monolayer of adsorbed molecules is always found sufficient to give the high energy solid surface the same wettability properties with respect to all liquids as the low energy solid having the same surface constitution.

Applications of the results of this investigation are too numerous for presentation here. The mechanisms reported here account completely for the non-spreading properties observed in various mineral, animal and vegetable oils as well as in the synthetic liquids reported by many workers including Woog,[28] Bulkley and Snyder,[29] Barker, *et al.*,[30] and Bielak and Mardles.[31] Clock oils, which have been troublesome and expensive for producers and users of watches and clocks as well as of timers, fuses, and other instruments, can now be synthesized and/or controlled adequately. In the production and use of paints, varnishes, plasticizers, cements and printing inks, hitherto unexplainable changes in adhesiveness, spreadability, or permeability can be understood and can be avoided by eliminating compounds capable of converting the solid surfaces involved into ones having undesirably low adhesion or poor wettability. Also, it should now be established once and for all that high lubricity in a liquid need not be associated with ability to spread and wet surfaces completely, for poor boundary lubricants like polymethylsiloxanes spread over all metals and good boundary lubricants like tri-*o*-cresyl phosphate do not spread on such surfaces.

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(28) P. Woog, *Compt. rend.*, **81**, 772 (1925), and "Contribution a 'etude du graissage onctuosite," Delagrave, Paris, France, 1926.

(29) R. Bulkley and J. Snyder, *J. Am. Chem. Soc.*, **55**, 194 (1933).

(30) G. E. Barker, U. S. Patent 2,355,616 (August 15, 1944); also G. E. Barker, G. E. Alter, C. E. McKnight, J. R. McKleven and D. M. Hood, A.S.T.M. Bull. No. 138, 25 (March 1946).

(31) E. B. Bielak and E. W. J. Mardles, *J. Colloid Sci.*, **9**, 233 (1954).

NOTES

SORPTION-HYSTERESIS PROPERTIES OF GASES ON CARBONYL IRON POWDER

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Adsorption–desorption isotherms of argon, nitrogen, carbon monoxide and carbon dioxide have been determined on iron powder produced from iron carbonyl. The work was undertaken primarily to examine the effect of pretreatment of a relatively pure iron surface on the sorption hysteresis properties of the above gases.

Experimental

Apparatus and Procedure.—The apparatus and procedure used to determine the isotherms were comparable to those described by Emmett.[1]

Materials.—The iron powder known as "HP" grade, was obtained from the General Aniline and Film Corp. The method of preparation of the iron was briefly as follows: iron was converted to $Fe(CO)_5$ at a temperature of *ca.* 175° and a pressure of *ca.* 1000 p.s.i. The $Fe(CO)_5$ was decomposed to iron powder at *ca.* 250° and atm. pressure. The iron powder was then reduced in H_2 at *ca.* 500°. The powder consisted of spherical particles having an average diameter on a weight basis of 10 μ. The impurity content of the sample was less than the following: 0.002% N_2, 0.30% O_2, 0.04% C, 0.03% sulfide, 0.0005% As, 0.04% insoluble in H_2SO_4, and 0.03% water soluble substances. An iron content of at least 99.6% by weight was guaranteed.[2]

The gases used were obtained from the Matheson Company. Argon, nitrogen and carbon dioxide had minimum purities of 99.8%. The carbon monoxide had a known purity of 97.1%, the impurities consisting of 2.1% N_2, and 0.8% H_2. Prior to entering the sorption apparatus, the gases were dried by passage over anhydrous magnesium perchlorate.

Results and Discussion

In one particular series of runs (shown in Fig. 1 up to a relative pressure of only 0.5 to expand the plots), iron was first reduced at 400° (standard reduction temperature used throughout) in flowing hydrogen (200 cc./min.) for 24 hours and then outgassed for 24 additional hours. The subsequent sorption of argon (run 1) at −195° up to a relative pressure of 0.88 resulted in a typical Type II isotherm and showed no hysteresis. Further successive treatments consisting of outgassing the iron at room temperature for 12 hours (run 2), reducing in hydrogen for 1 hour and outgassing for 12 hours at 400° (run 3), and outgassing at room tempera-

(1) P. H. Emmett, *Am. Soc. Testing Materials*, **41**, 95 (1941).

(2) A more detailed description of the iron can be obtained from the manufacturer. The same product, known as C.P. iron powder, is marketed by J. T. Baker Chem. Co.

ture for 12 hours (run 4) had a negligible effect on the three subsequent sorption isotherms of argon.

Similar pretreatment of the iron prior to nitrogen sorption runs at −195° also resulted in Type II isotherms (runs 5 and 6), running slightly higher than those of argon but again showing no hysteresis nor pretreatment effect.

