Equilibrium constants.*</p>

Temp., °K.	392	403	413	425	431	437	463	473	482
K_p (this work)	0·23	0·40	0·57	0·87	1·05	1·22	—	2·51	3·10
K_p (lit.)	—	8·0 [1]	—	—	—	—	2·3 [2]	—	—
Temp., °K.	492	498	503	509	523	539	542	548	
K_p (this work)	3·51	—	3·66	3·86	—	—	—	—	
K_p (lit.).	—	3·5 [3]	—	—	6·9 [4]	7·75 [5]	8·3 [7]	1·0 [1]	

[1] Pease and Yung, *J. Amer. Chem. Soc.*, 1924, **46**, 2397. [2] Mailhe and de Godon, *Bull. Soc. chim.*, 1916, **5**, 565. [3] Jatkar and Watson, *J. Indian Inst. Sci.*, 1926, **9**, A, 71. [4] Clark, Graham, and Winter, *J. Amer. Chem. Soc.*, 1925, **47**, 2748. [5] Newitt and Semerano, *Proc. Roy. Soc.*, 1936, **157**, A, 348. [6] Alvarado, *J. Amer. Chem. Soc.*, 1928, **50**, 790.

Procedure for Equilibrium Measurements.—The autoclave containing 100 g. of catalyst was brought up to the required reaction temperature and evacuated. Alcohol (30 c.c.) were pumped in with a controlled-volume pump, conditions were kept constant until equilibrium was attained, and two samples (*ca.* 2 g. each) were withdrawn at an interval of 15 minutes and totally condensed. The water formed in the reaction was adsorbed more strongly than the alcohol, causing a slight fall in pressure inside the autoclave as the reaction proceeded. Completion of the reaction was indicated by the pressure becoming constant, and was confirmed by the concordant analyses of the two samples. The total time required for the reaction varied from 6 hours at the lowest temperature to 2 hours at the highest.

Results.—The pressure in the autoclave was kept at *ca.* 3 atm. and, since in the reaction there is no change in the number of molecules, K_p was taken as equal to K_c within the limits of the experimental error. Results are given in the table.

The experimental results are represented by the empirical equation

$$\log K_p = 7·70 - 2200T^{-1} - 1·00 \log T \pm 0·04$$

Thence other thermodynamic functions for the reaction were calculated, as follows :

$$\Delta F° = 10·061 + 4·573T \log T - 35·21T$$
$$\Delta H° = 10·061 - 1·986T$$
$$\Delta C_p° = -1·986$$
$$\Delta S° = 52·8 - 4·55 \log T - 10·020T^{-1}$$

To minimise errors the following equation was used in calculating the entropy change

$$\Delta S° = R \left(\frac{\mathrm{d} \log K_p}{\mathrm{d} \log T} + \log_e K_p \right)$$

<p align="center">DISCUSSION.</p>

Thermodynamic data for ether are calculated from those for the reaction, the best available data for alcohol and water being used. For alcohol

$$C_p° = 3·578 + 49·847 \times 10^{-3}T - 169·91 \times 10^{-7}T^2$$
$$H° = -51·762 + 3·578T + 24·924 \times 10^{-3}T^2 - 54·64 \times 10^{-7}T^3$$
$$S° = 31·93 + 8·239 \log T + 49·85 \times 10^{-3}T - 84·9 \times 10^{-7}T^2$$

[from Spencer and Flanagan (*J. Amer. Chem. Soc.*, 1942, **64**, 2511), Brickwedde, Moskow, and Aston (*J. Res. Nat. Bur. Stand.*, 1946, **37**, 263), and Aston (*Ind. Eng. Chem.*, 1942, **34**, 514)].

For water

$$C_p^{\circ} = 7\cdot219 + 2\cdot374 \times 10^{-3}T + 2\cdot67 \times 10^{-7}T^2$$
$$H^{\circ} = -57\cdot016 + 7\cdot219T + 1\cdot187 \times 10^{-3}T^2 + 0\cdot89 \times 10^{-7}T^3$$
$$S^{\circ} = 4\cdot08 + 16\cdot623 \log T + 2\cdot374 \times 10^{-3}T + 1\cdot34 \times 10^{-7}T^2$$

[from Spencer and Flanagan (*loc. cit.*), Brickwedde, Moskow, and Aston (*loc. cit.*), Giauque and Archibald (*J. Amer. Chem. Soc.*, 1937, **59**, 56), and Gordon (*J. Chem. Physics*, 1934, **2**, 65)].

Then for ether

$$C_p^{\circ} = 2\cdot049 + 97\cdot320 \times 10^{-3}T - 342\cdot49 \times 10^{-7}T^2$$
$$H^{\circ} = -36\cdot447 - 2\cdot043T + 48\cdot661 \times 10^{-3}T^2 - 112\cdot39 \times 10^{-7}T^3$$
$$S^{\circ} = 112\cdot58 - 4\cdot695 \log T + 97\cdot33 \times 10^{-3}T - 171\cdot1 \times 10^{-7}T^2 - 10\cdot020T^{-1}$$
$$F^{\circ} = -36\cdot447 - 95\cdot05T - 48\cdot77 \times 10^{-3}T^2 + 56\cdot92 \times 10^{-7}T^3 + 4\cdot718T \log T.$$

These results are recorded in the following table, together with values in the literature, extrapolated values being marked with an asterisk.

Thermodynamic values for ethyl ether.

Temp., °K.	285	293	372	400	450	500
C_p° (this work)	—	—	29·4 * 3	31·4	34·6	37·9
C_p° (spec.) [a]	—	—	30·6	32·3	35·3	38·2
H°	—	−33,149 * 2	—	−30,196	−28,530	−26,714
S°	92·5 * 1	—	—	111·6	119·2	124·3

[a] Calc. from spectroscopic functions by Dobratz's method (*Ind. Eng. Chem.*, 1941, **33**, 759).
[1] Parks and Huffman (*J. Amer. Chem. Soc.*, 1924, **46**, 1753) give 88·9.
[2] The heat of combustion recorded by Stohmann, Rodatz, and Herzberg (*J. pr. Chem.*, 1887, **35**, 410) leads to H° −44,935.
[3] Jennings and Bixler (*J. Physical Chem.*, 1934, **38**, 747) give 32·1.