Adsorption of Hydrogen on Zinc Oxide

Energy of Interaction and Related Mechanisms

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The heat of adsorption of hydrogen on zinc oxide (Kadox 25) has been measured at room temperature using a Calvet microcalorimeter.

Two main forms of adsorbed hydrogen have been found, coinciding with the literature types I and II. Both always occur simultaneously (although with different kinetics) and a clear-cut separation between the two forms is not achieved on the basis of their reversibility. Differential heats of adsorption decrease with coverage from 60 to 14 kJ mol^{-1}. Apart from the lowest coverages, where a real heterogeneity in site energies is present, the decrease is basically due to the simultaneous adsorption of type I (*ca.* 40 kJ mol^{-1}) and type II (*ca.* 14 kJ mol^{-1}), the latter prevailing at increasing coverage. The surprising feature that the 'irreversible' type II has a lower adsorption heat than the reversible type I is interpreted as evidence for diffusion of the adsorbate into the bulk, in agreement with kinetic observations.

The interaction of hydrogen with ZnO has been the subject of many investigations because of the role adsorbed hydrogen plays in both methanol synthesis and the hydrogenation of unsaturated hydrocarbons. Various adsorption processes are known to occur, characterized by different mechanisms, kinetics and stability of adsorbed species, as shown in a recent review.[1] At room temperature two main processes have been identified, yielding two species called type I and type II by Dent and Kokes,[2] but more than two peaks have been found by thermal desorption analysis.[3-6] Type I has been defined as rapid, dissociative, reversible and i.r. active; type II as slow and irreversible.[2, 7] Type I participates directly in catalytic reactions such as methanol synthesis, hydrogenation and H$_2$–D$_2$ exchange, whereas it is not clear whether type II plays any role at all, as its effect on the rate of hydrogenation is still the subject of debate.[2, 8]

The two forms of adsorption have been assigned to the interaction with the two different crystal faces known to occur predominantly on ZnO Kadox,[9] namely the polar ones (000$\bar{1}$) for type I and the apolar ones (0$\bar{1}$01) for type II.

The model adopted for type I adsorption on the basis of i.r. investigations identifies a Zn—O pair as active site on the (000$\bar{1}$)-type faces.[2] Boccuzzi *et al.*[10] hypothesize a site originating from a triplet of Zn^{2+} exposed by an oxygen vacancy and at least one reactive O^{2-} ion. Hydrogen undergoes heterolytic dissociation thus yielding surface hydroxyls and hydrides. Taking into account that only 10% of the actual surface is involved in this type of adsorption, lateral interaction between adsorbed species should be ruled out and a substantial homogeneity in this adsorption process is expected, unless adsorption occurs in very well defined patches of the surface. T.p.d. peaks corresponding to type I are indeed unaffected by coverage;[5] however, accurate kinetic analysis by Aharoni and Tompkins[11, 12] and the continuous shift of the i.r. bands with coverage found by Boccuzzi *et al.*[10] indicate the existence of slight heterogeneity or mutual interaction. Moreover, two different mechanisms giving rise to these species,

one involving charge transfer and one not, have recently been proposed by Murphy *et al.*[13] which can easily account for slight differences in the final surface arrangement.

Type II hydrogen is less well defined. It is desorbed below 373 K but the t.p.d. peak temperature varies irregularly with coverage.[5] It has long been considered an i.r. inactive species[2, 7] although recently a broad i.r. band in the low-frequency region has been assigned to hydrogen bridge-bonded to couples of Zn^{2+} or O^{2-} on the apolar faces.[10]

In spite of the many investigations of H_2 adsorption and catalytic mechanism on ZnO, energy data related to these processes are almost non-existent, the only calorimetric data available being those reported by Garner and Veal[14] many years ago.

We have therefore measured the heat of interaction of H_2 with ZnO as a function of coverage in order to characterize the different processes, assign energy values to the various species, detect possible surface heterogeneity and, finally, find out whether different binding energy can account for the difference in reversibility and catalytic activity between hydrogen adsorbed as type I and as type II.

EXPERIMENTAL

The heat of adsorption and related values were measured in a Tian-Calvet microcalorimeter connected to a volumetric apparatus.[15, 16]

ZnO samples were slowly heated under vacuum up to 673 K and 50 kPa O_2 were admitted and removed several times; the sample was then cooled under O_2 and transferred into the calorimeter. Complete evacuation was monitored through the endothermic signal arising from desorption of O_2.

Adsorption was obtained by successive admission of increasing doses of the gas, up to *ca.* 3 kPa. Each dose was admitted only when equilibrium conditions were attained (constant pressure, no deviation from the calorimetric base-line). Stepwise desorption was obtained by expansion of the gas phase into a defined volume. Eventually the sample was pumped off by direct connection to high vacuum, in order to remove all the adsorbate that was reversible at the operating temperature. These procedures were performed several times on the same sample and will be hereafter indicated as runs I, II and III. In one case the sample was contacted with an excess of H_2 (50 kPa) in order to saturate all sites and to define the maximum adsorption capacity.

The calorimeter was kept at a constant temperature of 298 K.

Zinc oxide (Kadox 25, New Jersey Zinc Co.) with 10 m^2 g^{-1} B.E.T. surface area was used.

