Summary

1. Supported catalysts of iron, cobalt, nickel, copper and silver have been prepared by as nearly similar methods as possible and their activity in the hydrogenation of ethylene has been determined. Cobalt and nickel caused instantaneous action at $-20°$, iron was moderately active at $0°$, copper at $50°$ and silver at $100°$. The effect of the support appears to be to increase the effectiveness of all but copper. This is discussed.

2. Adsorption measurements show much more hydrogen adsorbed by nickel and cobalt than by the other metals, and more ethylene is adsorbed by iron.

3. Reaction kinetics in the presence of silver at $100°$ show that the rate is proportional to the hydrogen and independent of the ethylene concentration, as was found for copper. In the presence of iron at $0°$, excess of hydrogen increases the rate while excess of ethylene exerts little influence.

4. Attention is called to the periodicity among the metals in catalytic properties and the correlation with complex ion formation. An association rather than a dissociation theory of catalytic hydrogenation is indicated.

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A SIMPLE TYPE OF FLOWING JUNCTION

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In connection with a study of the relation of the potential of an antimony electrode in contact with a solution saturated with antimony trioxide to the acidity of that solution, the problem of obtaining a reproducible liquid junction potential between the antimony electrode and the reference electrode (Ag, AgCl, 3.5 M KCl) became of prime importance. The electrode vessels used were modifications of the type described by Brönsted,[1] in which the solution flows slowly down through a deep layer of the saturating substance, past the electrode proper, to the junction; therefore, a flowing junction device requiring only small volumes of electrolyte and possessing an easy flexibility of adjustment to solutions of widely varying density was highly desirable. None of the arrangements previously described[2] meet these requirements. It was found, however, that by interposition of a thin mica plate vertically between the ends of the pair of horizontal exit tubes from the electrodes so that the streaming electrolytes flow slowly down opposite faces of the plate past a small hole, through which alone the solutions make contact, the resulting junction is satisfactory in all respects.

[1] Brönsted, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, **3**, No. 9 (1920).

[2] Lamb and Larson, THIS JOURNAL, **42**, 229 (1920); (b) MacInnes and Yeh, *ibid.*, **43**, 2563 (1921); (c) Scatchard, *ibid.*, **47**, 696 (1925).

A diagram of the arrangement of the electrodes and of the mica plate is presented in the figure, which also illustrates the shape of plate finally adopted. M is the type of electrode vessel developed for the calomel electrode as a simply made, convenient form for use with a flowing junction. S is the type of vessel employed either for the silver-silver chloride electrode used in testing the reliability and value of this type of junction, or for the antimony-antimony trioxide electrode to be discussed in a later paper;
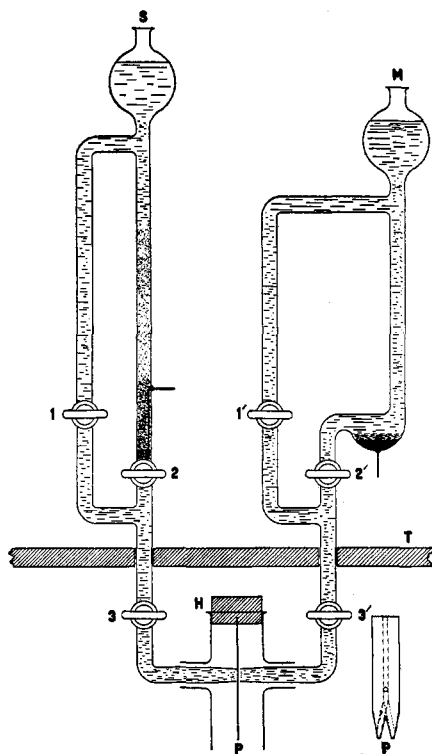

its length above the upper stopcocks is about 20 cm., the capacity of the bulb being 25–50 cc. The lower end of each vessel is bent horizontally, tapered, if necessary, to an internal diameter of 2–3 mm. and paraffined near the tip to obviate creeping of the liquid. These tips slip into side tubes in a glass tube H and are adjusted so that the issuing drops of liquid touch the mica plate P, conveniently held in a gash in a rubber stopper in H. The detail drawing of the plate shows its construction. A hole about 1 mm. in diameter is drilled in a thin strip of mica (about 1.5 by 7 cm.) by means of a glass-rod drill, working from both sides of the plate so that the edges are as smooth as possible; it is placed about 5 mm. below the exit tubes of the electrodes. The lower edge of the plate is notched and the faces are painted with hot paraffin, except for a narrow channel (indicated by dotted lines) past the

Fig. 1.—Arrangement of apparatus and detail of mica plate for liquid junction.

hole to one of the points, opposite points on the two sides; this insures that the only liquid junction is at the aperture in the plate.

