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LETTER TO THE EDITORS

Kinetics of Oxygen Exchange

In a recent paper Avetisov *et al.* (*1*) presented calculations and arguments which, they claim, show that the experimental procedure used by me (*2*) in studying the oxygen-exchange characteristics of oxides is unsatisfactory. They suggest that the unreliability is because: (a) variations in the amount of oxygen desorbed during the 3-min pumping period employed by me immediately before adding ^{18}O-enriched oxygen at the commencement of the exchange reaction could seriously affect the extent of the "exchangeable surface," calculated by ^{18}O-balance at the end of the reaction; and (b) the 3-min pumping could alter the thermodynamic equilibrium between the oxide surface and the gas phase and so introduce errors into the determination of the pressure dependence of the reaction.

In making these comments Avetisov *et al.* ignore evidence to the contrary presented in Ref. (*2*). The procedure adopted involved, essentially, leaving the oxide in contact with $^{16}O_2$ gas at 1.5 cm pressure for 18 hr at the reaction temperature, pumping for exactly 3 min, and then commencing the reaction by adding immediately and rapidly the enriched gas; most exchange runs were performed at 1–2 cm, and the pressure dependence was measured over the range 1–10 cm. Tables 2 and 3 of my paper (*2*) show that generally speaking the kinetic parameters are not seriously affected by the procedure used, comparison being made with a substantial number of experiments in which the oxide was outgassed for 18 hr in high vacuum at a temperature greater than the reaction temperature, and cooled *in vacuo* to the latter before adding the enriched gas: Table 1 of the paper also shows that the quantity of readily desorbable oxygen left on the surface after 3 min pumping did not introduce serious error in the determination of the extent of the exchangeable surface; this is also evident from Tables 2 and 3 in Ref. (*2*).

A few comments upon the paper of Avetisov *et al.* (*1*) seem pertinent: Eq. (6) should read

$$E_{O_2} = \tilde{R}\,\frac{\partial \ln (R)}{\partial(-(1/T))} = \text{etc.};$$

Eq. (33) is wrongly printed—the denominator should be squared (cf. Fig. 4); Eq. (34) is incorrect and should read

$$E_{O_2} = \frac{(k_aP_{O_2})^{\frac{1}{2}}E_d + (k_d)^{\frac{1}{2}}E_a}{(k_d)^{\frac{1}{2}} + (k_aP_{O_2})^{\frac{1}{2}}},$$

so that the subsequent discussion in the text as to the conditions under which, on the model used, E_{O_2} is independent of P_{O_2} reduces simply to the condition that E_d must equal E_a when $k_d \approx k_aP_{O_2}$ (and then it follows that $E_{O_2} \approx E_a \approx E_d$); alternatively, if $k_d \ll k_aP_{O_2}$ then E_{O_2} is again independent of P_{O_2} and equal to E_d.

The latter situation is the one which I have demonstrated to be the most likely

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in the case of many oxides (*2*), assuming the homogeneous surface model. [This conclusion is independent of the detailed mechanism of the exchange reaction; for example, it can apply whether the reaction proceeds via dissociative adsorption of oxygen, followed by atom-by-atom exchange (rate R^1 in my notation) or whether the reaction proceeds by the exchange of whole molecules (rate R^2).] Thus, if $E_{O_2} \approx E_d \approx E_a$, the maximum possible rate of reaction at temperature T and pressure P (mm) is for oxygen

$$R = \frac{3.51 \times 10^{22} P\sigma}{(32T)^{\frac{1}{2}}} \times \exp\left(\frac{-E_{O_2}}{RT}\right) \text{ mol cm}^{-1} \text{ sec}^{-1},$$

where σ is the accommodation coefficient and E_{O_2} is the observed activation energy of the exchange reaction. Even assuming $\sigma = 1$ this equation gives rates which are much lower than those observed. Hence $E_a < E_{O_2}$ and therefore desorption or some reaction located in the solid surface or in the bulk solid must be the rate-determining step (*2*). [This conclusion may also be drawn in the case of V_2O_5 studied by Avetisov *et al.* (*1*); thus from values of R and $k_{obs}{}^0$ in their Table 1, and assuming $\sigma = 1$, the maximum possible values of E_a at the three pressures used are 38, 43, and 43 kcal mol^{-1}, compared with the quoted values of E_{obs} of 44, 51, and 60 kcal mol^{-1}. Incidentally, using the values of R and $k_{obs}{}^0$ given in this table, the values of E_{obs} appear to be 50, 53, and 59 kcal mol^{-1}.]

The results of Avetisov *et al.* thus do not justify rejection of the homogeneous surface model. The subsequent discussion (*1*, pp. 10–13) of the reasonableness of their heterogeneous surface model (which leads to fairly complex formulas) involves so many assumptions and approximations as to be of no practical value in deciding between the two models. Additionally, the data presented upon pressure dependence may be affected by transport problems; we have found (*3*) (as did Avetisov *et al.*) that, when using a capillary to transfer continuously a fraction of the reactant gas phase to the mass spectrometer, transport through the capillary becomes rate determining in the region 200–300 mm P_{O_2}; this is just the pressure range over which the data in Fig. 2 (*1*) show an inflection.

The choice of V_2O_5 as the material with which to attempt to demonstrate the presence of a heterogeneous surface is also curious. This is one of a small number of materials, all possessing similar structures, which rapidly exchange the oxygen in the whole bulk of the solid—not just the surface layer—with gaseous oxygen. Such an extreme degree of lability—almost fluidity—in the solid lattice would suggest an even greater lability in the surface so that statistically an energetically uniform surface would be expected.

Finally, although the one test of mechanism [using presumably a highly enriched nonequilibriated mixture of $^{16}O_2$ and $^{18}O_2$ (*4*, *2*)] showed that only the whole-molecule exchange mechanism (my R^2) was present, there is substantial evidence for the simultaneous presence of both that and the dissociative mechanism (my R^1) on V_2O_5 (*2*, *5*). The two mechanisms have differing pressure dependencies, $P_{O_2}{}^n$ (n = 1.0 ± 0.2 and 0.32 ± 0.1), and activation energies (80 ± 10 and 20 ± 5 kcal mol^{-1}) (*2*). The possibility of the occurrence of the two reactions introduces further uncertainty into the interpretation of the kinetics, as the procedure adopted by Avetisov *et al.* measures $k_{obs}{}^0$ which is proportional to $(2R^2 + R^1)$ (*2*); the presence of the two reactions could well account for the significant increase of E_{obs} with pressure shown in their Table 1, although, as noted above, the situation may be complicated because of possible transport difficulties.

REFERENCES

1. Avetisov, A. K., Gol'dshtein, N. D., Dulin, D. A., Mischenko, Yu. A., and Gel'bshtein, A. I., *J. Catal.* **52**, 1 (1978).
2. Winter, E. R. S., *J. Chem. Soc. (London)*, A2889 (1968).
3. Barnard, J. A., Winter, E. R. S., and Briscoe, H. V. A., *J. Chem. Soc. (London)*, 1517 (1954); Winter, E. R. S., unpublished observations.
4. Boreskov, G. K., *Advan. Catal.* **15**, 285 (1964); Klier, K., Nováková, J., and Jírů, P., *J. Catal.* **2**, 479 (1963).
5. Muzykantov, V. S., Jírů, P., Klier, K., and Nováková, J., *Collect. Czech. Chem. Commun.* **33**, 829 (1968).

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