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State Institute of the Nitrogen Industry

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CHARGING CURVES ON POWDERED METALS

G. A. Bogdanovskii, G. P. Khomchenko, and G. D. Vovchenko.

The application of electrochemical methods to the investigation of disperse catalysts became more effective when it became possible to record charging curves on powders. At the present time two methods — the gauze and impact methods — are available for powdered metals[1,2]. In the former method, the metal powder wrapped in a fine platinum gauze forms the electrode, on which the charging curve is determined by the usual technique employed for compact electrodes. In the impact method the powder is charged by collision with a platinum electrode polarised from an external source of current. The reliability of these methods, and their promise for studying the properties of disperse catalysts, are indicated by comparison of the results obtained with data for compact electrodes.

An important difference between the gauze and impact methods is that in the latter case the charging curves are recorded under conditions of vigorous agitation[3,4]. In the absence of stirring, the charging of platinised platinum in the potential range 0.02–0.7 V (with respect to a reversible hydrogen electrode in the same solution) is reversible, and hence the charging curve here is an equilibrium curve. Cathodic charging curves, obtained from a potential of 0.7 V under various conditions of stirring, coincide with the equilibrium curve only as far as 0.1 V. At potentials more negative than 0.1 V, the polarising current becomes comparable with the diffusion current in the solution due to molecular hydrogen formed on the electrode. As a result, the recording of charging curves gives satisfactory results over a narrower potential range (0.09–1.3 V) in stirred than in unstirred systems. Therefore the gauze method probably represents the more soundly based technique.

In several cases, however, the surface of the gauze itself cannot be ignored in recording charging curves by this method. It is also possible that some of the powder may be lost both on immersion of the wrapped weighed quantity in the solution and when hydrogen and nitrogen are passed through the system, which distorts the results. In view of this, we somewhat modified the technique of recording charging curves on powders metals in the absence of stirring. A weighed quantity of the powder, instead of being wrapped in a platinum gauze, was placed at the bottom of a specially designed cell, in contact with the platinum wire *1* sealed into the base of the cell (Fig. 1). The volume of solution in the cell did not exceed 10 ml, which appreciably diminished depolarisation effects.

The upper part of the body of the cell has four inlets, for the reference electrode *2*, the auxiliary electrode *6*, saturating the system with hydrogen *4*, and the escape of gas *5*. The auxiliary electrode consisted of the ground-glass joint *3*, at the end of which was sealed the glass filter *7* separating anode and cathode compartments. The platinum wire of the auxiliary electrode *8* was inserted inside the ground-glass attachment. The powder was saturated with hydrogen by simultaneous cathodic polarisation and passage of molecular hydrogen through the system. In other respects the usual technique[5] was employed to record a charging curve.

Thus the proposed method for recording charging curves on powdered metals differs from the gauze method only in that the weighed quantity of powder is placed at the bottom of the cell and the volume of solution is sharply decreased. In our view this procedure is more convenient, and we have termed it the direct contact method, in contrast to the gauze method.

Fig. 2 shows a charging curve obtained by the direct contact method. The adsorption of hydrogen by a weighed quantity of the platinum powder, calculated from the anodic charging curve, was 3.5 ml g^{-1}. The quantity of hydrogen adsorbed is directly proportional to the amount of adsorbent taken (Fig. 3).

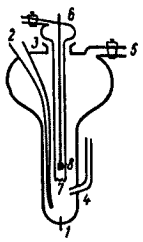

Fig. 1. Cell for determining charging curves on powdered metals.

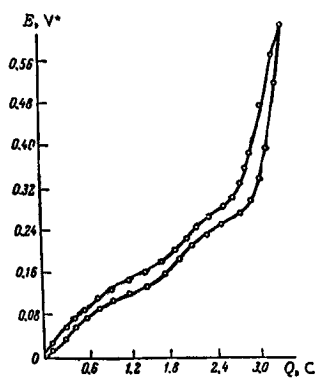

Fig. 2. Charging curve for 0.1 g of platinum black in 1 N H_2SO_4.

* All potentials given relative to that of a reversible hydrogen electrode in the same solution.

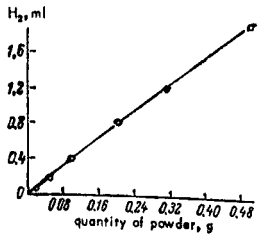

Fig. 3. Dependence of quantity of hydrogen adsorbed on weight of platinum taken.

