

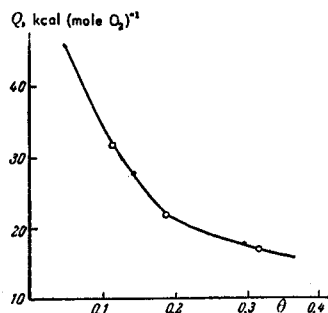


Fig. 3. Variation of the heat of adsorption with degree of surface coverage with oxygen; circles — results of two different experiments.

evacuation lasted not less than 70 h. Small portions of oxygen were then applied to the specimen, the experiments being carried out at 100°. The oxygen pressure during the adsorption and the heat evolved were measured. In calculating the degree of surface coverage, it was assumed that each surface Ag atom is capable of binding one oxygen atom. On increasing the degree of surface coverage from 0.05 to 0.4, the differential heat of adsorption calculated per mole of oxygen fell from 46 to 17 kcal mole⁻¹. Fig. 3 presents the results of two experiments on the determination of the variation of the heat of adsorption of oxygen with surface coverage. The points lie on a single curve.

The design of the calorimeter allows it to be used not only for measurement of heats of chemisorption but also for the heats of other processes which occur at a sufficiently high rate at temperatures up to 200°.

In conclusion we would like to thank S. M. Skuratov and A. A. Isirikyan for valuable consultations and T. S. Zimin for assembling the electrical measuring circuit.

SUMMARY

A differential double calorimeter has been developed for the measurement of the heats of chemisorption of gases at 25°–200° with automatic recording and control. The instrument allows measurements of amounts of heat between 0.02 and 0.5 cal at a heating rate of 5×10^{-5} – 2×10^{-3} cal sec⁻¹ with an accuracy of 2–5%. The differential heats of adsorption of oxygen on silver have been measured for the first time. The calorimeter, unlike those described in the literature, makes it possible to measure the heats of processes which are slow at room temperature.

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THE ZERO-CHARGE POTENTIAL OF PLATINUM

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According to several independent methods¹⁻⁴, the zero-charge potential of platinum is close to 0.15–0.2 V†. Only the zero-charge potentials found by the capacitance method in dilute solutions differ sharply from this value^{5,6}, and in one investigation have actually been found to be pH dependent⁷. The differences among the zero-charge potentials based on the capacitance method and the overall discrepancies between these values and those obtained by other methods renders the former suspect. The present paper deals with the investigation of the double-layer capacitance in sulphuric acid solutions of various concentrations at different a.c. frequencies.

The experimental technique used for the capacitance measurements and the preparation of the electrode have already been described⁸. The impedance of the platinum electrode was measured by a compensation method, series-connected capacitances C_1 and resistances R being switched into the compensating arm. In subsequent calculations the resistance of the solution R_s was subtracted from R : $R - R_s = R_1$.

At a sufficiently high a.c. frequency, when the impedance due to the adsorption capacitance⁹ may be neglected by comparison with the resistance R_2 due to the discharge of hydrogen ions, $H^+ + e \rightarrow H_{ad}$, the model circuits assume the simple form of parallel-connected double-layer capacitance C_2 and the resistance R_2 . For 0.01 N H₂SO₄ solution this condition holds approximately even at 10–20 kc/s. Since under these conditions the product $\omega^2 R_1^2 C_1^2$ is not small compared with unity, in calculating C_2 from the equation $C_2 = C_1 / (1 + \omega^2 R_1^2 C_1^2)$ it is necessary to know R_1 very accurately and hence also the resistance of the solution R_s . In a previous paper¹⁰ R_s was assumed to be approximately equal to the resistance measured by means

† The potentials are given relative to the normal hydrogen electrode.

