The authors believe that determinations of the Sörensen value of sea water by the method of Barnett and Barnett, with the applications of the corrections given above, afford the most exact results attainable by any colorimetric method as yet developed. This is true also of straight sodium chloride solutions (Wells, Ref. 2), and probably of solutions of other uni-univalent salts of this general type.

As the indicator constant for cresol red (8.13) was determined on the basis of the standard borate and phosphate mixtures of Clark and Lubs, the corrections given should apply as well to tube determinations of the Sörensen value of saline solutions in which the buffered standards of those authors are used.

Summary

The salt error of cresol red (*o*-cresolsulfonephthalein) in solutions containing from 5 to 35 parts per 1000 of sea salts has been determined on the basis of comparative colorimetric and electrometric studies of the Sörensen values of samples of sea water of known salinity. The results are presented in tabular form.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

THE CATALYTIC COMBINATION OF ETHYLENE AND HYDROGEN IN THE PRESENCE OF METALLIC COPPER

III. CARBON MONOXIDE AS A CATALYST POISON

BY ROBERT N. PEASE AND LELAND STEWART

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Facts of some importance to the adsorption theory of contact catalysis were established in a previous investigation[1] of the catalytic and adsorbent properties of metallic copper granules before and after "poisoning" with mercury. The adsorption isotherms at 0° of hydrogen, ethylene and carbon monoxide were displaced nearly parallel to themselves in the direction of less adsorption after the poisoning; that is, the mercury had the effect of preventing the "strong" (low-pressure) adsorption, though not affecting the weaker (high-pressure) adsorption appreciably. At the same time, the catalytic activity of the copper at 0° toward a hydrogen-ethylene mixture was almost completely destroyed. A correlation of catalytic activity and "strong," as opposed to general, adsorption was thus observed in the fact that poisoning brought about simultaneous disappearance of the two.

A detailed investigation of this relation promised to be somewhat laborious and unsatisfactory because of the difficulty of introducing very small but accurately known quantities of mercury and because this sub-

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[1] Pease, THIS JOURNAL, **45**, 2296 (1923).

stance is a permanent poison. The work was therefore dropped. It appeared, however, that much might be learned from a study of the effects of a poison. For this purpose, carbon monoxide seemed to possess many advantages in that it is well known to be a powerful poison to hydrogenation catalysts, it was shown in the previous investigation to be adsorbed in greater quantity at low pressures than ethylene or hydrogen, and its adsorption was reversible. A set of measurements was accordingly made in which the effect of carbon monoxide on the activity of a copper catalyst toward a hydrogen-ethylene mixture at 0° was determined.

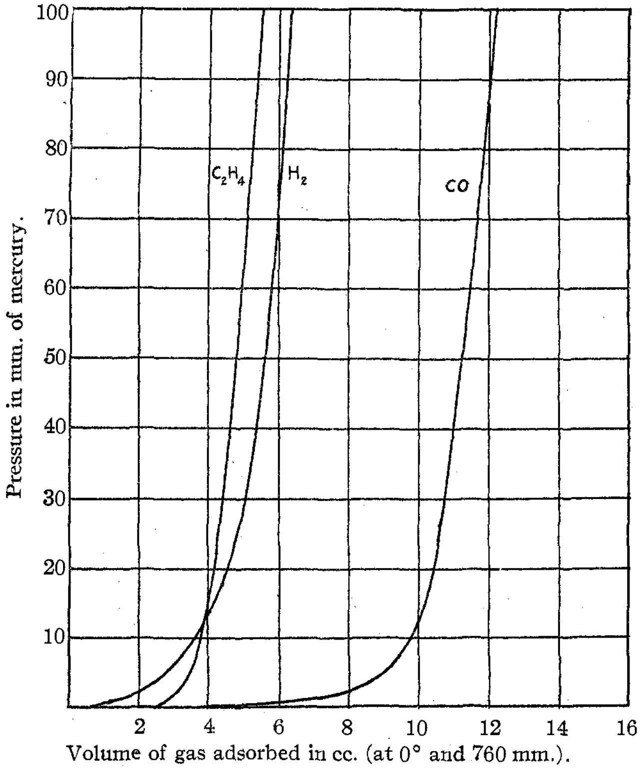

Fig. 1.—Adsorption isotherms of hydrogen, ethylene and carbon monoxide on active copper at 0°.

Procedure.—The details of the methods of preparation of catalyst and gases and of making the measurements were the same as those described by Pease.[2] About 100 g. of copper granules was used as catalyst.

In the preliminary experiments the carbon monoxide was introduced admixed with the reacting gases. The results were somewhat unsatisfactory because an appreciable time elapsed before the full effect of the

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[2] Pease, This Journal, **45**, 1196 (1923). Ref. 1.

poison was apparent, and during this period reaction had sometimes proceeded nearly to completion, the catalyst being a very active one. In the final experiments, the poison was introduced into the catalyst bulb some time before the reactants. This proved much more satisfactory.