The electrodes were kept in an air thermostat maintained at $25 \pm 0.02°$, the exit tubes passing through the floor of the air chamber, T. The temperature of the surroundings was usually about 3° below that of the thermostat but the junction potentials encountered in the solutions investigated were sufficiently low so that changes due to fluctuations in the room temperature could be neglected. The cocks 3 and 3′, attached to the electrodes by means of rubber tubing for convenience in filling the vessels, have their keys scratched near the bore at both ends, the scratches

being diametrically opposite, to facilitate the adjustment of the rate of flow.   Cocks 2 and 2' serve for the thorough washing of the metal electrode with the electrolyte when the electrode is set up and at frequent intervals when it is in use but they are kept closed during the actual measurements, the by-pass cocks 1 and 1' being open.   Before the mica plate is set in place the flow of the electrolytes is made as nearly equal as possible, 4–6 drops per minute being a suitable rate; then the plate is inserted and the exit tubes are brought against the opposite faces.   The potential very quickly adjusts itself to a constant value, the time required being usually a matter of seconds and never more than a few minutes.   Under favorable conditions (that is, small junction potentials) the variation in the potential proved to be less than 0.05 mv. over a period of several days.

The Liquid Junction Potential Between 0.1 M HCl and 0.1 M KCl at 25°

In order to test the accuracy and reproducibility of the junction potentials obtained with the device described, the potential between 0.1 M HCl and 0.1 M KCl, which has been investigated by MacInnes and Yeh,[2b] was measured.

Preparation of Material

Silver.—Crystals of metallic silver were prepared by the rapid electrolysis of a solution of silver nitrate between small platinum wire electrodes, the anode being placed in a porous cup to prevent contamination of the metal with silver peroxide.   The silver crystals were packed in a close mass around the platinum lead wire in the electrode vessel, held in place by a cotton plug at the bottom and covered with a layer of *crystalline* silver chloride about 10 cm. deep.

Silver Chloride.[3]—Silver chloride was precipitated from a solution of silver nitrate by the addition of a solution of constant-boiling hydrochloric acid and the carefully washed precipitate dissolved in redistilled ammonium hydroxide.   The resulting solution was filtered and the ammonia removed by absorption in sulfuric acid under a bell jar.   The crystals of silver chloride were filtered and dried in a vacuum.   The salt was protected from the action of light by a red lacquer coating on the electrode vessel and on the heating lamps of the thermostat.   No appreciable darkening had occurred after five months' use of an electrode.

Mercury.—Mercury was purified by running it in a fine stream several times through a solution of mercurous nitrate and nitric acid, followed by distillation in a vacuum.

Calomel.—Pure mercury was dissolved in nitric acid, the mercury being present in considerable excess, and mercurous chloride precipitated by the addition of a solution of constant-boiling hydrochloric acid.   After washing many times by decantation, the mixture of mercury and mercurous chloride was sucked dry on a Büchner funnel and shaken several days with water, changing the water every few hours.   The material was kept under water in a brown bottle until required, when it was washed repeatedly with the particular solution to be used in the electrode under construction.

Potassium Chloride.—Ordinary "c. p." potassium chloride was recrystallized three times.

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[3] Crystalline silver chloride prepared by this method has been used by Professor J. N. Brönsted.

Hydrochloric Acid.—A strictly 0.1 M solution of hydrochloric acid was prepared by diluting a slightly stronger, carefully analyzed solution of the constant-boiling acid.

The following single electrodes were made up: (1) Ag, AgCl, 0.1 M HCl; (2) Ag, AgCl, 0.1 M KCl; (3) Hg, Hg$_2$Cl$_2$, 0.1 M KCl. The solutions used in all the electrodes were saturated with the corresponding metal chloride by shaking with an excess of the salt for from three to twelve hours in the thermostat before they were put into the electrode vessels. It is evident that the difference in potential between the first and second electrodes is a direct measure of the junction potential if the usual assumption is made that the activity of chloride ion in two fairly dilute solutions of equal ionic strength is the same. It is also apparent that there is no junction potential between the second and third electrodes and that the junction between the first and third is sensibly the same as between the first and second. Therefore, the difference in potential between the two possible cells comprising the calomel electrode as one pole is a measure of the junction potential. The experimentally determined potentials and their deviations over the period of observation are listed in Table I.

