HEATS OF CHEMISORPTION OF CO_2, CO AND H_2 ON ZINC OXIDES WITH AND WITHOUT VALENCY INDUCTION

By P. M. G. Hart and F. Sebba

Department of Chemistry, University of Cape Town

Adsorption isotherms of CO_2, CO and H_2 on pure zinc oxide, zinc oxide containing 0·5 mole % Ga_2O_3 and zinc oxide containing 0·5 mole % Li_2O were measured in the temperature range 250°C to 320°C and below a pressure of 1 mm Hg. Isosteric heats of adsorption were calculated and plotted against surface coverage of the adsorbents. The quasi-free electron concentration in the adsorbents was found to influence the heats of adsorption considerably, especially at low coverages.

It has been shown that addition of foreign monovalent or trivalent metal ions to the zinc oxide lattice will respectively decrease or increase the semi-conductivity of the zinc oxide.[1, 2] The influence of these modifications of the concentration of charges may be regarded as a raising or a lowering of the Fermi level.[3] Thus the activity of the zinc oxide as an electron donor should be affected.

If heterogeneous processes at the surface of a solid involve transfer or sharing of electrons than it may be expected that changes in the electron concentration in the solid will effect the heterogeneous processes. This has been tested experimentally and found to be true for a number of reactions catalyzed by zinc oxide.[4-6] However, little work has been done on the changes in adsorption brought about by altering the semi-conductivity of the adsorbents, apart from the measurements of hydrogen adsorption on zinc oxides by Cimino, Cipollini and Molinari.[7]

Wiggill [6] studied the reaction

$$CO_2 + H_2 \xrightarrow{\text{ZnO}} CO + H_2O$$
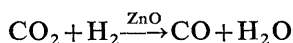
between 250°C and 320°C and found that its activation energy was decreased slightly by addition of a small percentage of gallium oxide to the zinc oxide, and increased slightly by addition of lithium oxide. Pretreatment of the catalyst with oxygen was found to have a poisoning effect.

It was decided to carry this work further by measuring the adsorption of CO_2, CO and H_2 on zinc oxide with and without valency induction caused by addition of gallium oxide and lithium oxide. No attempt was made to measure heats of adsorption calorimetrically because of the high working temperatures, but adsorption isotherms were measured where possible and isosteric heats of adsorption were calculated from the data obtained.

EXPERIMENTAL

Pure zinc oxide was obtained by decomposing the oxalate by treating for 10 h at 450°C in a stream of air.[6-10] $ZnO + 0·5$ mole % Ga_2O_3 was prepared by making pure zinc oxide into a paste with gallium nitrate solution, drying at 110°C, and heating for 10 h at 450°C in a stream of air to decompose the nitrate to the oxide.[4, 6, 7, 11] $ZnO + 0·5$ mole % Li_2O was prepared by making pure zinc oxide into a paste with lithium oxalate solution. Drying and heating were carried out as before. No carbonization of the lithium oxalate [12] could be detected when it was heated in this way with a large excess of zinc oxide.

The gases used were prepared and purified in gas trains which were part of the high-vacuum apparatus used for the adsorption experiments. CO_2 prepared by heating sodium bicarbonate, was dried over silica gel and anhydrone, $Mg(ClO_4)_2$. Carbon monoxide generated by dehydrating formic acid with conc. H_2SO_4 was purified by passing it over

soda lime and anhydrone.   Hydrogen, prepared electrolytically from sodium hydroxide, was purified over silica gel, palladized asbestos at 300°C and anhydrone.   The sulphur dioxide used for surface-area determinations was taken from a siphon.   It was condensed, permanent gases were boiled off, and then it was dried over silica gel and anhydrone.
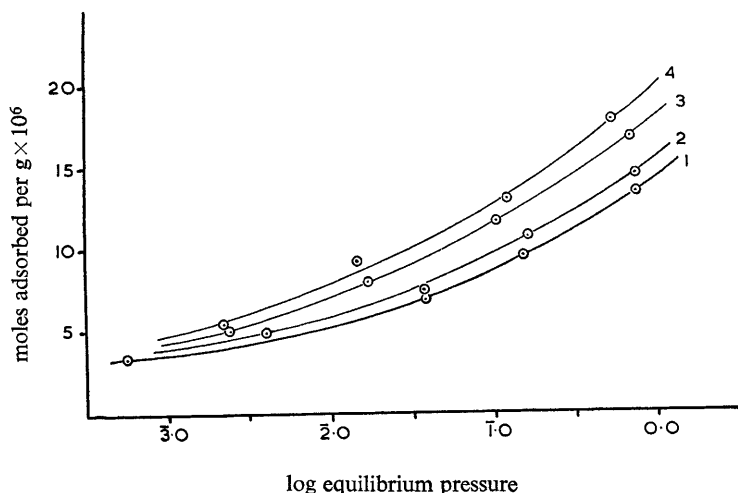

