NOTE.

The Free Energy of Methyl Ether from the Methanol–Methyl Ether Equilibrium $2\mathrm{MeOH(v.)} = \mathrm{Me_2O} + \mathrm{H_2O(v.)}$. 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° 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 $\Delta G^0_{298\cdot1} = -26{,}350$ cals. 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° and 403° K. Kennedy, Sagenkahn, and Aston (*J. Amer. Chem. Soc.*, 1941, **63**, 2267) found the entropy of methyl ether at 298·16° K. and 1 atm. to be $63\cdot72 \pm 0\cdot20$ 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°, 300·76°, 333·25°, and 370·42° K.; these values when plotted against temperature give a straight line whose equation is :

$$\Delta C_p = 5\cdot40 + 0\cdot0335T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation gives the variation of heat capacity with temperature over the range 0—100°; 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 : $2\mathrm{MeOH(v.)} = \mathrm{Me_2O} + \mathrm{H_2O}$; $\Delta H^0_{291} = -7{,}300$ cals., and for the formation of methyl ether, $\Delta H^0_{291} = -46{,}400$ cals.

Using equation (1), we find :

$$2\mathrm{C} + 3\mathrm{H_2} + 0\cdot5\mathrm{O_2} = \mathrm{C_2H_6O}; \ \Delta H^0_{298\cdot1} = -46{,}500 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The experimental equilibrium constants are : $K = 3\cdot18$ at 623° K. (McKee and Burke), 15·4 at 503° K., 48·5 at 403° K (both due to Gajendragad, Jatkar, and Watson). From these data, we can develop the free-energy equation

$$2\mathrm{MeOH (v.)} = \mathrm{Me_2O} + \mathrm{H_2O\ (v.)}; \ \Delta G^0 = -9100 - 10\cdot2T\log_e T + 0\cdot00142T^2 + 69\cdot58T \quad . \quad . \quad . \quad (3)$$

(The three values of the integration constant are $-69\cdot10$, $-69\cdot14$, and $-70\cdot5$.) Hence

$$\Delta G^0_{298\cdot1} = -4\cdot420 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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

$$2\mathrm{C} + 3\mathrm{H_2} + 0\cdot5\mathrm{O_2} = \mathrm{C_2H_6O}; \ \Delta G^0_{298\cdot1} = -27{,}700 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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

$$2\mathrm{C} + 3\mathrm{H_2} + 0\cdot5\mathrm{O_2} = \mathrm{C_2H_6O}; \ \Delta S^0_{298\cdot1} = -57\cdot3 \text{ E.U.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

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

$$2\mathrm{C} + 3\mathrm{H_2} + 0\cdot5\mathrm{O_2} = \mathrm{C_2H_6O}; \ \Delta G^0_{298\cdot1} = -29{,}400 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For the mean free-energy value, we may take

$$2\mathrm{C} + 3\mathrm{H_2} + 0\cdot5\mathrm{O_2} = \mathrm{C_2H_6O}; \ \Delta G^0_{298\cdot1} = -28{,}500 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

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 $\log_e K = 7300/RT - 4\cdot8$, $\Delta G^0 = -7300 + 9\cdot6T$, and

$$2\mathrm{MeOH\ (v.)} = \mathrm{Me_2O} + \mathrm{H_2O\ (v.)}; \ \Delta G^0_{298\cdot1} = -4{,}440 \text{ cals.}$$

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