TABLE I

THE MEASURED POTENTIAL AT THE JUNCTION OF 0.1 M HCL AND 0.1 M KCL AT 25°

Cell	Potential, mv.	Mean deviation, mv.
Ag, AgCl, 0.1 M HCl | 0.1 M KCl, AgCl, Ag	28.0$_0$	0.03
Ag, AgCl, 0.1 M HCl | 0.1 M KCl, Hg$_2$Cl$_2$, Hg	73.3	.15
Ag, AgCl, 0.1 M KCl, Hg$_2$Cl$_2$, Hg	45.3$_0$	.05
(By difference)		
Ag, AgCl, 0.1 M HCl | 0.1 M KCl, AgCl, Ag	28.0$_0$	

The difference in potential between a silver chloride electrode and a calomel electrode in the same chloride solution, the third cell in Table I, has been measured by Gerke[4] for 1.0 M KCl and 1.0 M HCl. He obtained 45.5 mv. at 25°, which is in close agreement with our value of 45.3 mv. Both sets of measurements were made with finely divided crystalline silver electrodes but Gerke used the granular silver chloride obtained by direct precipitation. The value computed by Scatchard[2c] from his revised activity data is 46.6 mv. The discrepancy between this last value and those obtained by direct measurement is probably due to the method of extrapolation used in deriving the activities, which is not entirely inarbitrary, since Scatchard found excellent uniformity between silver electrodes prepared by three different methods—finely divided crystalline metal made electrolytically by Linhart,[5] that obtained from the thermal decomposition of silver oxide by Noyes and Ellis,[6] and his own electroplated platinum.[7]

[4] Gerke, THIS JOURNAL, 44, 1684 (1922).

[5] Linhart, ibid., 41, 1175 (1919).

[6] Noyes and Ellis, ibid., 39, 2532 (1917).

[7] Scatchard, ibid., 47, 641 (1925).

A summary of a number of values for the liquid junction potential is given in Table II.

TABLE II

COMPARISON OF VALUES FOR THE POTENTIAL AT THE JUNCTION OF $0.1\ M$ HCL AND $0.1\ M$ KCL AT $25°$

	Potential, mv.
Measured directly	28.0_0
By difference	28.0_0
Measured directly, MacInnes and Yeh	26.78
Computed, Lewis and Sargent formula	28.4

It will be observed that our value is greater than that found by Mac-Innes and Yeh, lying between the value of the latter authors and that computed by the Lewis and Sargent formula,[8] $E_j = RT/F \ln \Lambda/\Lambda'$. The ratio of the equivalent conductances of 0.1 M HCl and 0.1 M KCl, Λ/Λ', calculated from our measured value of the junction potential, E_j, is 2.974. From the conductance data given by MacInnes and Yeh this ratio is 3.026. The difference, 1.7%, is far too great to be accounted for by any probable error in the conductivity measurements. It seems most plausible to ascribe the discrepancy to the abnormality of the potassium ion pointed out by MacInnes and Yeh, who found good correspondence between the calculated and measured junction potentials at the boundaries of a number of univalent chloride solutions except in the presence of potassium ion.

The reproducibility of the potentials at the liquid junctions formed in the manner described is certainly within 0.2 mv.; with regard to the absolute accuracy no definite statement can be made. The extreme simplicity of the arrangement, the ease and rapidity with which it can be set up and the fact that a small volume of liquid suffices for quite an extended series of measurements may be emphasized. Moreover, it eliminates the necessity of maintaining the column heights in the two arms of the cell in inverse ratio to the densities of the electrode solutions to insure equal rates of flow, a marked advantage over other forms of flowing junction.

In conclusion the authors wish to acknowledge their indebtedness to Dr. John Johnston for many valuable suggestions in connection with this work.

Summary

A simple arrangement for obtaining reproducible liquid junction potentials between two flowing electrolytes is described and its applicability tested by determining the potential at the boundary of 0.1 M HCl and 0.1 M KCl. The result obtained is in satisfactory agreement with that computed from the theoretical equation of Lewis and Sargent and in fair accord with the measured value of MacInnes and Yeh.

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[8] Lewis and Sargent, THIS JOURNAL, **31**, 363 (1909).