FIG. 1.—Isotherms of CO_2 on zinc oxide.
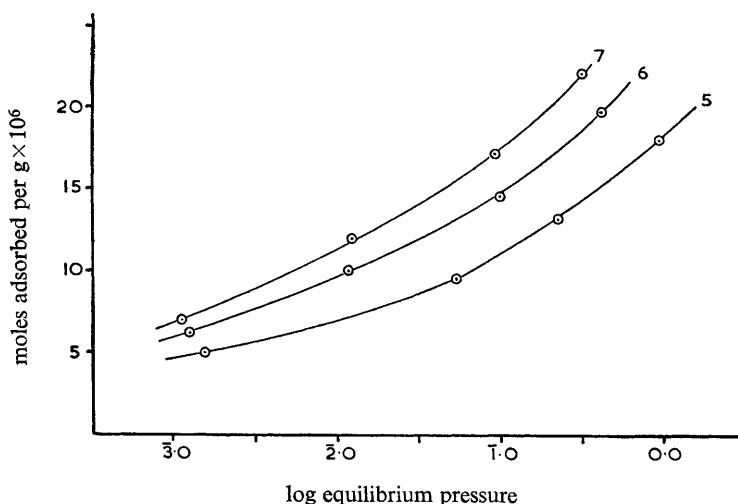isotherm 1, 310°C; 2, 292°C; 3, 268°C; 4, 251°C.

FIG. 2.—Isotherms of CO_2 on zinc oxide doped with gallium oxide.
Isotherm 5, 312°C; 6, 275°C; 7, 252°C.

The adsorption measurements were made in a high-vacuum apparatus very similar to that used by Frankenburg.[13]   Equilibrium pressures were read on McLeod gauges. A simple differential mercury manometer was used to measure pressures of gas before adsorption and also the vapour pressure of SO_2 in the surface-area measurements.   The adsorption furnace was electrically heated and the temperature was controlled to ±1°C over a period of a few days.   The adsorption bulb held 22 g of adsorbent in the form of small tablets.

Isotherms were measured by the method of cumulative additions.   For each gas on each adsorbent a family of isotherms was measured at various temperatures in the range

250°C to 320°C. The adsorbents were activated between isotherm runs by heating *in vacuo* at 450°C for $4\frac{1}{2}$ h.

RESULTS

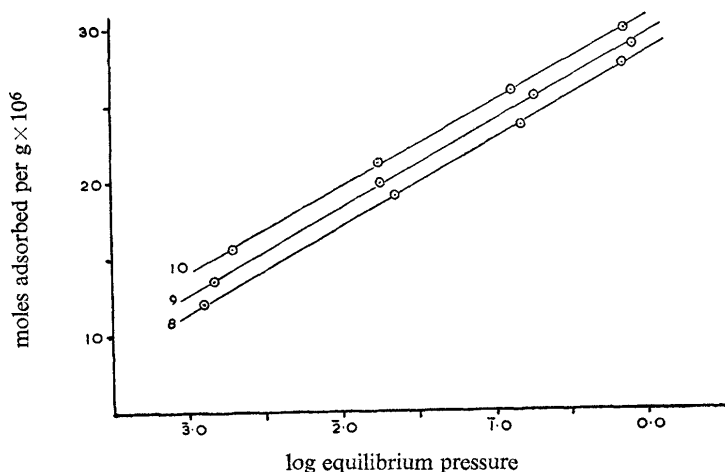The adsorption isotherms of CO_2 are shown in fig. 1, 2 and 3.   For convenience