The iron was next reduced in hydrogen for 2 hours, outgassed at 400° for 8 hours, and then at room temperature for 14 hours prior to carbon monoxide sorption at −195°. The adsorption isotherm (run 7) ran essentially parallel to that of argon but was 0.070 cc./g. higher. Even though this difference may be due completely to chemisorption of carbon monoxide on the iron powder,[3] it amounts to only 27% of a complete monolayer, agreeing qualitatively with the findings of Podgurski and Emmett,[4] who report that on a pure iron surface the chemisorption of carbon monoxide amounts to only a fraction of a monolayer. The desorption isotherm (run 7) also essentially paralleled but was 0.29 cc./g. higher than that of argon. The iron was next outgassed for 12 hours at −78°. In the subsequent sorption of carbon monoxide (run 8), the isotherm again paralleled that of argon but the adsorption and desorption volumes were still 0.035 and 0.10 cc./g. higher. This is thought to be indicative of the removal of a fraction of chemisorbed carbon monoxide when the iron was outgassed under the above conditions.

The sample was next reduced in hydrogen for 5 hours, outgassed at 400° for 5 additional hours, and then outgassed at room temperature for 10 hours. Free space determinations using helium agreed well with the original value, indicating the absence of carbides of iron and free carbon as possibly formed at elevated temperatures from the previously chemisorbed carbon monoxide. The subsequent sorption isotherm (−78°) of carbon dioxide (run 9) fell significantly below the argon curve but showed only slight hysteresis. After the sample was outgassed overnight at room temperature, run 10 not only found a slightly higher adsorption volume but also a considerably larger hysteresis than the preceding run. Next, the sample was reduced in hydrogen for 12 hours and cooled down to −78° with the hydrogen flow continuing. The subsequent carbon dioxide adsorption (run 11) is seen to parallel closely run 9 at low pressures but to continue to increase in divergence (greater adsorption) with increasing pressure. The desorption curve failed to close the isotherm, falling close to that of the preceding run.

The sample was next outgassed for 8 hours at room temperature and then exposed to a stream of oxygen for 16 hours. The subsequent sorption run (12) showed no marked effect of oxygen pretreatment over the three previous carbon dioxide isotherms, with the desorption curve agreeing particularly well with those of the two previous runs. It should be noted that the B.E.T. area for the four carbon dioxide runs was 0.76 ± 0.02 m.²/g. (using a molecular area of 17.0 Å.²) compared to 0.89 m.²/g. for argon adsorption (using a molecular area of 14.2 Å.²). Therefore, the combined physical adsorption and possible chemisorption volumes of carbon dioxide still produced a B.E.T. area less than the physical adsorption volume of argon.

(3) P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **59**, 310 (1937).

(4) H. H. Podgurski and P. H. Emmett, THIS JOURNAL, **57**, 159 (1953).

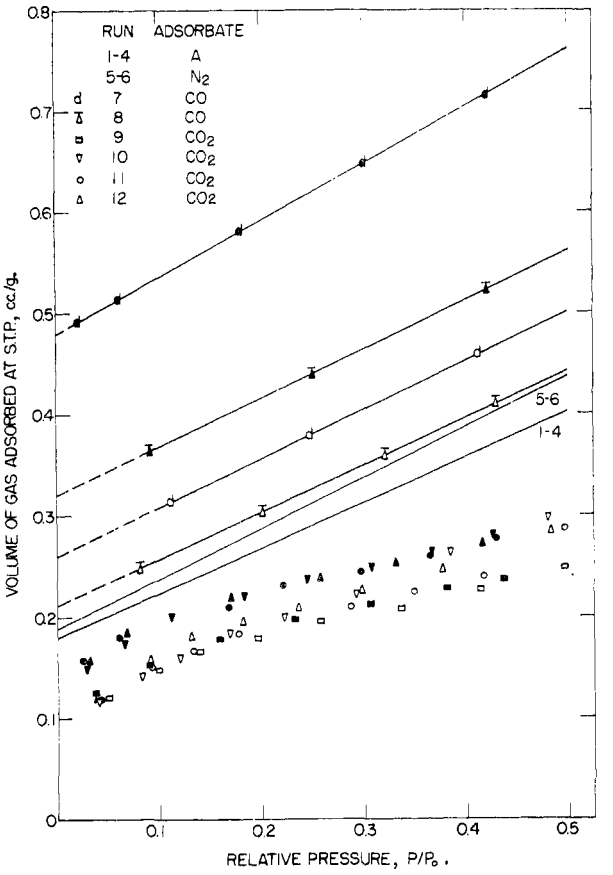

Fig. 1.—Sorption isotherms of gases on iron powder (closed symbols are desorption).

ON THE SUTHERLAND MODEL FOR THE VISCOSITY OF GASES

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Assuming the gas molecules to be hard elastic spheres, interacting with an attractive field, Sutherland obtained for the coefficient of viscosity of a gas, the relation

$$\eta = \frac{CT^{1/2}}{1 + S/T} \qquad (1)$$

where C and S are constants. η is the coefficient of viscosity of the gas, T the absolute temperature and S is called the Sutherland constant for the gas under consideration.

Although this equation was derived in non-rigorous way by Sutherland, it was found to hold successfully for many gases over a considerable range of temperatures. Some observers,[1] however, reported that equation 1 fits the experimental results

(1) Binkele, *Ann. Physik*, **9**, 839 (1931); Rilaud and Vasilesco, *Compt. rend.*, **208**, 884 (1939).