RESULTS

The adopted pretreatment procedure leads to a surface composition which is as near as possible stoichiometric and fairly reproducible as far as activity towards simple gases such as CO is concerned.[17] Loss of surface area, which is known to occur easily on ZnO,[3, 11] was observed only in particular cases when the same sample was reactivated many times. A test of the adsorption capacity of CO ensured that in all cases the surface area was the same. However, as has been described elsewhere,[17] slight differences in activity towards H_2 can be found from one sample to the other, due to the extreme sensitivity of the system.[3]

Results reported in the present paper have all been obtained on samples exhibiting similar activity towards H_2, the activity being close to the average value obtained using a larger set of specimens.

Three successive adsorption–desorption runs are reported in fig. 1 as Q^{int} against p. In runs II and III adsorption values are reported from the last desorption point, obtained by complete evacuation of the adsorbate. As a corresponding volumetric point is lacking, similar n_a against p curves cannot be drawn. However, they all follow the same trend for the first run (fig. 2) as the calorimetric ones.
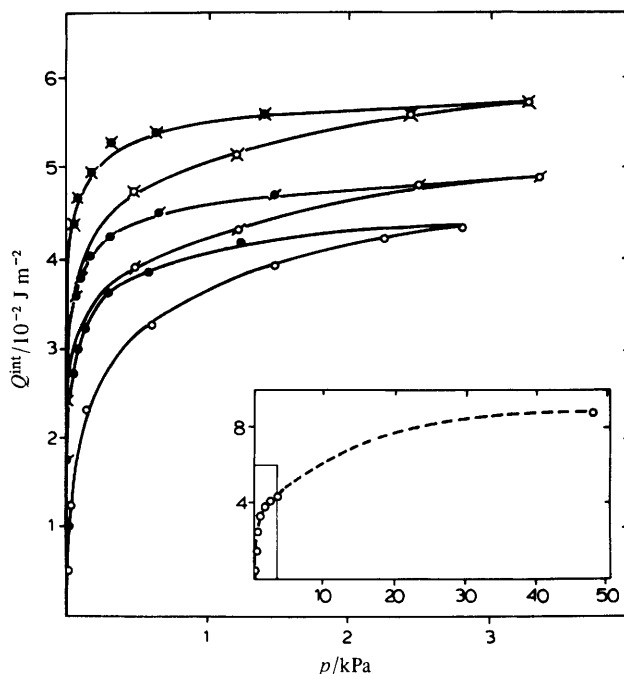
FIG. 1.—Heat related to hydrogen interaction in three successive adsorption–desorption runs (Q^{int} against p). Insert: saturation with an excess of H_2. Open symbols: adsorption; filled symbols: desorption.
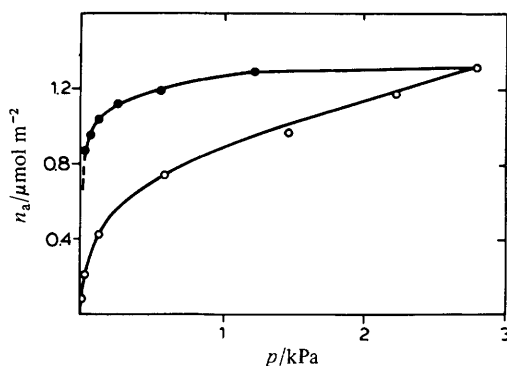

FIG. 2.—Adsorption and desorption in the first run (n_a against p). Open symbols: adsorption; filled symbols: desorption.

The main features of these curves are: (i) Adsorption is pressure dependent in the whole range examined. Even a very small adsorbed amount, such as the first point in fig. 1 and 2 (0.09 μmol m^{-2}), yields a pressure of 20 Pa over the sample. (ii) The slopes of the adsorption–desorption curves show that the adsorption process is far from finished at the end of each adsorption run. Higher pressure ranges have not been examined in detail; however, 'saturation' of a sample by exposure to a pressure of *ca.* 50 Pa for a period of four days involved a heat of adsorption (from 2.8 kPa to total saturation) of 4.35×10^{-2} J m^{-2}, which corresponds to *ca.* 50% of the total heat evolved (insert of fig. 1). (iii) Adsorption and desorption follow different paths in the whole range examined, not only in the first run but in all the successive runs as well.

This behaviour appears even in successive adsorption–desorption runs performed after 'saturation' of the ZnO sample with H_2. (iv) In each adsorption run some reactions occur yielding adsorbed species which are not removable by evacuation at room temperature. This fraction of adsorbate is measured on the ordinate axis in fig. 1 by the last desorption point, which represents the amount of heat evolved upon adsorption and not recovered upon desorption. Although a slight decrease in the amount of this fraction in successive runs can be detected, the formation of 'irreversible adsorbate' is far from being exhausted in the third run. This fraction seems to be related to the time of contact of H_2. Points in fig. 1 and 2 have therefore to be considered pseudo-equilibrium ones, although taken when the system appeared to be in equilibrium as far as was detectable by our instruments.

