

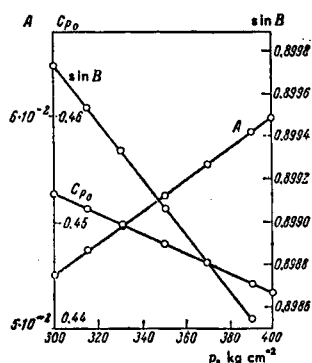


Fig. 3. Pressure dependence of parameters in Eqn. (4) for water vapour.

possibility was made by setting up, on the basis of data for water vapour between 300 and 370 kg cm⁻², the linear equations

$$A = 3.623 \times 10^{-3} + 7.467 \times 10^{-6} p, \quad (8)$$

$$\sin B = -0.90383 + 1.355 \times 10^{-5} p, \quad (9)$$

$$C_{p0} = 0.4859 - 1.067 \times 10^{-4} p. \quad (10)$$

Their accuracy is illustrated in Fig. 3. Extrapolation on the basis of these equations to $p = 400$ kg cm⁻² gives completely satisfactory results (see Table 3). Values of C_p in Table 3 were calculated from Eqn. (4), the coefficients in which were determined on the basis of Eqns. (8)–(10).

Similar calculations for air and other substances also gave satisfactory results.

The authors express their gratitude for assistance in the work to Chang Hsien and Ch'ên Chung-hou.

SUMMARY

The approximate method of calculating the properties of substances in polar coordinates proposed previously¹ has been used to calculate the temperature dependence of the heat capacity of compressed gases.

The method has been tested on the heat capacity at constant pressure of H₂O ($p = 1$ –400 kg cm⁻²), N₂ (50–700), CO₂ (25–500), CO (50–3000), Ar (50–2000), NH₃ (60–200), 95% C₂H₅OH + 5% H₂O (80–200), and air (20–220). The mean error in the calculation is 0.4%.

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MEASUREMENT OF HYDROGEN OVER-POTENTIAL AT A DROPPING GALLIUM ELECTRODE

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The periodic renewal of the electrode surface and the possibility of allowing for concentration polarisation have ensured the extensive use of the dropping mercury electrode for investigating the mechanism of electrochemical reactions. In several cases, however, it is important to ascertain the role in an electrochemical process of the nature of the metal forming the electrode. In this connection it is useful to employ a dropping gallium electrode as well as a dropping mercury electrode. The melting point of gallium (29.78°) is close to room temperature, which allows measurements to be made in solutions of different concentrations in the usual apparatus. A dropping gallium electrode was first constructed by Giguère and Lamontagne¹, who pointed out the complexity of work with such an electrode resulting from the ready oxidisability of gallium, and the limited opportunities for applying it in analytical chemistry because of its comparatively low hydrogen overpotential (0.3 V lower than on mercury). Grahame² made capacitance measurements at a dropping gallium electrode by means of an a.c. bridge, using slightly acidified solutions to diminish oxidation of the gallium.

In the present work we have assembled a dropping gallium electrode and measured its hydrogen overpotential in 0.1 N HCl and in 0.01 N HCl + x KCl solutions of constant pH as a function of the logarithm of the total concentration of electrolyte in the solution. The design of the dropping gallium electrode was the same as that of the usual dropping mercury electrodes. Because gallium is readily oxidised in air and tends to stick to glass, relatively short capillaries were used, ~5–6 cm and of diameter 0.1 mm, so that the drop time was 1–2 sec. Such a short drop time ensured relatively slight fluctuation in the current flowing through the dropping electrode from the instant of birth of the drop to its breaking away, although the limiting size of the gallium droplets was relatively large. The limiting surface area of a droplet was 0.1 cm², and its diameter ~1.78 mm. Such a large size of droplet was due to the high surface tension, $\sigma \approx 600$ dyn cm⁻¹, and low specific gravity, 6.13 g cm⁻³, of gallium. When capillaries of large diameter were used, divergence of the growing drop from a spherical form became quite appreciable.

