Nitrogen and Stearic Acid Adsorption by Supported and Unsupported Catalysts

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On Steric Effects

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STERIC effects have long been recognized in both equilibrium and rate studies. Quantitative experimental data are now available in a number of instances.[1] However, on the theoretical side, it appears that only qualitative interpretations have been attempted. The purpose of this note is to suggest a very obvious and simple (but apparently new) semi-quantitative theoretical approach to the problem which might be found useful at least in some cases.

The forces involved in steric effects are well known: (1) groups or atoms (within a molecule) may repel each other if too close together .(just as two gas molecules do for sufficiently small inter-molecular distances); (2) in order to decrease this interaction, the groups or atoms will tend to move apart, but this will generally require the stretching or bending of bonds with a related increase in energy. The final configuration will thus be the result of a compromise between the two types of force, and will be the configuration of minimum energy. The above simple argument (which can be generalized) applies when we may neglect entropy effects, all configurations but the one of lowest energy, polar effects, solvent effects, etc.

The suggestion to be made here is that it may sometimes prove worthwhile to attempt to formulate the above discussion quantitatively. For example, we might express approximately the steric energy, E^s, of a molecule as follows:

$$E^s = u_0\left(\frac{r_0}{r}\right)^{12} - 2u_0\left(\frac{r_0}{r}\right)^6 + \tfrac{1}{2}k_s(l-l_0)^2 + \tfrac{1}{2}k_b(\theta-\theta_0)^2, \quad (1)$$

where additional terms are necessary if there is more than one pair of interacting groups, more than one bond being stretched, or more than one bond angle being bent. In Eq. (1), l is a bond distance, θ a bond angle, k_s and k_b are force constants, l_0 and θ_0 are the values of l and θ in the absence of steric effects, r is the distance between the two interacting groups, and $-u_0$ is the minimum value of the interaction energy (at $r=r_0$). Equation (1) assumes, as an approximation, that the Lennard-Jones form of the interaction potential is appropriate here and that Hooke's law holds (for large displacements in some cases).

The minimum value of E^s in Eq. (1) is desired. This is found using $r=r(l, \theta)$, $\partial E^s/\partial l=0$ and $\partial E^s/\partial\theta=0$. The constants u_0 and r_0 may be estimated from van der Waals constants and radii, or other data. The force constants are hypothetical force constants. They are not the force constants which might be determined experimentally, but rather those which would exist in the absence of steric effects. Hence, they must be estimated by analogy, guessed, or calculated backwards from experimental data.

Calculations of this kind might also be of interest from the point of view of studying (classically) polar and steric effects on molecular structure.[2]

The best type of equilibrium experimental data for comparison with theoretical calculations is of the sort obtained by Brown[1]: measurement of ΔH, ΔF, and ΔS for a series of gas phase reactions in which there is a systematic change in substituents. The procedure then is to calculate E^s for the reactants and products of the different reactions in the series (generally E^s may be taken as zero for some of these substances), and compare calculated values of ΔE_i^s (where i refers to the ith reaction in the series) with the deviations of ΔH_i from the values of ΔH_i which would be expected in the absence of steric effects (e.g., in the absence of steric effects, ΔH_i might be a linear function of i). A corresponding treatment of steric effects on reaction rates involves calculation of E^s for the reactants and the activated complexes in the series.

Sufficient preliminary equilibrium calculations have been made for the gas phase addition reaction between trimethylboron and the methylamines (and ammonia) to indicate that forces of the sort discussed here can give effects of the type and order of magnitude found experimentally by Brown. However, a discussion of results will be deferred until time is available to carry out more detailed and refined calculations (e.g., including polar effects).

Note added June 25, 1946: It has come to the author's attention that F. H. Westheimer has been developing independently a similar approach to this problem, with particular reference to reaction rates.

[1] See, for example, H. C. Brown and co-workers, Science **103**, 385 (1946); J. Am. Chem. Soc. **67**, 374, 378, 503, 1452, 1765 (1945).
[2] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945), pp. 78–80.

Nitrogen and Stearic Acid Adsorption by Supported and Unsupported Catalysts

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June 21, 1946

IT has been suggested earlier[1] that diatomaceous earth supports of low area (and relatively large pores) may be responsible for the high area small pore structure of certain supported catalysts. Considerable evidence supporting this viewpoint and bearing on the structure of supported catalysts has recently been obtained in these laboratories by means of nitrogen adsorption at low temperatures[2] and stearic acid adsorption from solution.[3] The following observations strongly indicate that the unsupported catalyst precipitated in the absence of diatomaceous earth forms finely-divided essentially non-porous particles, whereas the supported catalyst precipitated in the presence of the low area diatomaceous support develops a small pore structure of much greater area.

UNSUPPORTED CATALYST

The nitrogen and stearic acid areas of an unsupported catalyst, U,[4] are, respectively, 91 and 93 sq.m per g (ignited weight). This good agreement indicates that the large stearic acid molecules reach all the surface available to the smaller nitrogen molecules and that the particles

are effectively non-porous. With the great majority of similar materials studied in the range of this and higher areas the nitrogen values are greater than the stearic acid values by a factor of two or more. Furthermore the nitrogen adsorption-desorption isotherm for catalyst U in the 0.4 to 0.6 relative pressure region does not show the hysteresis effect characteristic of the high area supported catalyst and generally attributed to small pores.[5] Finally the small non-porous particle size required for an area of 91 sq.m per g is qualitatively confirmed by the extremely slow sedimentation rate in benzene observed in the stearic acid experiments. Relatively large pores are, of course, not excluded by the above observations.