Integral heats of adsorption on various samples (run I) are reported in fig. 3 as a function of adsorption. The integral heat of desorption obtained by successive expansions in all runs (I, II, III) and on various samples are reported in fig. 4, as a function of desorption.
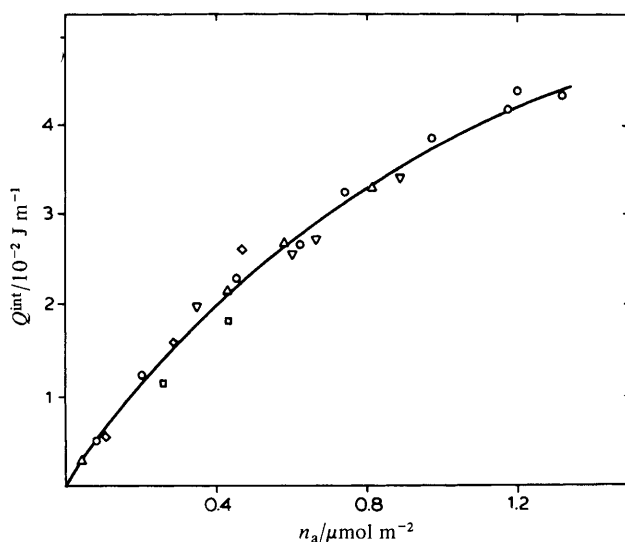

FIG. 3.—Integral heat of adsorption against amount adsorbed (run I) on various samples. Different symbols indicate different samples.

Fig. 3 shows a smooth curve, whose slope decreases with coverage, indicating a heterogeneity in site energy distribution. On the other hand, all the points in fig. 4, although scattered, lie on a straight line passing through the origin. The differential heat of desorption calculated from the slope (37 kJ mol^{-1}) is thus fairly constant over the coverage range examined by stepwise desorption. The variation of differential heat of adsorption with coverage has been obtained by differentiation of the curve in fig. 3 and it is reported in fig. 5 as a solid line. The same data for run II are also reported; run III coincides with run II. The heat of desorption is reported in fig. 5 as a broken line at the appropriate coverage value. Three main features emerge from the figure: (i) Differential heats of adsorption strongly decrease with the coverage from an initial value of 60 kJ mol^{-1} down to *ca.* 14 kJ mol^{-1}. (ii) The heat of adsorption is lower than the heat of desorption, in the stepwise desorption range. (iii) The initial heat of adsorption is higher in run II (69 kJ mol^{-1}) than in run I (60 kJ mol^{-1}). Such an increase of *ca.* 15% has been observed on various samples.
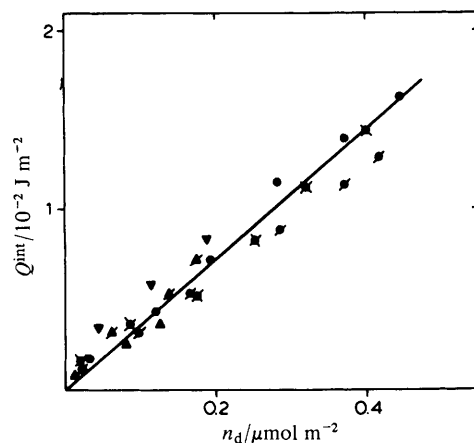
FIG. 4.—Integral heat of desorption against amount desorbed (runs I, II and III) on various samples. Different symbols indicate different samples. Dashed symbols: run II; crossed symbols: run III.
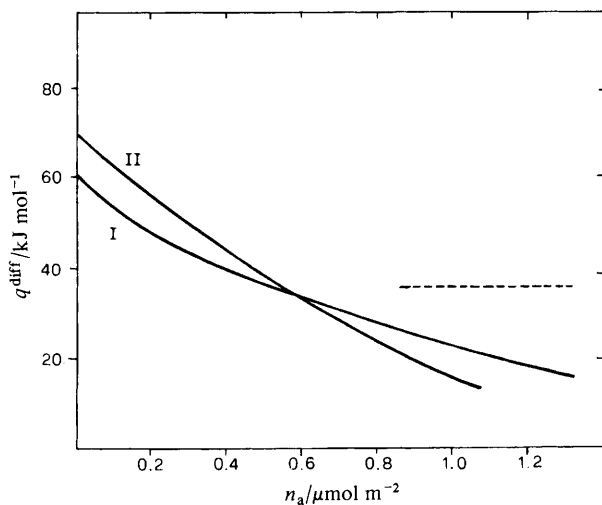

FIG. 5.—Differential heat of adsorption against amounts adsorbed (runs I and II). Broken line: differential heat of desorption.

The heat of emission peaks corresponding to the adsorption of the first dose (runs I and II) are reported in fig. 6(a). They both exhibit the characteristic thermokinetic behaviour of activated chemisorption,[16] $i.e.$ the curve is less sharp than the standard one for instantaneous heat evolution and the calorimetric zero is attained after a much longer time than the zero due to instrumental inertia. Note that in our case this time was always $ca.$ 6-7 h for the first peak of the first run. Subsequent adsorption either in the same or in successive runs was accomplished within $2\frac{1}{2}$ h. Something peculiar is thus occurring with the first contact of H_2 with ZnO samples.