FIG. 3.—Isotherms of CO_2 on zinc oxide doped with lithium oxide. isotherm 8, 312°C; 9, 291°C; 10, 272°C.
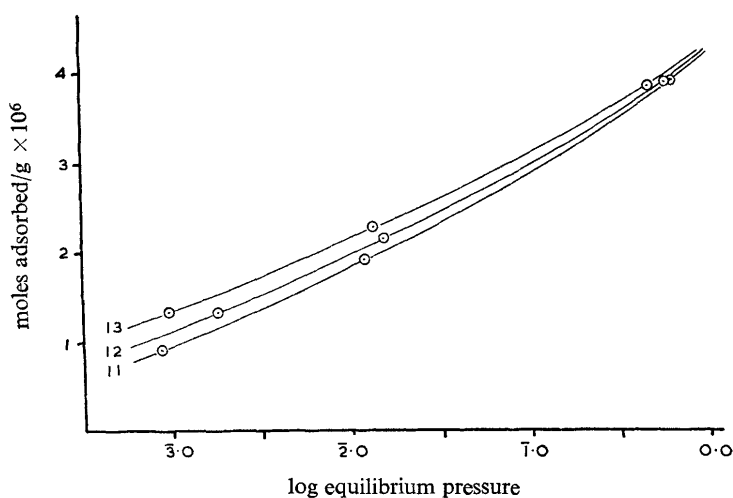

FIG. 4.—Isotherms of CO on zinc oxide. Isotherm 11, 318°C; 12, 299°C; 13, 264°C.

all the isotherms are plotted with pressure on a log_{10} scale.   Normal chemisorption occurred in all three cases.   Adsorption of CO amounted to only about one-fifth of that obtained for CO_2, and with the adsorbent containing Li_2O reduction by the CO occurred too rapidly for the adsorption isotherms to be measured.   Isotherms on the other two adsorbents are shown in fig. 4 and 5.   For hydrogen on all three absorbents there was too much reduction for reliable isotherms to be measured.

Equilibrium pressures were determined by drawing graphs of pressure against time after admission of gas sample, and extrapolating to constant pressure when sufficient of the curve had been measured to do so accurately.   The time required varied from a few hours to more than 100 h depending mainly on the amount of gas already adsorbed.   The longer times were required for the greater amounts adsorbed.
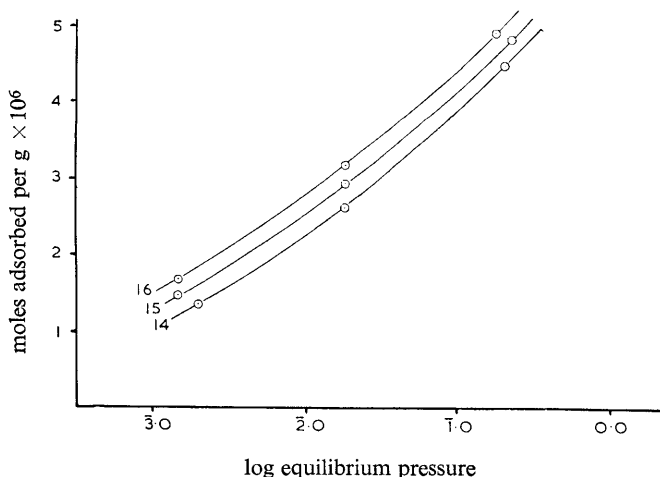

FIG. 5.—Isotherms of CO on zinc oxide doped with gallium oxide.
Isotherm 14, 320°C; 15, 292°C; 16, 263°C.

Indications of reduction of the adsorbent were (i) a disinclination of the pressure against time curve to flatten out to a constant pressure value, (ii) a darkening of the adsorbent and (iii) the formation of a grey-black deposit of zinc in the tube leading to the adsorption bulb at the point where it emerged from the adsorption furnace.   For CO these indications were only obtained at the higher pressures (0·1 to 1·0 mm Hg) except with the adsorbent containing Li_2O.   With hydrogen, reduction took place at all pressures and was especially rapid for the adsorbent containing Li_2O.

The physical adsorption of SO_2 at $-20·5°C$ on the three adsorbents was measured and the surface areas of the adsorbents determined by the B.E.T. method. In spite of the possibility of some chemisorption and the uncertainty as to the effective cross-section area of the molecule, SO_2 was the most convenient gas to use considering the equipment which was available.   The cross-section area of the molecule was calculated as $16·2 Å^2$ using Emmett and Brunauer's formula.[14]   The surface areas as calculated were:

ZnO	4·6 m²/g,
ZnO+0·5 mole % Ga_2O_3	9·1 m²/g,
ZnO+0·5 mole % Li_2O	5·5 m²/g.