The platinum black was prepared by adding a small excess of concentrated alkali to a solution of hexachloroplatinic acid containing formaldehyde. The true surface of the powders obtained in this way, determined by the BET method from the low-temperature adsorption of krypton, was 9 $m^2 g^{-1}$. [6,7] This shows good agreement with the value of 10 $m^2 g^{-1}$ which we have calculated from the hydrogen region of the charging curve. It was assumed in the calculation that 28×10^{-5} C cm^{-2} is consumed in ionising the hydrogen adsorbed on the platinum[8]. If, however, the calculation is based on the slope of the charging curve in the region of formation of the electrical double layer, the capacitance of smooth platinum being taken as 20 μF cm^{-2}, the value obtained for the surface is far too high.

Thus the result obtained for the true surface of platinum black again supports the previously expressed opinion[9] that the true surface can be determined quite reliably from the hydrogen section of the charging curve.

Fig. 4 shows a charging curve for palladium black obtained by the direct contact method. The sorption capacity of the weighed portion for hydrogen, calculated from the anodic charging curve, was 68 ml g^{-1}. The palladium black was prepared by a similar method to that used for platinum black. The true surface of this black, determined from the low-temperature adsorption of krypton, is 23 $m^2 g^{-1}$. [7,10] Direct determination of the surface of palladium black from the hydrogen region of the charging curve is complicated by the specific behaviour of palladium itself, which is able to absorb hydrogen in amounts considerably exceeding that which is adsorbed The true surface of 0.05 g of palladium black, determined from the low-temperature of krypton, is 1150 cm^2. The quantity of electricity required to remove the hydrogen sorbed by this weight of palladium is 30 C according to the charging curve. Hence the quantity of electricity needed to extract the hydrogen sorbed by 1 cm^2 of palladium is 28×10^{-4} C. This is ten times the value for platinum.

If it is accepted that, under similar conditions, the total quantity of hydrogen on palladium exceeds that on platinum by a factor of 10, removal of the adsorbed hydrogen from 1 cm^2 of palladium requires the same quantity of electricity as from platinum, which is 28×10^{-5} C. The rest of the electricity is consumed in extracting the absorbed hydrogen.

Fig. 5 shows charging curves obtained with the same weight (0.1 g) of platinum and palladium blacks 0.1 N H_2SO_4. The quantity of electricity necessary to remove hydrogen from the palladium is seen to exceed that for platinum by a factor of 20. However, comparison of charging curves obtained with double the weight of platinum compared with palladium (i.e. roughly in the ratio of the atomic weights) shows that in this case the quantity of electricity consumed in the removal of hydrogen from palladium does in fact exceed that for the removal of hydrogen from platinum by a factor of 10 (see Figs. 2 and 4).

Fig. 6 shows a charging curve for palladised platinum foil. Palladisation was carried out from $PdCl_2$ solution at a current density of 0.002 A cm^{-2}, the amount of palladium deposited being 0.02 g. In this case calculation gives for the true surface of the electrode, determined from the hydrogen region of the charging curve, 4500 cm^2, or 23 $m^2 g^{-1}$.

Thus in order to determine the true surface of palladium from the hydrogen region of the charging curve, it is necessary to determine the quantity of electricity in coulombs consumed in removing hydrogen from the palladium, and divide the results by 28×10^{-4} C. This will give a value for the surface of the same accuracy as that obtained by the BET method.

Fig. 7 shows a charging curve obtained by the direct contact method with 0.05 g of rhodium black. The adsorption capacity for hydrogen of the rhodium, calculated from the anodic charging curve, is 11 ml g^{-1} Calculation of the true

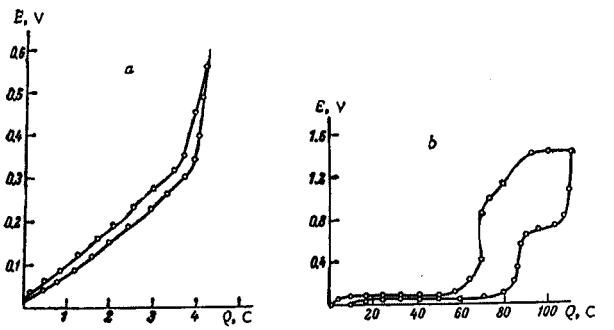

Fig. 5. Charging curves obtained by the gauze method for 0.1 g of: *a*) platinum black; *b*) palladium black.

