

LETTER TO THE EDITORS

Determination of the Excess Energy of Carbon Formation in the Decomposition of Carbon Monoxide and Methane

In a recent paper, Rostrup-Nielsen (1) correlates the excess free energy of decomposition reactions of carbon monoxide and methane over nickel catalysts with the diameter of the catalyst particles. This paper, taken together with the observations of Baird, Fryer and Grant (2) on high resolution electron microscopy of carbon obtained by decomposition of methane over nickel, led us to establish an expression for the partial molar excess free energy of carbon, using only surface tensions and the dimensions of the small crystals of carbon. The validity of this expression was checked with the data of Rostrup-Nielsen (1) and with the data of Legalland (3) who completed his work in our laboratory.

I. SURFACE ENERGY OF CARBON CRYSTALS

Baird, Fryer and Grant pointed out that carbon obtained by decomposition of methane over nickel (2) forms tubules with three principal regions. According to these authors, "in the center is an irregular particle of metal (in this case it would be nickel) and surrounding this is a highly crystalline carbon with the (0002) lattice planes parallel to the surface of metal par-

ticle; on the periphery of tubule there is a narrow region of amorphous carbon." Tubule growth has also been observed for carbon obtained by disproportionation of carbon monoxide (4) and recently on our samples (5).

Figure 1 represents the part of a tubule of carbon growing around a catalyst particle of diameter d . The tube consists of carbon crystals with their (0002) axis in a radial position. The walls of the cylinder are built by (0002) lattice planes and the bases by (0100) planes.

The catalytic reaction take place on the surface of the catalyst particle and the parts of the carbon tube without contact to the metal particle cannot alter the reaction. Therefore only the partial molar excess free energy of the carbon atoms surrounding the catalyst particle modifies the energetic balance of the reaction.

The surface energy of this part of the tube (see Fig. 1) is:

$$E = \pi d(d + 2h)\gamma_{0002} + \pi d^2\gamma_{0002, Ni} + 2\pi h(d + h)\gamma_{0100},$$

where γ_{0002} is the surface tension of the 0002 plane of graphite; $\gamma_{0002, Ni}$ the interfacial tension of the 0002 plane of graphite in contact with nickel; γ_{0100} the surface tension of the 0100 plane of graphite.

Thus the partial molar excess free energy of formation of carbon as a tube around a nickel particle is

$$\overline{\Delta G^{xs}} = \frac{M}{\rho} \left[\left(\frac{d + 2h}{d + h} \gamma_{0002} + \frac{d}{d + h} \gamma_{0002, Ni} \right) \frac{1}{h} + 2\gamma_{0100} \frac{1}{d} \right],$$

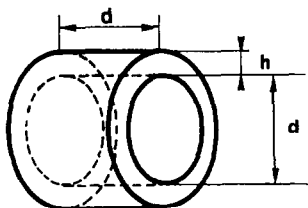


FIG. 1. Carbon tube obtained over a nickel particle of diameter d .

where M is the mass of a mole of carbon and ρ the density of carbon.

When the height of carbon crystal is smaller than the metal particle diameter ($h \ll d$),

$$\overline{\Delta G^{xs}} \simeq \frac{M}{\rho} \left[(\gamma_{0002} + \gamma_{0002, Ni}) \frac{1}{h} + 2\gamma_{0100} \frac{1}{d} \right]. \quad (1)$$

We can write Eq. (1) in a form similar to that of Rostrup-Nielsen [$\overline{\Delta G^{xs}} = \mu^* + (M/\rho) (2/d)\gamma$]. In Eq. (1) the term equivalent to μ^* represents the contribution from the surface energy of the basal planes of crystals whereas the contribution from structural defects was suggested by Rostrup-Nielsen.

II. EVALUATION OF $\overline{\Delta G^{xs}}$

γ_{0002} is known to be equal to 130 erg cm⁻² (6) for graphite in vacuum.

$\gamma_{0002, Ni}$ is calculated with the values of γ_{0002} , γ_{Ni} (7) and the contact angle of a nickel drop on graphite (8)

$$\gamma_{0002, Ni} = \gamma_{Ni} \cos 65^\circ + \gamma_{0002}$$

with $\gamma_{Ni} \simeq 2100$ erg cm⁻²; $\gamma_{0002, Ni} \simeq 1020$ erg cm⁻².