Blank experiments (in which no carbon monoxide was added) were run as checks with results which were for the most part satisfactory. The only drawback was that when large amounts of the poison had been used in a previous run the activity was found to have increased noticeably. The reason for this is not clear unless it is that some slight oxidation had occurred through a series of runs and that the oxide, reduced at a low temperature by the carbon monoxide, left a little very active copper. For the rest it can be said that carbon monoxide is a perfectly temporary poison, pumping out at 250° being sufficient to restore the activity of the catalyst.

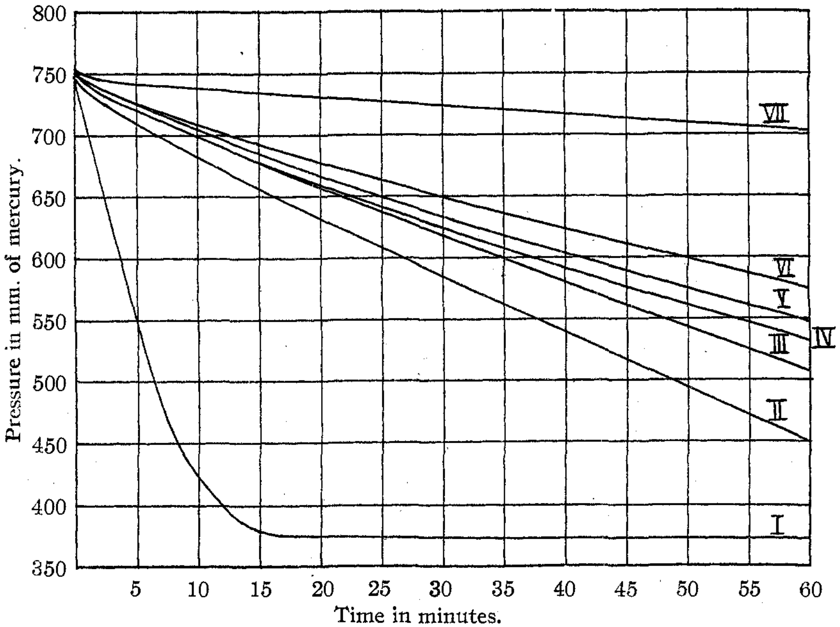

Fig. 2.—Velocity measurements on ethylene-hydrogen mixtures at 0° in the presence of carbon monoxide.

Curves I—no CO; II—<0.05 cc. CO; III—0.08 cc. CO; IV—0.33 cc. CO; V—0.69 cc. CO; VI—1.97 cc. CO; VII—9.14 cc. CO.

Results.—Adsorption isotherms of hydrogen, ethylene and carbon monoxide at 0° are shown in Fig. 1. These are similar in essentials to those obtained by Pease except that the adsorption of ethylene at higher pressures is somewhat less, relative to the other two gases. Carbon monoxide is adsorbed in much greater quantity than either hydrogen or ethylene over the whole range.

The velocity measurements in which carbon monoxide was introduced prior to the reactants are shown in Fig. 2. Although a marked effect had been expected of the carbon monoxide, the magnitude of that observed was something of a surprise. Curve I, Fig. 2, corresponds to the standard run in the absence of carbon monoxide. Curve II corresponds to a run in which less than 0.05 cc. of carbon monoxide (that is, the amount required to fill the bore of the stopcock plug) had first been introduced. A comparison of the two reveals the fact that this minute quantity of carbon monoxide reduced the activity to approximately 11% of its normal value (based on the time taken for the pressure to fall from 700 to 600 mm.). Larger quantities of carbon monoxide produced somewhat greater effects, 1.97 cc. bringing the activity to 5% (Curve VI) and 9.14 cc. to 1% (Curve VII) of the normal. The relatively greater efficacy of the smaller quantities needs no comment, however. A graph of relative activity against volume of carbon monoxide is given in Fig. 3.

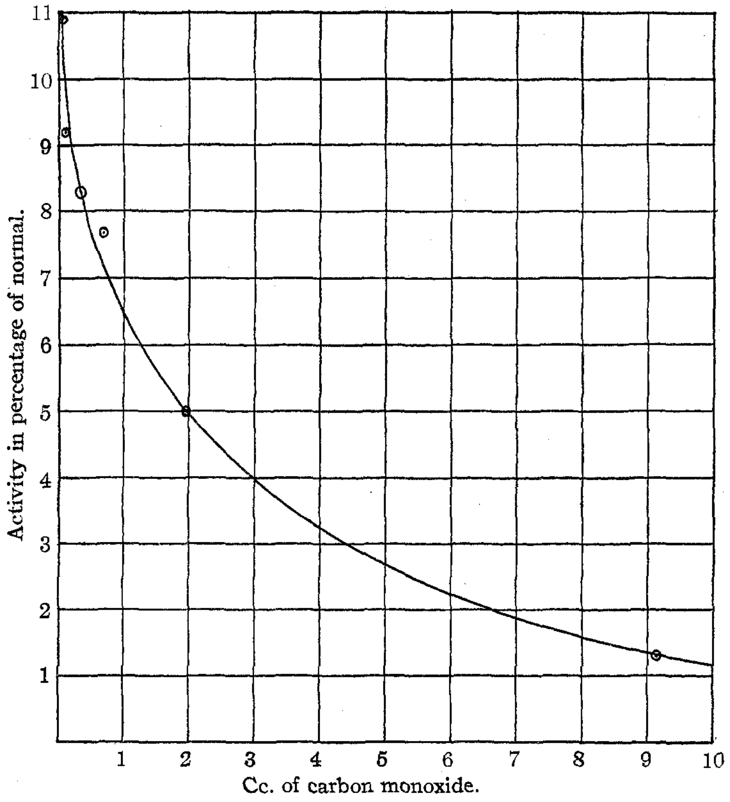

Fig. 3.—Activity of the catalyst as a function of the volume of carbon monoxide introduced.

