

A New Method of Estimating the Surface Area of Powder

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This has an activation energy of ~ 7 kcal.,⁴ which is close to Smith's value; moreover, the equilibrium is well over to the right, accounting for Taylor and Lavin's result that hydroxyl radicals disappear more rapidly than hydrogen atoms.

Our conclusions are therefore that the experimental investigations have given information as to the rate of the gas-phase removal of hydroxyl radicals, and that the surface reaction is very much slower. To complete the argument it is necessary to show that the rate measured is consistent with the assumption of homogeneous reaction. The γ calculated above was $\sim 2 \times 10^{-7}$ at 453°K, and since $\gamma = 2kr/\bar{v}$ (Eq. (4) of Part I), and with $r = 0.55$ cm³ the first-order rate constant is $\sim 2 \times 10^{-2}$ sec.⁻¹. If the reaction is really a second-order gas reaction involving molecular hydrogen at a concentration of H_2 , the second-order rate constant is $\sim 2 \times 10^{-2}/\text{H}_2$ liter mole⁻¹ sec.⁻¹. With a frequency factor of 10^{12} sec.⁻¹ and an activation energy 7 kcal., the calculated second-order rate constant is $\sim 3 \times 10^8$ liter mole⁻¹ sec.⁻¹. The homogeneous and heterogeneous reactions then have about the same rates if the hydrogen pressure is $\sim 10^{-4}$ mm, and the homogeneous will predominate at higher pressures. The actual hydrogen pressure in the system is not known, but the water vapor pressure was 5×10^{-2} mm. Taking a lower limit of about 20 percent for the degree of dissociation in the discharge, there is certainly enough molecular hydrogen to account for the experimental rate of disappearance of OH radicals by the reaction proposed.

The true value of γ for the surface recombination therefore remains unknown, but it can be bracketed: at 453°K it must be less than the apparent figure of $\sim 2 \times 10^{-3}$ and is probably greater the previously calculated value of $\sim 2 \times 10^{-7}$, since the activation energy for the surface recombination is probably less than the 9 kcal. quoted by Smith and used in our calculations.

Some recently published results of Byrne⁵ are also consistent with our conclusions.

* AEC Postdoctoral Fellow.

¹ K. E. Shuler and K. J. Laidler, *J. Chem. Phys.* (to be published); cf. also, K. J. Laidler, *Bull. soc. chim.* 16, D171 (1949); *J. Phys. Colloid Chem.* 53, 712 (1949).

² H. S. Taylor and G. I. Lavin, *J. Am. Chem. Soc.* 52, 1910 (1930).

³ W. V. Smith, *J. Chem. Phys.* 11, 110 (1943); thesis, Harvard University (1941).

⁴ K. H. Geib, *Ergeb. d. exakt. Naturwiss.* 15, 44 (1936).

⁵ J. F. Byrne, *Third Symposium on Combustion and Flame and Explosion Phenomena* (Williams and Wilkins, Baltimore), p. 481.

A New Method of Estimating the Surface Area of Powder

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THERE are three methods now to estimate the surface area of powder: Methods of Brunauer-Emmett-Teller¹ and Harkins-Jura,² using adsorption isotherm, and the thermal meas-

urements of the latter.³ In this note a new method will be suggested.

Let us consider the following thermodynamic process (Fig. 1):

- (1) vaporize the ample amount of pure liquid (n molecules) at its saturation pressure p_s ,
- (2) then decrease the pressure of the vapor to p_0 , at which the first molecule of the vapor is adsorbed on the powder,
- (3) put the powder into the room,
- (4) increase the pressure, following up the adsorption isotherm, until the pressure of the vapor attains again its saturation value p_s .

In these processes, we assume that the adsorption is reversible and the amount of liquid is ample enough. All of the processes must be under isothermal condition.

The change in Gibbs' free energy in each step is easily calculated. In (1) $\Delta G = 0$, (2) $nkT \ln(p_s/p_0)$, (3) 0, (4) $kT \int_1^n \ln(p_0/p(v)) dv$; thus the total change is $\Delta G = kT \int_1^n \ln(p_s/p(v)) dv$, where v is the number of molecules adsorbed on the powder, and $p(v) = p$ is the adsorption isotherm.

This ΔG can be expressed in another way. The initial and the final states of the above process differ only in the point that the surface of the powder is clean or covered with liquid. From this point of view, we may put $\Delta G = a(\sigma_{SA} - \sigma_{LS})$, where a is the area of the powder, and σ_{SA} , σ_{LS} are the surface tensions (surface Gibbs' free energy) of the interface between powder and air, and between powder and liquid, respectively.

From these two formulas we obtain,

$$kT \int_1^n \ln \frac{p_s}{p(v)} dv = a(\sigma_{SA} - \sigma_{LS}), \quad (1)$$

or, introducing the contact angle θ between the powder and the liquid, by the Dupre's relation³ $\sigma_{AL} \cos \theta = \sigma_{SA} - \sigma_{LS}$, σ_{AL} : surface tension of the liquid. (1) becomes

$$a = kT \int_1^n \ln \frac{p_s}{p(v)} dv / \sigma_{AL} \cos \theta. \quad (2)$$

If we obtain the adsorption isotherm with some suitable liquid and the powder whose area we want to know, then, measuring the contact angle, we can calculate the required area by (2).

There are no suitable data to test (2), except that of Carver's old one.⁴ He obtained the adsorption isotherm with toluene and glass, whose surface area he measured directly. With his result we obtain

$$kT \int \ln \frac{p_s}{p(v)} dv / a = 44 \text{ erg/cm}^2. \quad (3)$$

The contact angle between glass and toluene is measured by Bertell,⁵ from whose result

$$\sigma_{LA} \cos \theta = 46.5 \text{ erg/cm}^2. \quad (4)$$

(3) and (4) agree within 5 percent, confirming our prediction (2).

¹ Brunauer, Emmett, and Teller, *J. Am. Chem. Soc.* 60, 316 (1938).

² W. D. Harkins and G. Jura, *J. Chem. Phys.* 11, 430, 431 (1943).

³ Dupre, *Théorie Mécanique de la Chaleur* (1869), p. 369.

⁴ Carver, *J. Am. Chem. Soc.* 45, 63 (1923).

⁵ Bartell and Merrill, *J. Phys. Chem.* 36, 1178 (1932).

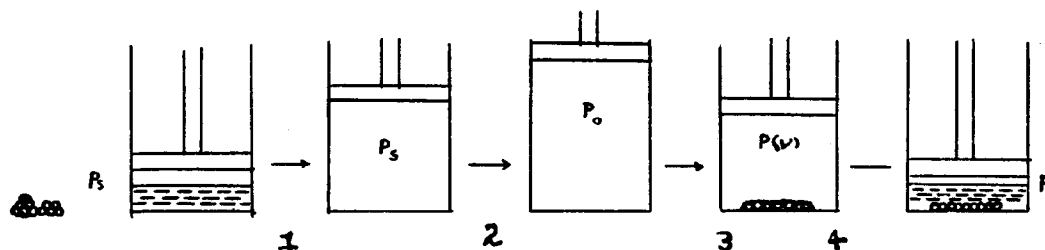


FIG. 1. A process diagram.