These values may not be very accurate considered as absolute surface areas, but they are of the right order.[15-17]   They are, however, useful as relative surface areas, which is important in this comparative study of the three adsorbents.

Isosteric heats of adsorption were calculated for CO_2 and CO, and they are shown in fig. 6 and 7 plotted against surface coverage of the adsorbents.

DISCUSSION

Based on the assumption [18] that the molecules of CO_2, CO and SO_2 all have effective cross-section areas of approximately $16 Å^2$, complete coverage of the

surface of any adsorbent would involve about 10×10^{-6} mole/m^2. It follows that the maximum coverage measured for CO_2 was about 50 % and for CO it was about 10 %.
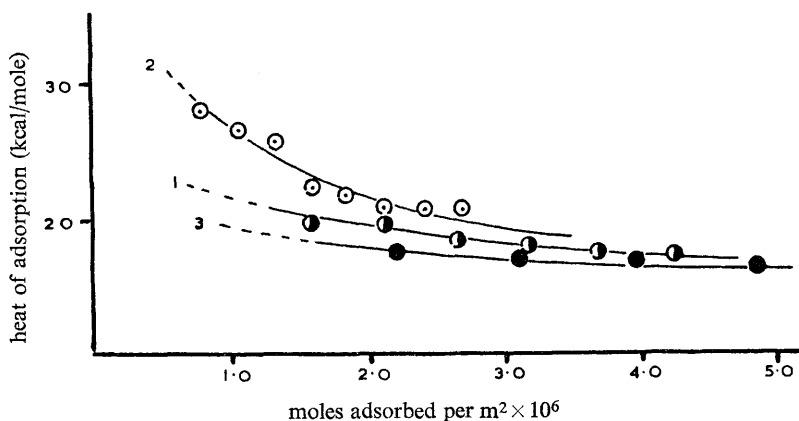

FIG. 6.—Heats of adsorption of CO_2 against surface coverage.
(1) on zinc oxide, (2) on zinc oxide doped with gallium oxide,
(3) on zinc oxide doped with lithium oxide.

The high figure for CO_2 on ZnO containing lithia corresponds to approximately 10^{20} molecules adsorbed per cm^3 of oxide. If CO_2 is behaving as an electron acceptor, this means that the minimum donor concentration in the ZnO is 10^{20} per cm^3. This is an extremely high figure, and may mean that the oxygen in the lattice is itself acting as a donor, i.e. that something akin to zinc carbonate is actually being formed.
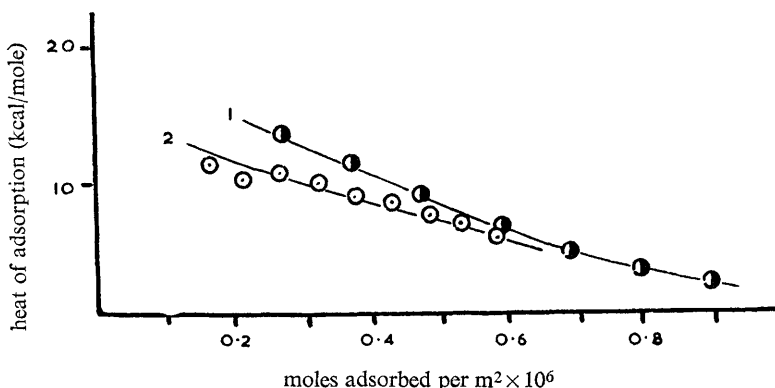

FIG. 7.—Heats of adsorption of CO against surface coverage.
(1) on zinc oxide, (2) on zinc oxide doped with gallium oxide.

Two facts emerge when the curves for the heat of adsorption (fig. 6 and 7) are studied. First, both for CO_2 and CO the curves for the different adsorbents diverge considerably at low coverages. At high coverages there is scarcely any difference between the heats on the three adsorbents. So it would appear that the Fermi level in the adsorbent was only of primary importance in determining the heat of adsorption at low coverages, and that as the coverage increased other factors such as repulsive interactions between molecules became more important. Secondly,

the curves show that the CO_2 acts as an electron acceptor in the adsorption, and the CO as an electron donor, because for the former, raising of the Fermi level in the adsorbent increased the heat of adsorption and for the latter it decreased the heat of adsorption.

