

According to Thomsen<sup>7</sup> the value of  $\Delta H$  for this reaction is  $-13,200$  cal. for  $1 \text{ Au}_2\text{O}_3$  (Aq.) whence  $\Delta S_{298} = (\Delta H - \Delta F)/T = (-13,200 - 19,100)/298 = -108.4$  cal./mol./degree.

The writers wish to express their appreciation to Professor G. N. Lewis, who suggested this investigation.

### Summary

1. Measurements have been made on the cell:  $\text{H}_2(\text{g})$ ,  $\text{H}_2\text{SO}_4(\text{x-M})$ ,  $\text{Au}_2\text{O}_3(\text{s})$ ,  $\text{Au}(\text{s})$ , at three concentrations of sulfuric acid and at  $25^\circ$ . The electromotive force is seen to be substantially independent of concentration of sulfuric acid, the general average value being  $1.364 \pm 0.001$  volts.

2. The free energy of formation of auric oxide from its elements, its dissociation pressure, and entropy of formation at  $298^\circ \text{A}$ . are calculated, all of which indicate that auric oxide is a very unstable compound.

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### NOTES

**Confirmatory Test for Aluminum.**—The test suggested is a modification of that proposed by Attack.<sup>1</sup> It has the advantage that the reagent need not be freshly prepared each time. Further, the color absorption is greater.

The reagent consists of a saturated solution of alizarin in concd. acetic acid.

After separating the aluminum hydroxide from any chromium and zinc, it is washed, dissolved in hydrochloric acid and then reprecipitated with a slight excess of ammonium hydroxide. To this solution is added one drop of the alizarin reagent which imparts an apple-blossom pink coloration to the aluminum hydroxide. The latter will soon settle out, leaving the solution above colorless.

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**Plastic Films and the Drop-Weight Method of Interfacial Tension Measurement.**—The drop-weight method of measuring surface and interfacial tensions has in recent years been greatly refined by Harkins and his co-workers.<sup>1</sup> Not only have they improved the apparatus in a

<sup>7</sup> Thomsen, "Thermochemistry," Longmans, 1908, p. 201.

<sup>1</sup> Attack, *Chem. Zentr.*, [1] **82**, 176 (1916).

<sup>1</sup> Harkins and Brown, *THIS JOURNAL*, **41**, 499 (1919).

mechanical sense but they have also shown that the law of Tate does not apply strictly, since the shape of the drop has an important effect upon the size of each drop, and therefore upon the number of drops formed from a given volume of liquid. It has been found that for reversible conditions a satisfactory correction for the shape effect can be made if the radius of the tip and the size of the drop formed are known.

In view of the importance of the shape development of the drops it is interesting to consider the possible effects of plastic film formation.

The work of Wilson and his students<sup>2</sup> is illuminating in regard to the thickness and mechanical properties of such films. They have determined that the surface films (solid or jell?) formed by sodium stearate on its aqueous dispersions may attain a thickness of 10 to 40 microns<sup>3</sup> and that such films exhibit frictional or plastic characteristics.<sup>4</sup> They also very cleverly demonstrated that a solution of saponin (1 to 1000) with Nujol or castor oil gives an interfacial film exhibiting distinct frictional qualities.<sup>5</sup> Holmes<sup>6</sup> also discusses the mechanism of the building up of thick solid films and describes a very thick film formed between water and a benzene dispersion of gum dammar. Bancroft<sup>7</sup> states that by adding salt to a soap solution the soap film can be made to come out so brittle that it will not form a satisfactory emulsion of oil in water. He believes that for good emulsification the film formed must be tough and elastic.

The above references are sufficient to show that one must consider the possibility of interfacial films being thick and either plastic and tough, or brittle. Plasticity, of course, connotes resistance to flow under low shear.

It has been commonly assumed that plastic films, if developed during the formation of a drop suspended from a dropping tip, would increase the drop size and the apparent interfacial tension. This assumption has as its corollary that plastic films can never be the cause of low apparent interfacial tensions. Is such an assumption justified? I believe not.

If a plastic film is formed around a partially developed drop the effect will be the same as though one had slipped a perfectly fitting casing of plastic material over the drop. If further solution tries to enter such an encased drop this plastic solid casing will resist distention and in order that the drop may increase its volume the body of the drop will be forced away from the dropping tip, thus tending to form an elongated drop.

<sup>2</sup> Wilson and Ries, "First Colloid Symposium Monograph," J. H. Mathews, University of Wisconsin, Madison, Wisconsin, 1923, p. 145.

<sup>3</sup> Ref. 2, p. 164.

