A RESEARCH ON THE ABSOLUTE SINGLE POTENTIAL OF THE ELECTRODE.

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"The absolute single potential" of an electrode determined by the electrocapillary curve and the drop mercury electrode has been subjected to various objections.(1) The potential across the Helmholz double layer might vanish at the maximum of electrocapillary curve, while the potential due to selective adsortion would persist. The latter effect may be neglected for the drop mercury electrode in the case of rapid flow of mercury; still we are not sure that the potential across the double layer vanishes in this case. We have tried the method described below by which the point of maximum interface tension is determined by means of a rapid jet of mercury into the solution.

(1) Frumkin, *Ergebnisse der exakten Naturwiss*, **7** (1928), 239. "Handbuch der Experimentalphysik, XII Elektrochemie," 2. Teil, 368.

Our method is based upon the following observations: the height of a mercury jet ejected upward through a small nozzle into a solution depends upon the electrical potential applied between the solution and the mercury; and the rate of the mercury flow is practically independent of the potential. It follows that the mercury is imparted with a constant kinetic energy as it leaves the nozzle. The kinetic energy is partly converted into the surface work which depends on the interface tension at the moment it spreads out into small mercury drops, and the rest of the energy determines the height of the mercury jet. The mininum in height should then correspond to the maximum interface tension.

The apparatus used is illustrated in Fig. 1. The mercury was allowed to flow down from a wide vessel and was ejected through an orifice of 0.08 mm.

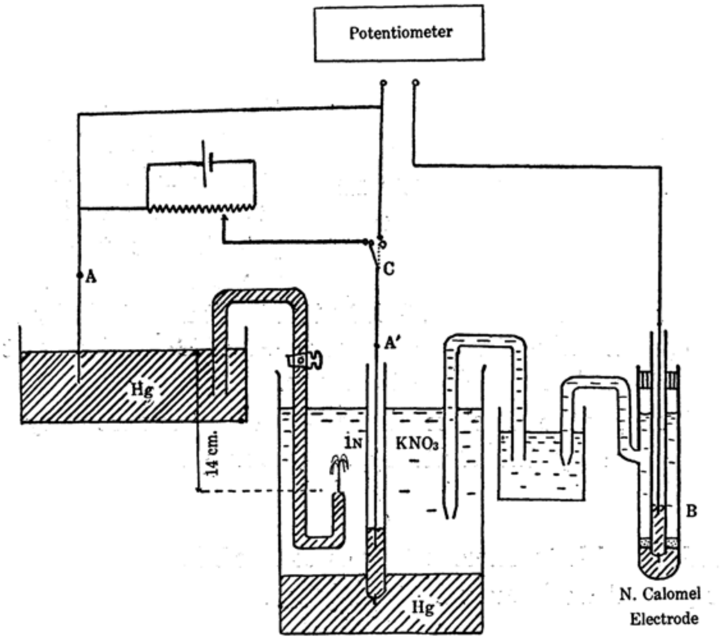

Fig. 1.

diameter into a normal potassium nitrate solution. The mercury head was practically constant during the experiment. The potential varying from zero to 1.5 volts was applied between A and A′, the corresponding potential of mercury jet against a normal calomel electrode B being measured by means of a potentiometer inserted between A and B. The height of the jet was measured with a microcathetometer accurately within 1/100 mm.

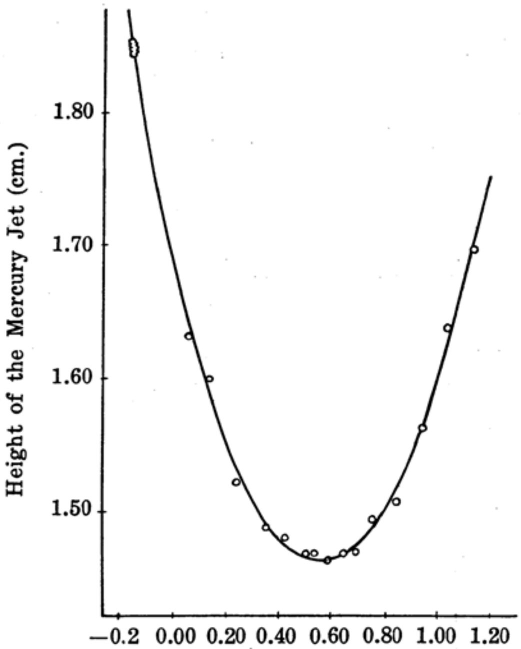

Fig. 2.

The height of the jet was plotted against the measured potential difference between the mercury jet and the normal calomel electrode. One of the series of measurements is shown in Fig. 2. A crowd of points on the upper part of the left branch of the curve shows measurements made in the absence of the applied potential (effected by the commutation C) from time to time between these experiments.

The curve runs parabolic fairly well as is expected from the foregoing reasoning. We obtained therefrom "the absolute single potential" of the normal calomel electrode as the potential at the minimum of the curve. The minimum of this parabola was determined as $+0.560 \pm 0.004$ volt at 20.1°C. by the method of the least square. The other series gave $+0.567 \pm 0.005$ volt at 21.0°C., giving $+0.563 \pm 0.004$ at 20.6°C. as the mean.

This value of "the absolute single potential" agrees very well with former ones given by the electrocapillary curve and the drop mercury electrode.

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