Although after the attainment of the calorimetric zero no further appreciable development of heat was observed, in agreement with previous results by Dent and Kokes,[2, 7] we noticed that, after several days of contact, the H_2 pressure over the ZnO samples decreased slightly. Adsorption corresponding to this decrease is such that the

corresponding heat, slowly evolved over a period of days, could not be detected in our apparatus.

Desorption obtained by evacuation of the sample is monitored on the calorimeter as a broad endothermic peak [fig. 6(b)]. Several such peaks obtained by evacuation at different pseudo-equilibrium pressures are reported. The general features of these curves are similar, except for the time taken for the attainment of the calorimetric zero and for a marked variation in the position of the maximum, which is displaced on the time axis as the coverage decreases. Fig. 6 also compares desorption heat peaks from both stepwise expansions [fig. 6(c)] and direct evacuation [fig. 6(d)] with the similar peaks obtained by desorption of CO from ZnO (broken line). The activation energy for desorption of hydrogen is clearly higher than the activation energy for desorption of carbon monoxide.
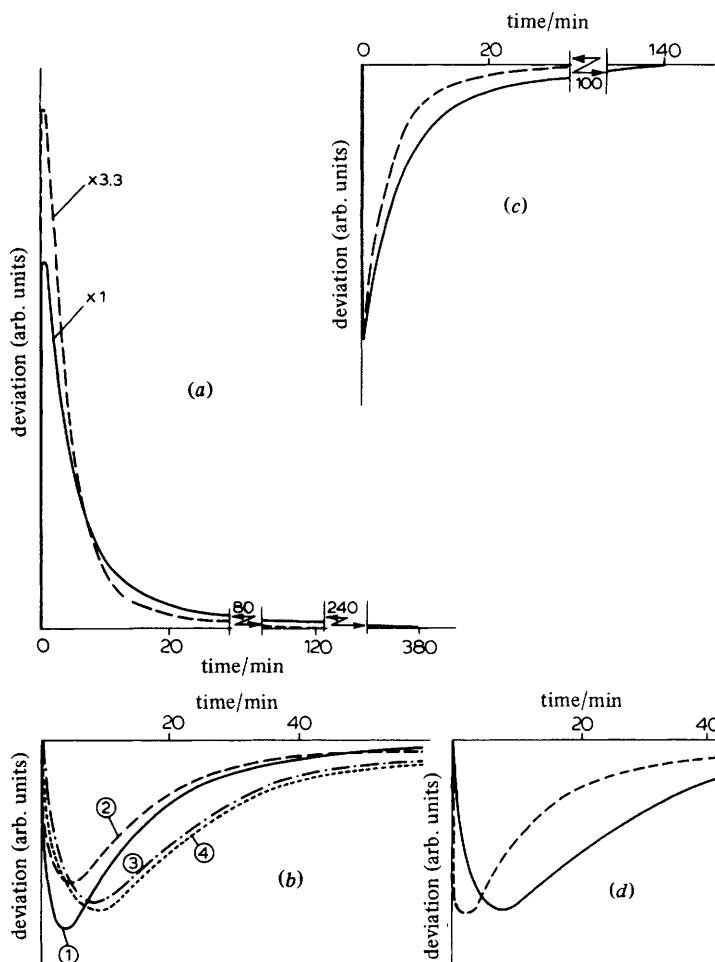

FIG. 6.—Thermokinetics. (a) Heat emission peak corresponding to adsorption of the first dose in run I (solid line) and run II (dashed line). (b) Desorption by evacuation of H_2 from ZnO at different coverages: curve 1, $p = 2$ kPa; curve 2, $p = 0.6$ kPa; curve 3, $p = 0.133$ kPa; curve 4, $p = 0.066$ kPa. (c) Stepwise desorption peaks of H_2 (solid line) and CO (broken line). (d) Desorption by evacuation of H_2 (solid line) and CO (broken line).

DISCUSSION

DIFFERENT FORMS OF ADSORBED HYDROGEN

At room temperature hydrogen interacts with ZnO in at least two different forms, which we will identify to a first approximation with the 'reversible' and 'irreversible' species type I and type II, hereinafter referred to as H(I) and H(II).

These two processes take place simultaneously and both depend on H_2 pressure so that they cannot be separated at different coverages along the same isotherm, as is possible in other cases.[18] Adsorption and desorption do not coincide in the whole range examined. Moreover, adsorption in the so-called irreversible form occurs to a considerable extent after successive adsorption–desorption cycles, so that we cannot draw conclusions as to the contributions from the two forms by a simple comparison of the first and second runs.

Adsorption values fall within the range of those obtained by other authors[2, 5, 19] at the same pressure. Dent and Kokes[2, 7] did separate H(I) from H(II) by simple evacuation (30 min) of a sample exposed to high H_2 pressure (17 kPa): all H_2 successively adsorbed on this sample was then assigned to the H(I) form.