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of a series-connected circuit at a frequency of 20 kc/s and a potential of 0.6 V. This involves the assumption that in the region of double-layer potentials the platinum electrode behaves as an ideal condenser with respect to a.c. However, Breiter *et al.*¹¹ have shown that at double-layer potentials the platinum electrode has the properties of a condenser with leakage†. Our assumption in the determination of the resistance of the solution did not permit accurate separation of the capacitances due to the double layer and to the electrochemical process and therefore the method of capacitance measurements in dilute solutions could not be used to determine the zero-charge potential of the platinum electrode.

In view of the above considerations, instead of the solution resistance measured at 20 kc/s we used the value calculated from the formula

$$R_s = \frac{1}{\kappa} K,$$

where κ is the resistivity of the solution and K the instrument constant. The capacitance curves thus obtained for 0.01 N H₂SO₄ (Fig. 1, curve 1) pass through a minimum at a potential of 0.18 ± 0.02 V and have the shape characteristic of the double-layer capacitance curves in the region of the zero-charge potential^{13,14}. However, the shape most characteristic of the double-layer capacitance curves in dilute solutions near the zero-charge point is obtained when the correction for the resistance of the solution is taken to be about 5% greater than the calculated value (Fig. 1, curve 2). It appears that the slightly higher correction compensates the small error caused by the assumption that at 20 kc/s the impedance due to the adsorption capacitance may be neglected.

A similar minimum and at the same potential is observed in 0.001 N H₂SO₄ (Fig. 2). Since the depth of the minimum obtained strongly depends on the accuracy of the determination of R_s , it is impossible to determine from our data the variation of the former with change in dilution of the solution from 0.01 to 0.001 N.

The absence of a similar minimum on the capacitance curves in 1 N H₂SO₄ confirms that the minimum in dilute solutions corresponds to the maximum diffuseness of the double layer near the zero-charge potential of platinum. This is also supported by the difference in the capacitances on either side of the zero-charge potential, which shows that near 0.18 V there is a change in the sign of the surface charge accompanied by a change in the thickness of the double layer. Within the limits of accuracy of the measurements the position of the capacitance minimum is independent of the pH of the solution.

The agreement between the potential at the capacitance minimum which we obtained in dilute solutions and the potential of the maximum diffuseness of the double layer found by the crossed-filament method⁴, as well as another procedure², suggests that the minimum on the capacitance curves obtained with correct allowance for the resistance

† It may be assumed⁸ that the "leakage of the condenser" is due both to the low rate of charging of the double layer¹¹ and to the presence of residual adsorbed gases. The amount of the latter and the rate of exchange in the region of the double-layer potentials may depend on the preliminary treatment of the electrode. Probably, this can also explain the higher double-layer capacitance, compared with the value found in our experiments, that some workers have found^{11,12} for platinum at $\phi = 0.4$ V.

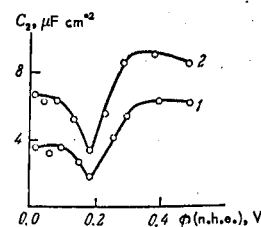


Fig. 1. Capacitance curves for 0.01 N H₂SO₄ at an a.c. frequency of 20 kc/s, recalculated in terms of a parallel circuit with various corrections for the resistance of the solution (R_s):

- 1) $R_s = 3.6 \Omega \text{ cm}^2$ (calculated);
2) $R_s = 3.8 \Omega \text{ cm}^2$.

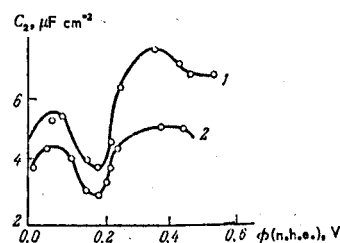


Fig. 2. Capacitance curves in 0.001 N H₂SO₄ at different a.c. frequencies (kc/s):
1) 10; 2) 20.

of the solution does indeed correspond to the maximum diffuseness of the electrical double layer on platinum. The zero-charge potential obtained agrees fairly well with the results of the adsorption method¹. The difference between the zero-charge potentials measured by different methods, reaching 0.09 V,^{1,2,4} may be explained by the difference in the extent of adsorption of hydrogen on platinum, depending on the preliminary treatment of the latter.