CATALYST SUPPORTED ON DIATOMACEOUS EARTH

The nitrogen and stearic acid areas of the catalyst supported on diatomaceous earth, H−G,[4] are, respectively, 270 and 46 sq.m per g (ignited weight), or expressed more significantly as area per gram of catalyst material, approximately 516 and 90 sq. m per g (see Table I). The increase in nitrogen area over that of the unsupported material is more than fivefold. Since the larger stearic acid molecules are adsorbed to the same extent as on the unsupported catalyst they evidently reach practically none of the internal surface of the high area supported material. The development of fine pore structure in the supported catalyst is also demonstrated by the marked adsorption-

TABLE I. Nitrogen and stearic acid adsorption by supported and unsupported catalysts.

| | Area, sq.m/g | | Nitrogen hysteresis (0.4 to 0.6 relative pressure) |
	Nitrogen (BET)	Stearic acid	
U (unsupported)	91 (91)*	93 (93)	None
H −G (on diatomaceous earth)	270 (516)	46 (90)	Marked
T (on titanium dioxide)	72 (134)	45 (82)	None

* Values in parentheses are areas per gram of *catalyst material*. Catalyst material constitutes approximately fifty percent by weight of the supported samples. In computing these values the maximum possible contribution of the support is subtracted (although a considerable portion of the support surface is undoubtedly covered). The nitrogen and stearic acid areas of the diatomaceous earth are, respectively, 23 and 2 sq.m/g and for the titanium dioxide, 10 and 8 sq.m/g.

desorption hysteresis effect observed with nitrogen in the 0.4 to 0.5 relative pressure region.[5]

CATALYST SUPPORTED ON TITANIUM DIOXIDE

In sharp contrast to the results obtained with a diatomaceous earth support are those found for the same catalyst supported on non-porous titanium dioxide. The nitrogen and stearic areas of this supported catalyst, T,[4] are, respectively, 72 and 45 sq. m per g or 134 and 82 sq. m per g of

catalyst material. No hysteresis is observed in the 0.4 to 0.6 relative pressure region of the nitrogen isotherm. Evidently the non-porous titanium dioxide support does not produce the high area fine pore structure obtained with the diatomaceous earth.

[1] Ries, Van Nordstrand, and Teter, Ind. Eng. Chem. **37**, 310 (1945).
[2] Brunauer, Emmett, and Teller, J. Am. Chem. Soc. **60**, 309 (1938).
[3] Harkins and Gans, J. Phys. Chem. **36**, 86 (1932).
[4] The unsupported catalyst, U, was prepared by the reation between sodium carbonate and a salt of a heavy metal whose oxide is readily reducible. The precipitation of the supported catalyst, H −G, was similarly performed in the presence of suspended diatomaceous earth. In the preparation of catalyst T, titanium dioxide was substituted for the diatomaceous earth. All catalysts were calcined at 350°C for two hours. Catalyst material constitutes approximately fifty percent by weight of the supported samples. The catalysts were prepared by Dr. Olson of these laboratories.
[5] Ries, Van Nordstrand, Johnson, and Bauermeister, J. Am. Chem. Soc. **67**, 1242 (1945).

The Interpretation of Pressure Dependence of Accommodation Coefficients

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IN a recent paper, Amdur[1] interprets the pressure dependence of the accommodation coefficients of several gases on platinum. He attributes the pressure dependence to simple Langmuir adsorption of the same gas as that of which the accommodation coefficient is being measured.

Probably this interpretation is the correct one for the gases H_2, D_2, N_2, CO, and O_2. However an alternative interpretation is possible for the inert gases He, Ne, A, Kr, and Xe.

In the paper giving the experimental results, Amdur, Jones, and Pearlman[2] report using neon of 99.9 percent purity. Thus in 0.1-mm pressure neon, there is impurity of 10^{-4}-mm pressure.

Morrison and Roberts,[3] using accommodation coefficient measurements, found that a clean tungsten surface adsorbs oxygen at pressures as low as 10^{-9} mm and becomes completely covered with molecular oxygen at a pressure of about 10^{-5} mm, always in the presence of neon at 0.1-mm pressure. Moreover, Roberts[4] found that clean tungsten adsorbs a saturated film of hydrogen at 4×10^{-4}-mm pressure in the presence of neon at 0.07-mm pressure.

Since the amount of impurity in each of Amdur's inert gases is directly proportional to the pressure of the inert gas, the adsorption of this impurity could account for the fitting of the Langmuir isotherm.

[1] I. Amdur, J. Chem. Phys. **14**, 339 (1946).
[2] I. Amdur, M. M. Jones, and H. Pearlman, J. Chem. Phys. **12**, 159 (1944).
[3] J. L. Morrison and J. K. Roberts, Proc. Roy. Soc. **A173**, 1 (1939).
[4] J. K. Roberts, Proc. Roy. Soc. **A152**, 445 (1935).