The fact that the adsorption of CO_2 was about five times as great as that of CO correlates with the fact that, in the former adsorption, the zinc oxide acted as an electron donor and the CO_2 as an acceptor and in the latter case zinc oxide had to act as an electron acceptor, an abnormal process for an n-type semi-conductor.

For the adsorbent containing Li_2O, acceptance of electrons was facilitated to the extent that reduction became very marked in the presence of carbon monoxide. This confirms Garner's suggestion that the irreversible adsorption of CO on zinc oxide takes place on acceptor sites.   For hydrogen the presence of the Li_2O was observed to accelerate the reduction considerably.

These results agree with Wiggill's activation-energy measurements for the reduction of CO_2 with hydrogen over zinc oxide.   He found that the addition of gallium oxide decreased the energy of activation and lithium oxide increased it. If the mechanism of the reaction is dependent on the adsorption of CO_2, then naturally the higher heat of adsorption on the gallium-oxide-impurity catalyst will cause a lowering of the activation energy of the reaction.   If carbon dioxide is adsorbed then carbon monoxide must be desorbed, and the lower heat of adsorption of the CO on the gallium-oxide-impurity catalyst will facilitate this.   For any particular reaction pressure, only about one fifth of the sites which could be covered with CO_2 could be covered with CO, so that on reduction of the dioxide it is most probable that a large proportion of the monoxide formed must desorb.

An apparently anomalous feature of the experimental results is that at a given pressure of CO_2, the surface coverages for the three adsorbents vary in the opposite way to the heats of adsorption.   For example, at $0\cdot1$ mm Hg, the quantities adsorbed on zinc oxide doped with lithium oxide, pure zinc oxide and zinc oxide doped with gallium oxide are $4\cdot5 \times 10^{-6}$ mole/m^2, $2\cdot7 \times 10^{-6}$ mole/m^2 and $1\cdot9 \times 10^{-6}$ mole/m^2 respectively.   A possible explanation may be that the proportion of active sites are different for each type of adsorbent.   Heats of adsorption would appear to be related to the Fermi level, but the number of adsorbed particles, which would be determined by the number of sites, may be determined by other considerations.

[1] Hauffe and Vierk, *Z. physik. Chem.*, 1950, **196**, 160.
[2] Wagner, *J. Chem. Physics*, 1950, **18**, 65.
[3] Boudart, *J. Amer. Chem. Soc.*, 1952, **74**, 1531.
[4] Molinari and Parravano, *J. Amer. Chem. Soc.*, 1953, **75**, 5233.
[5] Schwab and Block, *J. chim. physique*, 1954, **51**, 644.
[6] Wiggill, unpublished work (University of Cape Town).
[7] Cimino, Cipollini and Molinari, *Naturwiss.*, 1956, **43**, 58.
[8] Taylor and Sickman, *J. Amer. Chem. Soc.*, 1932, **54**, 612.
[9] Kubokawa and Toyama, *J. Physic. Chem.*, 1956, **60**, 833.
[10] Gmelin, *Handbuch der Anorg. Chem.*, 8 Auflage, no. 32, p. 775.
[11] Gmelin, 8 Auflage, no. 36, pp. 71-72.
[12] Gmelin, 8 Auflage, no. 20, p. 232.
[13] Frankenburg, *J. Amer. Chem. Soc.*, 1944, **66**, 1827.
[14] Emmett and Brunauer, *J. Amer. Chem. Soc.*, 1937, **59**, 1553.
[15] Gans, Brooks, Boyd, *Ind. Eng. Chem. (Anal.)*, 1942, **14**, 396.
[16] Schreiner and Kemball, *Trans. Faraday Soc.*, 1953, **49**, 190.
[17] Shekhter and Zhabrova, *Izvest. Akad. Nauk, Otdel. Khim. Nauk*, 1951, 500.
[18] Livingston, *J. Colloid. Sci.*, 1949, **4**, 447.
[19] Garner, *J. Chem. Soc.*, 1947, 1239.