The absolute magnitude of the capacitance proved to be smaller by a factor of about 2–3 than on mercury¹³. Thorough purification of the system from traces of surface-active substances did not result in an appreciable increase of the capacitance. The reason for the very low capacitance of platinum under our conditions is still not entirely clear.

SUMMARY

The zero-charge potential of the platinum electrode, 0.18 ± 0.02 V (with respect to the normal hydrogen electrode), obtained by measuring the impedance in 0.01 and 0.001 N H₂SO₄, is in good agreement with the values found earlier by several independent methods.

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MISCELLANY

A POTENTIOSTAT FOR KINETIC INVESTIGATIONS

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The kinetic parameters of an electrode process may be quantitatively determined from potentiostatic current-time curves^{1,2}; in this it is the initial sections of the curve that are of fundamental importance, and with rapid reactions these have to be recorded in a short time interval. The measurements must be carried out in a cell with anode and cathode compartments separated, which leads to a considerable increase in cell resistance. Gerischer² does not separate anolyte and catholyte, which is undesirable. In this connection more stringent requirements must be met by potentiostatic apparatus, in particular by the magnitude of the output voltage, on which the potential applied to the test electrode depends.

Most potentiostat circuits³⁻⁶ are applicable to the investigation of electrode processes that take place relatively slowly (10–0.1 sec). Potentiostats with very small potential regulation times (10⁻⁴–10⁻⁵ sec) are used for the investigation of rapid electrode processes^{2,7-11}. But the

output voltage of such apparatus is relatively low, of the order of tens of volts, and consequently it is impossible to work with high-resistance cells. A potentiostat circuit that we obtained from the Karpov Physicochemical Institute does not suffer from this disadvantage, since it has a high output voltage (500–300 V). But the supplies for this circuit are drawn from several sources, only some of which are stabilised, and this affects the stability of operation of the apparatus.

We have built a potentiostatic apparatus for kinetic investigations which has an adequate output voltage and good stability. It provides for the recording of potentiostatic *i-t* curves at a given potential, and also for transitions from one potential to another without disconnecting the polarising circuit. The current-potential curves are normally constructed from a large number of *i-t* curves obtained at various potentials. Our apparatus provides for the direct recording of both quasi-potentiostatic and stationary current-potential curves. The range of regulated potentials (-2.5 to +3.0 V) allows the investigation of both cathodic and anodic processes. The accuracy of potential regulation is ± 2 mV.

Fig. 1 shows a block diagram of the potentiostat. The potential difference between the test electrode and the reference electrode is applied to the first input of the balanced d.c. amplifier 1. If the potential of the working electrode under test varies from the prescribed value, the amplifier output current compensates this variation in the direction of the prescribed potential. The required electrode potential is set by a d.c. voltage, which is applied to the second input of the amplifier. When *i-t* curves are being recorded, this voltage is picked off from two parallel-connected PPTV potentiometers; the transition from one of these to the other is made by rapid operation of switch SI. For the recording of *i-φ* curves the voltage is taken from potentiometer RV1, which is driven by an electric motor whose speed can be varied in steps by gear-changing in the reduction gearbox.

The d.c. amplifier (Fig. 2) (valves V1-V8) consists of a voltage amplifier (V1-V6) and the power amplifier V7. The voltage amplifier consists of three push-pull stages directly

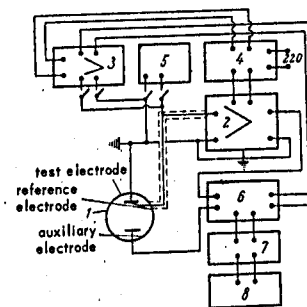


Fig. 1. Block diagram of potentiostatic apparatus:
1) cell; 2), 3) amplifiers; 4) power supplies; 5) valve voltmeter; 6) R1 resistance box; 7) N700 oscillograph; 8) P104 time-marker generator.