The drop size was determined by weighing a definite number of drops after solidification, which was necessary in order to remove solution. When water is removed from the surface of liquid gallium, the latter is rapidly oxidised

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and sticks to the glass. We observed no effect of polarisation on the drop time or size, since our measurements were concentrated within a relatively narrow range of electrode potentials, ~ 0.2 V. No correction was made for the charging current, the maximum value of which did not exceed one-tenth of the current involved in the reaction, so that the maximum error in the value of η corresponding to a given current density did not exceed 5 mV. The order of magnitude of the charging current in the test solutions was estimated from its value at a dropping gallium electrode in 0.01 N KCl solution at the same potentials. Our measurements of η at the dropping gallium electrode were made in a potential region in which the current through the electrode was far smaller than the limiting diffusion current of hydrogen ions, and therefore any possible movements of the surface of the drops, due to the rapid efflux of gallium from the capillary, did not appreciably affect the measurements. In several experiments the gallium droplets were broken off artificially by means of a glass spatula sealed to the end of the capillary†. The artificial cutting off of drops from the capillary was first proposed³ in the case of the dropping mercury electrode. We have observed no appreciable difference between the results obtained with and without the spatula. The anode was a platinum electrode isolated from the main cell by a tap. The potential of the dropping electrode was measured relative to a hydrogen electrode in a solution of the same composition. The apparatus comprising the dropping gallium electrode was placed in an air thermostat at $32 \pm 1^\circ$. The HCl was redistilled twice, and the KCl recrystallised twice and ignited. The purity of the gallium was 99.996%.

Fig. 1 shows the η - $\log i$ curve obtained at a dropping gallium electrode in 0.1 N HCl, allowance having been made in calculating the current density for the variation of the surface of the growing drop with time, as had been done earlier by Iofa *et al.*⁴ for the dropping mercury electrode. Fig. 2 shows the dependence of η on the logarithm of the total electrolyte concentration in the solution, $\log c$, at $i = 3.2 \times 10^{-4}$ A cm⁻² in solutions of constant pH, obtained from measurements of η in solutions containing 0.01 N HCl + x KCl. Values of η at a stationary gallium electrode, measured by the technique described previously⁵, are included in the diagrams for comparison. Good agreement is evident between results obtained on the two types of

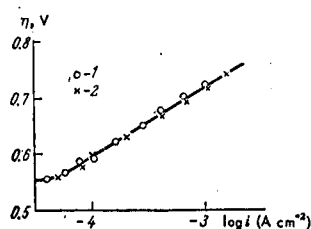


Fig. 1. Curve of η plotted against $\log i$ at gallium electrodes in 0.1 N HCl: 1) dropping electrode; 2) stationary electrode.

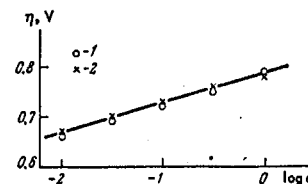


Fig. 2. Dependence of η at $i = 3.2 \times 10^{-4}$ A cm⁻² at gallium electrodes on logarithm of total electrolyte concentration in solutions of 0.01 N HCl + x KCl:

1) dropping electrode; 2) stationary electrode.

gallium electrode. The slope of the polarisation curve corresponds to 110 mV (Fig. 1), and hence $\alpha \approx 0.54$. In conformity with the slow-discharge theory⁶, the hydrogen overpotential on gallium falls by 50–55 mV for a tenfold increase in the total electrolyte concentration (Fig. 2), a value which is close to that predicted to a first approximation by the theory for $t = 32^\circ$, with an approximate expression for the ψ_1 potential in solutions of constant pH and variable c . This result tends to confirm a slow-discharge mechanism on gallium.

The agreement between measurements made at a dropping and at a stationary gallium electrode indicates the validity of results obtained at the dropping gallium electrode.

We express our deep gratitude to Academician A. N. Frumkin for valuable advice.

SUMMARY

1. A dropping gallium electrode has been set up, and the hydrogen overpotential at it has been measured in 0.1 N HCl and 0.01 N HCl + x KCl solutions.
2. The results agree satisfactorily with those obtained at a stationary gallium electrode.

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