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LETTERS TO THE EDITOR

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The Free Energy of the Producer-Gas Reaction, and the "Zero-Point" Entropy of Graphite[1]

In 1933, calculations made by Gordon[2] on the change in free energy for the producer-gas reaction indicated the possibility of the existence in graphite of a "zero-point" entropy of about 0.5 calorie per degree per mole. In an extensive study reported in 1934, Terebesi[3] compared, for five different reactions involving graphite, the experimentally determined equilibrium constants with those evaluated from calorimetric data and statistical calculations. According to Terebesi, the data on three of these reactions pointed strongly toward the nonexistence of a "zero-point" entropy for graphite, while the data on the other two reactions, one of them the producer-gas reaction, were inconclusive.

New calorimetric data on the heats of combustion of graphite[4, 5] yield new values, significantly different from the older ones, for the heats and free energies of formation of carbon dioxide[6] and carbon monoxide.[7] It seems desirable, therefore, to calculate a new value for the heat and free energy of the producer-gas reaction, and to ascertain the effect of the new values on the question of the "zero-point" entropy of graphite.

The new values for the heat and free energy of formation of carbon dioxide are, per mole:[6]

$$\mathrm{C}\ (c,\ \text{graphite})+\mathrm{O_2}\ (g)=\mathrm{CO_2}\ (g), \tag{1}$$

$$\Delta H^0_{298.16}=-393{,}355\pm46 \text{ NBS international joules, or } -94{,}030\pm11 \text{ calories,}^8 \tag{2}$$

$$\Delta F^0_{298.16}=-394{,}228\pm58 \text{ NBS international joules, or } -94{,}239\pm14 \text{ calories.} \tag{3}$$

For carbon monoxide, the writer[7] gives the following recalculated value for the heat of combustion, per mole:

$$\mathrm{CO}\ (g)+\tfrac{1}{2}\ \mathrm{O_2}\ (g)=\mathrm{CO_2}\ (g), \tag{4}$$

$$\Delta H^0_{298.16}=-282{,}937\pm120 \text{ NBS international joules, or } -67{,}635\pm29 \text{ calories,} \tag{5}$$

and for the heat and free energy of formation, per mole:

$$\mathrm{C}\ (c,\ \text{graphite})+\tfrac{1}{2}\ \mathrm{O_2}\ (g)=\mathrm{CO}\ (g), \tag{6}$$

$$\Delta H^0_{298.16}=-110{,}418\pm129 \text{ NBS international joules, or } -26{,}395\pm21 \text{ calories,} \tag{7}$$

$$\Delta F^0_{298.16}=-137{,}160\pm133 \text{ NBS international joules, or } -32{,}788\pm32 \text{ calories.} \tag{8}$$

Combination of the foregoing values, together with appropriate values[6, 7] of $H^0_{298.16}-H^0_0$, yields for the producer-gas reaction, per mole:

$$\mathrm{C}\ (c,\ \text{graphite})+\mathrm{CO_2}\ (g)=2\mathrm{CO}\ (g), \tag{9}$$

$$\Delta H^0_{298.16}=172{,}519\pm244 \text{ NBS international joules, or } 41{,}240\pm58 \text{ calories.} \tag{10}$$

$$\Delta F^0_{298.16}=119{,}908\pm248 \text{ NBS international joules, or } 28{,}663\pm59 \text{ calories,} \tag{11}$$

$$\Delta H^0_0=165{,}603\pm244 \text{ NBS international joules, or } 39{,}587\pm58 \text{ calories.} \tag{12}$$

Combination of the above value for ΔH^0_0 with the appropriate values of $(F^0-H^0_0)/T$, reported by Clayton and Giauque,[9] Johnston and Davis,[10] and Kassel,[11] permits calculation of the equilibrium constant for reaction 9 for any given temperature:

$$\log_{10} K=-(1/2.3026R)[\Delta H^0_0/T+\Delta(F^0-H^0_0)/T]. \tag{13}$$

In this manner, there may be calculated the following values of $\log_{10} K$: 1000°K, 0.2689; 1100°K, 1.0772; 1200°K, 1.7467; 1300°K, 2.3093; 1400°K, 2.7891; 1500°K, 3.2022. These values of the equilibrium constant are found to be in excellent accord with the experimentally determined equilibrium constants within the relatively large limits of uncertainty of the latter (see the summaries by Eastman,[12] Chipman,[13] and Terebesi[3]). It may be concluded, therefore, that the data on the producer-gas reaction are in accord with the nonexistence of a "zero-point" entropy for graphite.

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National Bureau of Standards,
Washington, D. C.,
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[1] Publication approved by the Director of the National Bureau of Standards, United States Department of Commerce.
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