

## NOTE.

*The Free Energy of Methyl Ether from the Methanol-Methyl Ether Equilibrium*  $2\text{MeOH}(v.) = \text{Me}_2\text{O} + \text{H}_2\text{O}(v.)$ . By P. H. GIVEN.

PARKS and HUFFMAN ("The Free Energies of Some Organic Compounds," 1932) calculate, from a single value of the equilibrium constant of the reaction at  $623^\circ \text{K}$ . (McKee and Burke, *Ind. Eng. Chem.*, 1923, **15**, 793) and Thomsen's value of the heat of combustion of methyl ether (*Z. physikal. Chem.*, 1905, **52**, 347), that the standard free energy of methyl ether is  $\Delta G_{298.1}^0 = -26,350$  cal. Since 1932 new data have appeared, but the free energy has not been recalculated. Gajendragad, Jatkar, and Watson (*J. Indian Inst. Sci.*, 1932, **15**, A, 59) have determined two new equilibrium constants, at  $503^\circ$  and  $403^\circ \text{K}$ . Kennedy, Sagenkahn, and Aston (*J. Amer. Chem. Soc.*, 1941, **63**, 2267) found the entropy of methyl ether at  $298.16^\circ \text{K}$ . and 1 atm. to be  $63.72 \pm 0.20$  E.U. in the ideal vapour state. This value for the ideal state may justifiably be combined with other data referring to an actual vapour, since the correction for gas imperfection is small (0.08 E.U.; *loc. cit.*), and the other thermochemical determinations are not of such high precision as this of entropy.

Kistiakowsky and Rice (*J. Chem. Physics*, 1940, **8**, 618) determined the molar heat capacity of methyl ether vapour at  $272.2^\circ$ ,  $300.76^\circ$ ,  $333.25^\circ$ , and  $370.42^\circ \text{K}$ ; these values when plotted against temperature give a straight line whose equation is:

$$\Delta C_p = 5.40 + 0.0335T \quad \dots \dots \dots (1)$$

This equation gives the variation of heat capacity with temperature over the range  $0-100^\circ$ ; strictly, any free-energy equation developed from it is valid only within this range, but extrapolation to higher temperatures should not involve much error.

Bischowsky and Rossini ("Thermochemistry of Chemical Substances," 1936) prefer a recalculated value for the heat of combustion of methyl ether based on Thomsen's value. From their values for the heats of combustion of methyl ether and methanol, and for the heat of vaporisation of water, we obtain:  $2\text{MeOH}(v.) = \text{Me}_2\text{O} + \text{H}_2\text{O}$ ;  $\Delta H_{291}^0 = -7,300$  cal., and for the formation of methyl ether,  $\Delta H_{291}^0 = -46,400$  cal.

Using equation (1), we find:

$$2\text{C} + 3\text{H}_2 + 0.5\text{O}_2 = \text{C}_2\text{H}_6\text{O}; \Delta H_{298.1}^0 = -46,500 \text{ cal.} \quad \dots \dots \dots (2)$$

The experimental equilibrium constants are:  $K = 3.18$  at  $623^\circ \text{K}$ . (McKee and Burke),  $15.4$  at  $503^\circ \text{K}$ .,  $48.5$  at  $403^\circ \text{K}$  (both due to Gajendragad, Jatkar, and Watson). From these data, we can develop the free-energy equation

$$2\text{MeOH}(v.) = \text{Me}_2\text{O} + \text{H}_2\text{O}(v.); \Delta G^0 = -9100 - 10.2T \log_e T + 0.00142T^2 + 69.58T \quad \dots \dots (3)$$

(The three values of the integration constant are  $-69.10$ ,  $-69.14$ , and  $-70.5$ .) Hence

$$\Delta G_{298.1}^0 = -4.420 \text{ cal.} \quad \dots \dots \dots (4)$$

Using Parks and Huffman's values for the free energies of the vapours of methanol and water, we obtain for the formation of methyl ether

$$2\text{C} + 3\text{H}_2 + 0.5\text{O}_2 = \text{C}_2\text{H}_6\text{O}; \Delta G_{298.1}^0 = -27,700 \text{ cal.} \quad \dots \dots \dots (5)$$

The entropy of formation of methyl ether (from the value of Kennedy and co-workers, and atomic entropies) is

$$2\text{C} + 3\text{H}_2 + 0.5\text{O}_2 = \text{C}_2\text{H}_6\text{O}; \Delta S_{298.1}^0 = -57.3 \text{ E.U.} \quad \dots \dots \dots (6)$$

From the third law, using  $\Delta G = \Delta H - T.\Delta S$ , we thus find:

$$2\text{C} + 3\text{H}_2 + 0.5\text{O}_2 = \text{C}_2\text{H}_6\text{O}; \Delta G_{298.1}^0 = -29,400 \text{ cal.} \quad \dots \dots \dots (7)$$

For the mean free-energy value, we may take

$$2\text{C} + 3\text{H}_2 + 0.5\text{O}_2 = \text{C}_2\text{H}_6\text{O}; \Delta G_{298.1}^0 = -28,500 \text{ cal.} \quad \dots \dots \dots (8)$$

This value is still somewhat uncertain, but it must be more reliable than that given by Parks and Huffman. The chief uncertainty lies in the heat of combustion of methyl ether. It may be noted that, if we assume  $\Delta C_p = 0$  for the dehydration of methanol, we obtain  $\log_e K = 7300/RT - 4.8$ ,  $\Delta G^0 = -7300 + 9.6T$ , and

$$2\text{MeOH}(v.) = \text{Me}_2\text{O} + \text{H}_2\text{O}(v.); \Delta G_{298.1}^0 = -4,440 \text{ cal.}$$