In our case, adsorption of H(I) is accompanied in all successive runs by adsorption of H(II). It could be inferred that, as H(II) adsorption is a very slow and pressure-dependent process, the adsorption capacity up to 3 kPa is not exhausted in the first run. In that case the 'irreversible' adsorption seen in later runs could be interpreted as a mere continuation of the slow process interrupted in the preceeding run. Although this can account for some irreversible adsorption taking place after many adsorption–desorption runs, we discard this as a unique interpretation for two reasons: (i) At the end of each run, the adsorption rate is very slow so we can confidently consider the isotherms in fig. 2 as pseudo-equilibrium isotherms. If adsorption of H(II) in the next run were just a continuation of it, it should occur at an even lower rate, being at a lower pressure than the final one in the first run. This is not the case. Adsorption in form II occurs in each successive run in the same way, with the same kinetics and in considerable amounts. Only a slight decrease in the total irreversible adsorption (fig. 1) occurs run after run. (ii) Adsorption and desorption after evacuation of the H_2-saturated sample still show the same features, *i.e.* different adsorption and desorption paths and new sites for 'irreversible' adsorption.

Note also that the time lag of desorption in our system (4 h directly pumping-off) is much longer than the one adopted by Dent and Kokes (30 min); even when the pressure over the adsorbent is very low, the calorimeter monitors the presence of endothermic processes still occurring, ascribable at a first approximation to the desorption of the more strongly held absorbate. Therefore some of the so-called 'irreversible' adsorption becomes 'reversible' in our apparatus.

Nevertheless, some indications of the adsorption energies related to the two forms can be drawn by molar heats, obtained by partial separation of the two processes.

Final total values in run I of both n_a and Q^{int} (fig. 1 and 2) are slightly higher than the corresponding values in run II, if the run II isotherms are computed from a zero initial point. This difference has to be ascribed to irreversible chemisorption, which occurs to a higher extent in run I. The partial molar heat of this fraction measured at 3 kPa is 16 kJ mol^{-1}, much lower than the overall molar heat at the same pressure (33 kJ mol^{-1}). Accordingly the initial differential heat is higher in run II than in run I (fig. 5). Moreover the heat of desorption in the range of stepwise desorption is much higher (37 kJ mol^{-1}) than the heat of adsorption in the same coverage range (20 kJ mol^{-1}).

These findings clearly indicate that the heat of adsorption related to the formation of H(I) (fast and reversible) would be higher than the heat of adsorption related to H(II) (considered as slow and irreversible). This fact is very unusual. As a general rule an irreversible adsorption has always been considered to have a higher heat of adsorption than a reversible adsorption. This would account for the higher energy of desorption and hence the different possibilities of removing the adsorbate by pumping-off. In some cases, where both molecular and dissociative adsorption were present, an inversion of these characteristics has been observed, caused by a significant difference in the entropic content of the two adsorbates.[20] In the present case we are dealing with two dissociative chemisorptions on two different crystal faces.[9, 10] It seems very difficult to envisage such a great difference in adsorption mechanisms, able to account for such a different kinetic behaviour, when heat of adsorption values indicate the opposite.

We have to discard any hypothesis concerning desorption of gases other than H_2, in order to justify a heat of desorption higher than the heat of adsorption in the same coverage range: in that case the heat of desorption would not be constant in such a wide coverage range and could by no means be the same in different runs (fig. 4). Moreover none of the authors who investigated the same system by t.p.d.[5, 6] mentioned the possibility of desorption peaks not arising from H_2 desorption.

We have therefore to look at the complexity of the adsorption features of H(II) (p and t dependence, occurrence at each run) for the cause of its peculiarly low heat of adsorption.

On the basis of one adsorption–desorption cycle (run I) we have attempted a breakdown of calorimetric and volumetric isotherms, in the range where data are available for both (0.133-3 kPa). The decomposition scheme is illustrated in fig. 7(a). At any pressure value (p_n) the difference between the adsorption and the desorption branches (a_n) represents the amount adsorbed (or heat evolved) related to irreversible processes occurring from that point to the end of the run. Considering a set of regular pressure intervals, the difference $a_n - a_{n+1}$ measures irreversible adsorption in the pressure interval $p_n - p_{n+1}$. A set of data related only to the irreversible processes can thus be obtained from a limiting value (133 Pa) up to the end of the run and is reported in fig. 7(b) and (b') as calorimetric and volumetric isotherms. The corresponding 'reversible' isotherms, obtained by subtraction, are also reported (broken line). Adsorption below 133 Pa is here incorrectly reported as wholly reversible, even if a small fraction (0.2×10^{-2} J m^{-2}) is irreversible, the corresponding adsorption value being unknown. Relevant Q^{int} against n_a plots are reported in fig. 7(c).

The main results obtained by this decomposition are: (i) The 'reversible' adsorption has an asymptotic trend and most adsorption occurs below 0.7 kPa, whereas the 'irreversible' adsorption increases almost linearly with pressure and is not exhausted in the pressure range examined. This is nearly the opposite of what one could expect in classical reversible and irreversible adsorption. (ii) Both processes proceed in the pressure range examined with constant differential heat of adsorption; namely q^{diff} (reversible) = 40 kJ mol^{-1} and q^{diff} (irreversible) = 14 kJ mol^{-1}. These values are fairly consistent with the heat of desorption (37 kJ mol^{-1}) and confirm a very low heat of adsorption in the 'irreversible' form.

