

those of Stone and Tiley, is that two different 'chemisorbed' states are involved. In one case the adsorbed molecule may be completely incorporated in the surface with loss of its individual characteristics, so that the perturbation of the original averaged surface field may not be sufficient to have any appreciable influence at the distances of purely physical attraction. It is this type of chemisorption which may be expected in the case of carbon monoxide to occur on clean metallic areas at fairly low coverages, and is represented by the difference between curves I and II. In the second case, the adsorbed molecule may remain distinct from the surface, to which it may be attached by a weak semi-polar bond, and so retain its individual character. In this case the adsorbed molecule behaves as a fresh adsorption centre, the potential at which will certainly differ from the original. This type of carbon monoxide adsorption will probably take place at high coverages on metallic surfaces, and at all coverages on oxides, carbides³ and nitrides; it approximates to the difference between curves II and III.

A detailed experimental and theoretical investigation is in progress.

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¹ Stone and Tiley, *Nature*, **167**, 654 (1951).

² Emmett and Brunauer, *J. Amer. Chem. Soc.*, **59**, 1553 (1937).

³ Podgurski, Kummer, De Witt and Emmett, *J. Amer. Chem. Soc.*, **72**, 5382 (1950).

THE results of Joy and Dorling are not altogether surprising, and their suggested explanation is generally in agreement with our views. There are, however, two points of interest.

First, it does not seem in accord with the reported heats of adsorption to refer to carbon monoxide on an iron catalyst as being "strongly chemisorbed" in contrast to the "weak" chemisorption on cuprous oxide. The initial heat of carbon monoxide on iron is approximately 25 k.cal./mole¹, whereas on cuprous oxide it is 21 k.cal./mole². Moreover, after carbon monoxide adsorption at 20° C., prior to the krypton adsorption, we evacuated at a pressure of less than 10⁻⁴ mm. of mercury for 1 hour at room temperature, thus removing all gas adsorbed with a heat less than 18 k.cal., whereas Joy and Dorling pump off at -78° C., removing only the gas with a heat less than 12 k.cal. (These are only approximate heat values.) The question of strength of the chemisorbed bond is therefore not immediately significant.

The difference between these two cases surely lies in the nature of the chemisorbed state and its relationship to the nature of the substrate. In so far as carbon monoxide is held on a metallic surface by a form of bonding which is essentially metallic, then the chemisorbed film may be considered as extending the surface of the metal, and no profound modification of the van der Waals adsorption potential occurs. With carbon monoxide on cuprous oxide, the adsorbate molecule is held by a covalent bond to a (largely) ionic surface, with a consequent increase in adsorption potential. It should be noted, however, that on certain metallic oxides carbon monoxide is adsorbed

irreversibly, and Garner³ has suggested that it is then incorporated into the surface as a carbonate ion (CO₃²⁻). In such cases, it seems probable that the physical adsorption characteristics are not so markedly changed, and experimental investigation is proceeding on these lines.

Since our last communication, Mr. Reeves, in this laboratory, has repeated the work, using nitrogen instead of krypton, and a similar modification of the isotherm has been observed. It is felt that in our initial discussion we tended to over-emphasize the significance of E_L , the heat of liquefaction. In order to cause a drop in the apparent value of V_m , it is not theoretically necessary that $E_1' < E_L$ but only that E_1' (heat of adsorption on the chemisorbed film) should differ considerably from E_L (heat of adsorption on the bare surface). The 'dual surface' adsorption theory of Walker and Zettlemoyer⁴, in which they discuss hypothetical composite isotherms obtained from two surfaces with differing values of the Brunauer-Emmett-Teller parameter c , is of considerable interest in this connexion.

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¹ Beobe, R. A., and Stevens, N. P., *J. Amer. Chem. Soc.*, **62**, 2134 (1940).

² Stone, F. S., and Tiley, P. F., *Faraday Soc. Discussion on Heterogeneous Catalysis*, 252 (1950).

³ Garner, W. E., *J. Chem. Soc.*, 1239 (1947).

⁴ Walker, W. C., and Zettlemoyer, A. C., *J. Phys. Chem.*, **52**, 47 (1948).

Application of an Incomplete Block Design to the Assessment of Quality in Cacao

DURING the course of recent work at the West African Cacao Research Institute, it became necessary to evaluate the products of small-scale fermentations of different types of cacao. Hitherto, samples have been judged for degree of fermentation on the appearance in longitudinal section and condition of testa. These criteria have not been sufficiently discriminating, especially in laboratory fermentation work¹, where in some instances different cacao types have given similar percentages to fully fermented beans.

An attempt has therefore been made to form a local 'taste panel' for assessment of the chocolate flavour of liquors prepared by a standard procedure recommended by the British Food Manufacturing Industries Research Association (Cocoa Panel)². This consists essentially of pre-heating fermented beans at 95-100° C. for one hour before roasting them in a glass-jacketed tube placed in a glycerine bath at 148° C. for 55-60 min., depending on the state of division of the beans. The only difference from the method as recommended is that no sugar has been added to the liquors.

Preliminary work showed that with randomized blocks and 'taster Latin square' designs, panel members had to taste several samples per session, with consequent deterioration in taste perception. A method was sought which would be statistically sound and which required the tasting of only two samples on any one occasion. A given set of samples was arranged in pairs, each sample being matched against every other sample by each taster. Scoring was by pair differences, each taster being asked to distribute ten points between the two samples under test; for example, if the samples were of equal value