<sup>4</sup> Ref. 2, pp. 154-161.

<sup>5</sup> Ref. 2, p. 167, Fig. 18.

<sup>6</sup> Holmes, "Colloidal Behavior" (Bogue), McGraw-Hill Book Co., New York, 1924, pp. 222-232.

<sup>7</sup> Bancroft, "Applied Colloid Chemistry," McGraw-Hill, New York, 1926, p. 352.

Since this elongated drop is formed as the result of a mechanical constriction and the increased surface is not in harmony with the volume of the drop and the interfacial tension, the chances for the drop to snap off before reaching full development are very good.

In extreme cases, that is, in cases in which the interfacial film is both rapidly formed and very tough, the elongated drop shape will be stabilized, as in the case of the drop shown in Wilson's Fig. 18. Another complication which may well arise is the actual adhesion of such a film to the dropping tip. Harkins seems to have had this in mind in referring to a determination<sup>8</sup> in which he obtained an "interfacial tension" of 0.04 dyne/cm. by dropping water containing 0.1 *M* sodium hydroxide and sodium chloride into benzene containing 0.1 *M* oleic acid. He states (p. 77) "In this case a solid film forms, and this causes the drops to hang longer than usual, but the minute value of the tension indicates that the tensile strength of the film is very low." As pointed out above, the "minute value" of the "interfacial tension" may mean that the film is strong and prevents the development of the drop. McBain and Burnett<sup>9</sup> emphasize the tendency for the formation of solid soap curds when salt is present in a soap solution; it is likely that solid films were formed in the case of other determinations reported in Harkins' paper. It would be interesting to know the magnitude of the deviation of individual determinations from the reported mean in the case of certain of these determinations. The check data given on p. 79 are either misprinted or reveal a deviation of 50% among check determinations.

To return to the non-equilibrium "interfacial tension" which Harkins reports as 0.04 dyne/cm. it is worth while to consider, first, the conditions at this "interface" and, second, the definition of interfacial tension. Starting from the inside of the drop we have (1) aqueous solution, (2) interface between aqueous solution and solid soap phase, (3) solid soap phase, (4) interface between solid soap phase and benzene dispersion of fatty acid. *If the solid soap phase touches the dropping tip, there will be no liquid liquid-interface.* The soap film is solid; it will resist distention and will crinkle if the drop tends to grow smaller.

If the soap film does not touch the tip, there will be a true liquid liquid-interface next the tip, but not elsewhere.

Interfacial tension as defined by Willows and Hatschek<sup>10</sup> involves only reversible forces, the stress per cm. being independent of the size of the surface. Clearly, if a plastic solid film touches the dropping tip and completely surrounds the drop there can be no interfacial tension.

<sup>8</sup> Harkins and Zollman, *THIS JOURNAL*, **48**, 69 (1926).

<sup>9</sup> McBain and Burnett, *J. Chem. Soc.*, **121**, 1332 (1922).

<sup>10</sup> Willows and Hatschek, "Surface Tension and Surface Energy," P. Blakiston's Son and Co., Philadelphia, 1923, p. 2.

Measurements made under conditions which make it probable that such a condition existed during the determinations should not be reported as "interfacial tensions," because they can in no way satisfy the fundamental requirement of reversibility.

In case the plastic film merely approaches but does not touch the tip, a true liquid-liquid interface will exist next the tip and the plastic film can only affect the results by influencing the shape development of the drop. Since the correction factor, which is dependent upon the shape development, varies from 1.3 to 1.8, it seems conservative to state that it is impossible to ignore any condition or set of conditions which is capable of affecting this shape development.

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**The Purification of Toluene for Thermo-Regulators.**—For use in a mercury-toluene thermo-regulator the toluene must be free from traces of certain impurities, notably sulfur compounds, which will foul the surface of the mercury and interfere with the sharp adjustment of the regulator. According to Vanino,<sup>1</sup> toluene may be purified by washing it repeatedly with sulfuric acid, then with water until the washings are neutral to litmus paper, and finally drying the toluene over metallic sodium.

A quantity of c. p. toluene purified according to Vanino's directions was still found to corrode the mercury. It occurred to us to determine the effect of sodium amalgam. The toluene was accordingly boiled under a reflux condenser with sodium amalgam containing 1% of sodium. The toluene was then decanted, washed with water and finally distilled. The water remaining in the toluene was all removed with the first small fraction of the distillate, which was accordingly rejected.

The toluene purified in this manner has been in use for several months without showing any action upon the surface of the mercury.

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<sup>1</sup> Vanino, "Handbuch der präparativen Chemie," Organischer Teil, p. 345.