The reversible process, having a differential heat of 37-40 kJ mol^{-1} above 133 Pa, can be easily ascribed to the species denoted as H(I). On the other hand, the assignment of the irreversible processes with a low heat of adsorption to a well defined model is more difficult. Assignment of the whole irreversible adsorption to the species assigned by Boccuzzi et al.[10] to H atoms bridged on apolar faces has to be disregarded, the heat of adsorption being far too low [by comparison with that for H(I)] for an irreversible and dissociative chemisorption.

Some characteristics of the process would instead indicate that possible diffusion in the bulk onto sub-surface layers has also to be taken into account. This would be in agreement with: (i) The continuous irreversible uptake in subsequent adsorption–desorption runs. (ii) The correlation between time of contact and irreversibly adsorbed amounts. (iii) The linear isotherm trend, characteristic of dissolution and not of irreversible chemisorption. (iv) The very low heat related to this process.
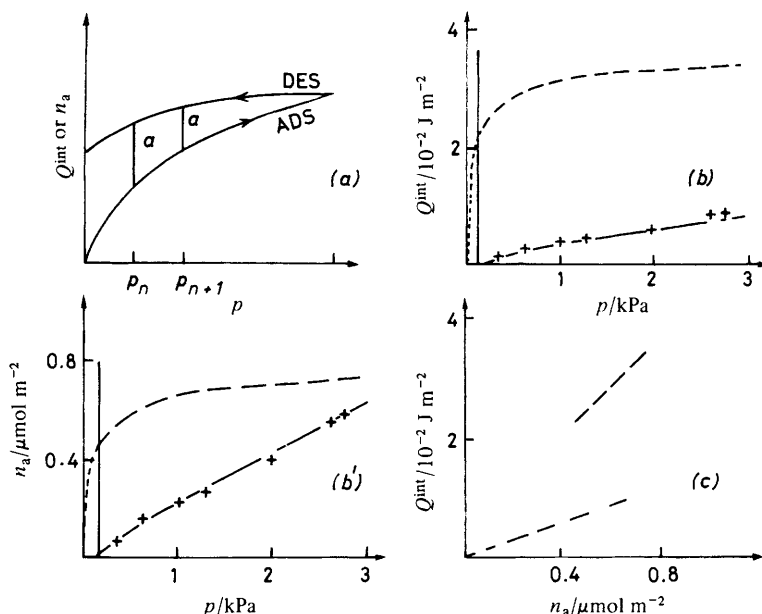

FIG. 7.—Decomposition of experimental Q^{int} and n_a against p curves in their reversible and irreversible fraction. (a) Decomposition scheme. (b) Q^{int} against p $(0.133 < p/kPa < 2.8)$. (b') n_a against p $(0.133 < p/kPa < 2.8)$. (c) Integral heat curves (Q^{int} against n_a).

It is well-known that in the case of absorption, *i.e.* any sort of penetration into the bulk from the surface, the heat evolution can be very low and in some cases[21] endothermic, as the process is mainly guided by entropic effects.

We recall here that the ZnO lattice has a very open structure with straight channels located on the apolar faces $(0\bar{1}01)$ of 0.2 nm diameter separated by a trigonal squeeze point of 0.12 nm through which a hydrogen atom or even a molecule can easily penetrate into the bulk.[22, 23] The squeeze point can account for the extreme slowness of the process and its substantial irreversibility. A schematic diagram for energy relationships in such a system is reported in fig. 8. The possibility of some penetration into the bulk had been also invoked by Dent and Kokes to account for the non-detectability by i.r. of type II and by Baransky and Galuzska to account for the irregular t.p.d. peak temperature.[5] Interstitial Zn^{+1} and oxygen[24] in ZnO have been identified. Mechanisms for diffusion of hydrogen in other oxides, *e.g.* TiO_2[25] and SiO_2,[26] have been described recently. On the ammonia synthesis catalyst, hydrogen is reversibly adsorbed but irreversibly dissolved in the subsurface layer.[27, 28]

The irreversible uptakes therefore would be comprised of at least two phenomena: the dissociative adsorption, yielding a bridged hydrogen as found by Boccuzzi *et al.*[10] and occurring at a first stage, followed by diffusion of the adsorbate in the bulk, through the wide channels present on the apolar faces.
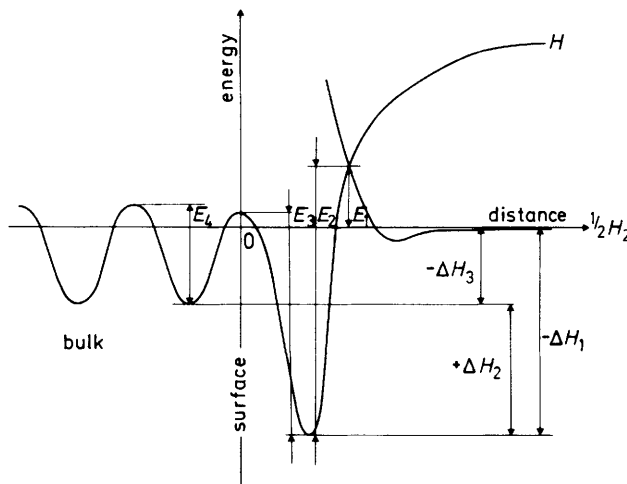
FIG. 8.—Schematic diagram for energy relationship in the case of hydrogen adsorption–absorption on ZnO. Activation energy for adsorption, E_1; for desorption, E_2; for penetration into subsurface layers, E_3; for diffusion in the bulk, E_4. $-\Delta H_1$, enthalpy change upon adsorption; $+\Delta H_2$, enthalpy change from adsorption to absorption; $-\Delta H_3$, enthalpy change from gaseous to absorbed state.