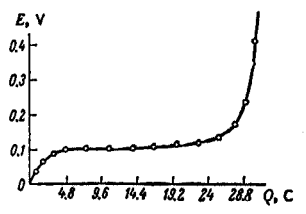

Fig. 4. Charging curve for 0.05 g of palladium black in 1 N H_2SO_4, obtained by the direct contact method.

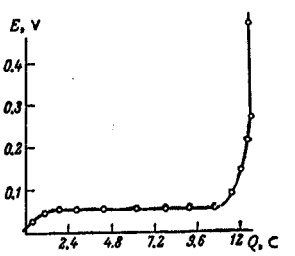

Fig. 6. Charging curve for pallidised platinum.

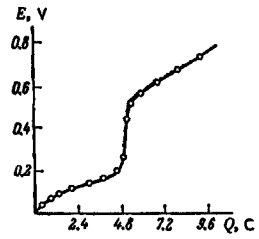

Fig. 7. Charging curve for rhodium black in 1 N H_2SO_4.

surface of the rhodium from the hydrogen region of the charging curve, on the assumption that removal of the hydrogen adsorbed on 1 cm^2 of rhodium consumes 28×10^{-5} C, yields a value of 1.7 m^2, or 34 $m^2 g^{-1}$. The true surface of rhodium black determined by the BET methods is 43 $m^2 \times \times g^{-1}$.[11] Similar results are obtained on ruthenium too. The quantity of electricity required to remove the hydrogen adsorbed on 1 cm^2 of ruthenium is also 28×10^{-5} C.[12]

The quantity 28×10^{-5} C is evidently a kind of characteristic constant of the platinum-group metals. Use of this value to determine true surfaces from the hydrogen region of the charging curve gives trustworthy results, and therefore the electrochemical method, in view of its relative simplicity, can compete with the BET method.

SUMMARY

1. What is termed the direct contact method is proposed for determining the charging curves of powdered metals.
2. Values of the true surfaces of powdered metals, calculated from the hydrogen region of charging curves recorded by the direct contact method, agree well with values obtained by the BET method.
3. The quantity of electricity required to remove the adsorbed hydrogen from 1 cm^2 of surface is 28×10^{-5} C, which is a characteristic parameter of the platinum-group metals.

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Lomonosov Moscow State University

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THE RELATION BETWEEN THE ENTHALPY AND FREE ENERGY CHANGES IN ELECTRODE REACTIONS AND IN THE DISSOCIATION OF THE ELEMENTS IN THE GAS PHASE INTO ATOMS AND IONS

N. E. Khomutov

In connection with the development of methods for the calculation of electrode potentials, the author has compared the free energy changes ΔG in electrode reactions and in the dissociation of the elements into atoms and ions in the gas phase with the corresponding enthalpy changes ΔH. For most elements, which are either solid or liquid (mercury, bromine) at 25° (Fig. 1), the relation between the free energy of formation of the atoms (ΔG_a°) and the corresponding enthalpies (ΔH_a°) is

$$\Delta G_a^\circ = b_a \Delta H_a^\circ + a_a, \qquad (1)$$

where $b_a = 0.96$ and $a_a = -7$ kcal are constants. The relation described by Eqn. (1) holds also for elements which exist at 25° in the gaseous state (Fig. 2). The constants

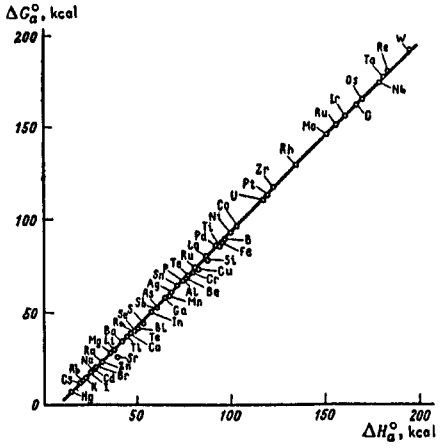

Fig. 1. Relation between the free energies and enthalpies of formation of atoms from elements which are liquid or solid at 25° and 1 atm.