It had been planned to determine the influence of carbon monoxide on the adsorptions of hydrogen and ethylene, after the completion of the velocity measurements. Unfortunately, a quantity of mercury was accidentally introduced and this part of the investigation was given up. Calculations based on the extrapolated initial pressures in the velocity measurements showed clearly enough that the adsorption of the reacting mixture was reduced by the presence of carbon monoxide. The effect was not marked, however, and by no means did it compare with the effect on reaction velocity. Roughly speaking, the adsorption of the mixture was decreased by an amount equal to the volume of carbon monoxide already in the bulb (and, hence, largely adsorbed), in the case of the smaller quantities used.

Discussion

In our opinion, the most important fact established by this investigation is that 0.05 cc. of carbon monoxide will reduce by 88% the activity (toward an ethylene-hydrogen mixture at 0°) of a copper catalyst that adsorbs at less than 1 mm. pressure approximately 1 cc. of hydrogen, 2 cc. of ethylene or 5 cc. of carbon monoxide. The following seems to be the only straightforward explanation of this result if we exclude the possibility of adsorption layers more than one molecule thick.

We assume that the catalyst surface is not all of equal activity, but that active centers or regions of different degrees of activity are scattered over it. Further, those centers on which are formed the most stable adsorption complexes are also those which have the greatest power of activating the reacting molecules. When carbon monoxide is introduced into the catalyst bulb, the molecules eventually come to rest on the most active centers and put these temporarily out of action. Its effectiveness in this regard will depend upon the distribution of activity among the centers. The fact that this particular catalyst surface adsorbs at least 5 cc. of carbon monoxide strongly but is incapacitated to the extent of 89% by 0.05 cc. of this gas, means that the surface owes 89% of its catalytic activity toward ethylene-hydrogen to less than 1% of the centers active in adsorption. Further, unless 0.05 cc. of carbon monoxide is capable of displacing quantities of ethylene and hydrogen of the order of 1 cc., which appears doubtful, the net result is that the adsorption of reactants at pressures even as low as 1 mm. is not going to serve as a quantitative measure of catalytic activity.

Experiments carried out by Maxted on the poisoning of catalysts used in the hydrogenation of oils are of interest in this connection. The first investigation[3] was designed to show the effect of varying percentages of carbon monoxide in the hydrogen employed in the hydrogenation of olive

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[3] Maxted, *Trans. Faraday Soc.*, **13**, 36 (1917).

oil in the presence of nickel. The results are considerably complicated by the fact that the partial pressure of carbon monoxide in the reaction vessel is constantly increasing. It is clear, however, that the poison is relatively more efficient in the smaller quantities. Its efficiency does not approach that found in the work just reported, the difference being perhaps partly traceable to the much higher temperature (180°) of the catalyst in Maxted's experiments. Later work[4] has been directed at the correlation of decreases in adsorption and catalytic activity of platinum and palladium catalysts due to addition of such permanent poisons as sulfur (as hydrogen sulfide), arsenic, lead and the like. It has been found that for small additions of poisons a linear relation exists between amount of poison and both adsorption (or occlusion) and activity. However, the poison is much more effective against catalytic activity than against adsorption, a result which is in harmony with the work of the authors.

Summary

In a quantitative study of the influence of carbon monoxide on the activity of a copper catalyst toward an ethylene-hydrogen mixture at 0°, it was found that the catalyst (which was a very active one) was excessively sensitive to this poison, less than 0.05 cc. of carbon monoxide being sufficient to reduce the catalytic activity by nearly 90%. This value is compared with the results of adsorption measurements and it is concluded that adsorptions at pressures even as low as one mm. are in all probability not a trustworthy index of catalytic activity for hydrogenation catalysts of this type.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 52]

THE INITIAL RATE OF DECOMPOSITION OF NITROGEN PENTOXIDE

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Introduction

The decomposition of nitrogen pentoxide is a reaction peculiarly well adapted for study in connection with theories as to reaction velocities and their temperature coefficients. It is perhaps the only known unimolecular gas reaction which is not appreciably catalyzed by the walls of the containing vessel, and it proceeds at moderate temperature at a rate convenient for measurement, the chief disadvantage being the corrosive action of the substance on mercury, rubber and other materials ordinarily used in handling gases.

[4] Maxted, *J. Chem. Soc.*, **119**, 1280 (1921).