KINETICS

As to the kinetic features of H_2 adsorption a possible interpretation is the following: (1) The first adsorbed dose of the first run is comprised of H(I) and H(II) in the i.r. active form. This latter process, being dissociative and irreversible, will probably be slower than the former, thus explaining the slow thermokinetics in this first step. The slow step could also be caused by generation of active centres upon chemisorption, as pointed out by Naito et al.[19] (2) Diffusion into the bulk, through channels present at the apolar faces, occurring all along the adsorption process, has a very low overall heat of reaction, probably due to some activated endothermic steps (fig. 8). As a consequence, although very slow, this process is not detectable as slow thermokinetics, but is mainly shown by the continuous decrease of the pressure over the adsorbent for a period of several days.

We now suggest that the characterization of the various processes as 'reversible' and 'irreversible' is misleading because we are dealing with pseudo-equilibrium data. H(I) and H(II) at the surface and H(II) diffusion into the bulk should probably be regarded as processes characterized by different kinetic behaviour accounting for their apparent reversibility and irreversibility. Note that previously some authors[2, 7, 29] already distinguished a fast part and a slow part in the adsorption of the H(II) form, probably corresponding to our surface and bulk processes.

Although adsorption of the H(I) form is the fastest process, thermokinetics indicate that this process is also activated. By comparing the peak for desorption of H_2 with those of CO we compare the kinetics of H(I) with those of a fast, instantaneous and reversible coordination of CO on similar sites[30] with a slightly higher heat of adsorption (44 kJ mol^{-1}).[31]

As the activation energy for desorption is higher for H_2 than for CO [fig. 6(c) and (d)] it must be that $E_a(\text{des}) \text{H(I)} = E_a(\text{ads}) \text{H(I)} + 35$ kJ mol$^{-1} > E_a(\text{des}) \text{CO} = 44$ kJ mol^{-1}; thus $E_a(\text{ads}) \text{H(I)} > 9$ kJ. Accordingly values of $E_a = 17$ kJ have been reported by Baransky et al.[5]

All forms of dissociative adsorption of H_2 on ZnO at room temperature have

therefore to be regarded as kinetically activated processes. The possibility for one species [H(II)] to diffuse into the bulk accounts for the apparent irreversibility and slowness of the process. On the other hand, the complete reversibility of adsorption of H(I), in spite of its dissociative and activated features, is probably connected with the characteristics of adsorption sites on polar faces, where O—H and Zn—H are located at such a short a distance that a low-frequency factor for desorption as H_2 can be invoked.

SURFACE HETEROGENEITY

The variation of the differential heat of adsorption against coverage shown in fig. 5 is characteristic of interaction of gases on heterogeneous surfaces and similar to data found by Garner and Veal.[14] ZnO heterogeneity towards hydrogen has been already pointed out and considered both as structural and induced on the basis of kinetic data.[11, 12] The limited shift of Zn—H and Zn—OH stretching frequencies with coverage in i.r. spectra[10] seems to confirm this hypothesis. On the other hand, t.p.d. data[3-6] indicated that adsorption at room temperature leads to three peaks, namely IA, IB and II, whose peak temperature did not vary with coverage as expected in the case of heterogeneous adsorption.

Our data indicate an intermediate situation; in a wide pressure range ($p > 133.3$ Pa), adsorption in forms H(I) and H(II) occurs with fairly constant heat (fig. 4 and 7) for each mechanism and the overall decrease in the heat of adsorption against coverage plot (fig. 5) is due only to the superposition of the two processes and the prevalence of H(II) compared with H(I) at increasing pressure (fig. 7). This accounts for the constancy of the peak temperature against coverage in t.p.d. data, although the presence of two different peaks (IA and IB) would suggest a different mechanism for thermal desorption.

Below 133.3 Pa, 0.4 mol m^{-2} are adsorbed mainly as H(I) or H(II) in the i.r. active, surface form. These processes occur with a higher heat of adsorption (partial molar heat of adsorption = 55 kJ mol^{-1}) which decreases markedly with coverage from a value of 60 kJ mol^{-1} (zero coverage) to a value of 40 kJ mol^{-1} (133.3 Pa). Most probably in this first range, not only do the two processes occur together but some heterogeneity in H(I) adsorption sites is present, in accordance with kinetic and i.r. data and with the possible existence of more than one mechanism yielding H(I).[13]

A confirmation of the substantial heterogeneity in adsorption of H_2 in the 'reversible form' at low coverage is given by fig. 6(b). The desorption curves obtained by pumping-off the sample are a representation of desorption rates, although deformed by the calorimeter inertia. Their general smoothed shape is obviously due to a decrease of the desorption rate along the desorption process itself. In the case of the desorption of a species characterized by a constant heat of adsorption, the desorption curve presents the same shape starting from any coverage, the only difference being in the overall heat measured, as in curves 1 and 2 (high H_2 coverage). On the other hand, significant variation occurs at low coverage (curves 3 and 4) indicating a variable energy of activation for desorption.