γ_{0100} values from the literature are estimates and according to Bruce (9) lie between 5470 and 6320 erg cm⁻². We may calculate an approximate value of γ_{0100} using the carbon-carbon bond energy in the (0002) lattice plane of graphite, as follows. To break all carbon-carbon bonds of graphite, the necessary molar enthalpy is $\Delta H^0 = 171.7$ kcal moles⁻¹. As the cohesion energy between (0002) planes is 260 erg cm⁻² (6), equivalent to 1 kcal mole⁻¹ (1 kcal mole⁻¹ = 4.18×10^{10} erg mole⁻¹), the bond energy of one atom in the (0002) plane is 170.7 kcal mole⁻¹. As each atom is bonded with three others, 170.7 kcal mole⁻¹ is the energy of simultaneous breaking of three carbon-carbon bonds. When a graphite crystal is broken as a (0100) lattice plane, three carbon-carbon bonds are broken per unit cell so the surface tension of the (0100) plane is:

With the surface of a unit cell section = 16.5×10^{-16} cm², it follows that $\gamma_{0100} \simeq 7200$ erg cm⁻²; this is only an approximate value, because the energetic model is the simplest and also because we neglected the contribution from entropy.

Finally, the molar free energy of carbon is:

$$\begin{aligned} \overline{\Delta G^{xs}} &= \frac{6.90 \times 10^3}{h} \\ &\quad + \frac{8.64 \times 10^4}{d} \text{ erg mole}^{-1}, \\ \text{or } \overline{\Delta G^{xs}} &= \frac{16.5}{h} + \frac{206}{d} \end{aligned} \quad (2)$$

where $\overline{\Delta G^{xs}}$ is in kilocalories per mole and h and d are in angstroms.

III. CORRELATION WITH EXPERIMENTAL DATA

1. Results of Rostrup-Nielsen (1)

From the experimental data of Rostrup-Nielsen the mean partial molar excess free energies at 550°C are:

for disproportionation of CO

$$\overline{\Delta G_{CO}^{xs}} = 2 + \frac{222}{d} \text{ kcal mole}^{-1};$$

for decomposition of CH₄

$$\overline{\Delta G_{CH_4}^{xs}} = 0.7 + \frac{219}{d} \text{ kcal mole}^{-1}.$$

The values 222 and 219 are only different by 10% from the value of 206 in Eq. (2). The first term allows us to evaluate the h values of crystals grown at 550°C. The data of Rostrup-Nielsen for decomposition of methane above 500°C and particle size $d = 2500$ Å give $\overline{\Delta G_{CH_4}^{xs}} - (220/d)$ nearly constant and equal to 0.5 kcal mole⁻¹. This value corresponds to $h = 33$ Å. For decomposition of CH₄ over nickel at 700°C Baird (2) observed carbon crystals about 40 Å high. Thus this result agrees with the

$$\gamma_{0100} = \frac{170.7 \times 4.18 \times 10^{10}}{\text{surface of unit cell section} \times \text{Avogadro No.}} \text{ erg cm}^{-2}.$$

value calculated with Eq. (2) and with the results of Rostrup-Nielsen.

2. Results of Legalland (3)

With nickel catalyst ex-formate Legalland pointed out three values of $\overline{\Delta G^{zs}}$:

$$\begin{aligned} \text{at } 425^\circ\text{C } \overline{\Delta G^{zs}} &= 5.1 \text{ kcal mole}^{-1}; \\ \text{at } 440^\circ\text{C } &= 4.3 \text{ kcal mole}^{-1}; \\ \text{at } 470^\circ\text{C } &= 3.8 \text{ kcal mole}^{-1}. \end{aligned}$$

The data of Rostrup-Nielsen for disproportionation of CO at 450°C over particles of 2500 Å lead to a first term of Eq. (2) equal to 2.2 kcal mole⁻¹; using this value we determine the particle sizes of Legalland's catalyst as:

$$\begin{aligned} d &= 76 \text{ \AA} \text{ at } 425^\circ\text{C}; \\ d &= 105 \text{ \AA} \text{ at } 440^\circ\text{C}; \\ d &= 138 \text{ \AA} \text{ at } 470^\circ\text{C}. \end{aligned}$$

Now a nickel catalyst prepared in the manner of Legalland's (10) catalyst has 40–70 m² g⁻¹ as specific area and consequently the diameter of the particle is in the range 100–170 Å. Therefore the Legalland results agree with those of Rostrup-Nielsen and confirm the validity of Eq. (2).

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