CONCLUSIONS

On the basis of calorimetric and thermokinetic results, the two main species arising from hydrogen adsorption on ZnO, denoted as H(I) and H(II), have to be distinguished more on a kinetic basis (slow and fast) than on their reversibility or irreversibility.

The slow and irreversible process [H(II)] probably comprises two different steps: an adsorption at the apolar faces forming a stable bridged H complex, i.r. active, and a very slow diffusion into the bulk, which escapes detection by surface techniques but

is probably the prevailing form from a quantitative point of view, at the highest coverage. Diffusion process can account for the very low heat values (14 kJ mol^{-1}) in spite of the 'irreversibility' of the process.

Adsorption as H(I) on the polar faces occurs to some extent with a constant heat of adsorption, on isolated and similar sites; nevertheless at low coverage some heterogeneity is found, which indicates the presence of a fraction of high-energy sites.

Although such a process has been regarded as fast, it has a definite activation energy in accordance with the proposed dissociative mechanism.

[1] C. S. John, *Catalysis by Zinc Oxide*, in *Catalysis*, ed. C. Kemball and D. A. Dowden (Specialist Periodical Report, The Chemical Society, London, 1980), vol. 3, p. 169.
[2] A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, 1969, **73**, 3781.
[3] A. Baranski and R. J. Cvetanovic, *J. Phys. Chem.*, 1971, **75**, 208.
[4] A. Baranski, R. J. Cvetanovic, T. Dal and J. Galuszka, *Proc. IInd Int. Symp. Heterogeneous Catalysis*, Varna, November 1971, *Commun. Dept. Chem., Bulg. Acad. Sci.*, 1973, **6**, 135.
[5] A. Baranski and J. Galuszka, *J. Catal.*, 1976, **44**, 259.
[6] M. Watanabe, *J. Res. Inst. Catal., Hokkaido Univ.*, 1978, **26**, 63.
[7] R. J. Kokes and A. L. Dent, *Adv. Catal.*, 1972, **22**, 1.
[8] D. Narayana, T. J. Lal and V. Kesavulu, *J. Phys. Chem.*, 1970, **74**, 4150.
[9] T. Morimoto and L. Moriskige, *J. Phys. Chem.*, 1975, **79**, 1573.
[10] F. Boccuzzi, E. Borello, A. Zecchina, A. Bossi and M. Camia, *J. Catal.*, 1978, **51**, 150.
[11] C. Aharoni and F. C. Tompkins, *Trans. Faraday Soc.*, 1970, **66**, 434.
[12] C. Aharoni and F. C. Tompkins, *Adv. Catal.*, 1970, **21**, 1.
[13] W. R. Murphy, T. F. Veerkamp and T. W. Leland, *J. Catal.*, 1976, **43**, 304.
[14] W. E. Garner and F. J. Veal, *J. Chem. Soc.*, 1935, 1436 and 1487.
[15] G. Della Gatta, B. Fubini and G. Venturello, *J. Chim. Phys.*, 1973, **70**, 64.
[16] B. Fubini, *Rev. Gen. Therm.*, 1979, **18**, 297.
[17] E. Giamello and B. Fubini, *React. Kinet. Catal. Lett.*, in press.
[18] G. Della Gatta, B. Fubini and L. Stradella, *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**, 1040.
[19] S. Naito, H. Shimizu, E. Hagiwara, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, 1971, **67**, 1519.
[20] B. Fubini, G. Della Gatta and G. Venturello, *J. Colloid Interface Sci.*, 1978, **64**, 470.
[21] T. B. Flanagan, *Hydrides Energy Storage*, ed. A. F. Andresen (Pergamon Press, Oxford, 1977), p. 135.
[22] A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, 1969, **73**, 3781.
[23] W. Gopel, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 744.
[24] A. Hausmann and B. Schallenberger, *Z. Phys. B*, 1978, **31**, 269.
[25] J. B. Bates, J. C. Wang and R. A. Perkins, *Phys. Rev. B*, 1979, **19**, 4130.
[26] J. Vitko Jr, C. M. Hartwig and P. L. Mattern, *Proc. Int. Conf.*, New York, 1978, ed. R. Pantelides (Pergamon Press, Oxford, 1978), p. 215.
[27] V. E. Ostrovskii and E. G. Ingranova, *Kinet. Catal. (USSR)*, 1978, **19**, 681.
[28] E. G. Igranova, V. E. Ostrovskii and M. I. Temkin, *Kinet. Catal. (USSR)*, 1976, **17**, 1257.
[29] R. P. Eischens, W. A. Pliskin and M. J. Low, *J. Catal.*, 1962, **1**, 180.
[30] F. Boccuzzi, E. Garrone, A. Zecchina, A. Bossi and M. Camia, *J. Catal.*, 1978, **51**, 160.
[31] E. Giamello and B. Fubini, to be published.
[32] R. J. Kokes, C. C. Chang, L. T. Dixon and A. L. Dent, *J. Am. Chem. Soc.*, 1972, **94**, 4429.