In other cases, the only legitimate deduction is that the equations tested serve very well as interpolation equations over a restricted range.

5. No confirmation of the theory of Ghosh is afforded by the experimental data for (a) the variation of equivalent conductivity with dilution for salts in aqueous solution, (b) the temperature coefficient of the ratio μ_v/μ_∞, (c) the electrical conductivity of non-aqueous solutions, (d) the molecular number i and the Clausius theorem, (e) the ionization of strong acids, (f) the ionization of weak acids, (g) the ionization of transition acids, (h) the electrical conductivity of pure salts in the solid and fused states, (i) the conductivity of salts in mixtures of pyridine and water, (j) the ionization of salts in solvents of low dielectric constant, (k) the distribution of a salt between an ionizing and a non-ionizing solvent, (l) the vapor pressure of the hydrogen halides in aqueous solution.

6. The rôle of the solvent in ionization, which is ignored altogether by Ghosh, must be taken into account in any complete theory of conducting solutions.

7. In its present form, the ionization hypothesis of Ghosh is unacceptable, and certain of the postulates upon which it is based must be either modified or rejected.

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THE PREFERENTIAL CATALYTIC COMBUSTION OF CARBON MONOXIDE IN HYDROGEN*

By ARTHUR B. LAMB, CHARLES C. SCALIONE AND GRAHAM EDGAR

An important factor in the commercial success of the Haber process for the synthesis of ammonia is the cost of the pure hydrogen which it requires. At present this hydrogen is usually obtained by "converting" mixed water- and producer- gas using a considerable excess of steam and a suitable catalyst, into a mixture relatively rich in hydrogen and carbon dioxide, and poor in carbon monoxide. The carbon dioxide is then largely removed by a thorough water-scrubbing under moderate pressures. The compositions of these gaseous mixtures are as follows, according to R. S. Tour.[1]

[1] Tour, *J. Ind. Eng. Chem.*, 12, 844 (1920).

	After conversion %	After water-scrubbing %
H₂	52–52	73–72
N₂	17–17	24–23
CO₂	29–27	0.1–1.0
CO	2–4	3–5
X	0.4–0.8	0.5–1.0

where X = argon, methane, etc.

To remove the 3 to 5% of carbon monoxide remaining in the gaseous mixture after the water-scrubbing, the practice has been to scrub thoroughly under high pressure with ammoniacal solutions of cuprous salts. By this means the carbon monoxide content can be reduced to between 0.1 and 0.01%. This degree of purity may be adequate, but the process is difficult and costly. It is desirable therefore, if possible, to devise one which is simpler and more economical.

With this requirement in mind, we have investigated the behavior of an absorbent for carbon monoxide called Hopcalite, developed during the war by the U. S. Bureau of Mines and the Chemical Warfare Service of the U. S. Army.[2] This material, consisting of a mixture of metallic oxides, is not strictly speaking an absorbent, for it operates by burning the carbon monoxide catalytically at the expense of the oxygen of the air; and if the air is adequately dried, it is not itself altered in the process. If this material should prove to be unaffected by hydrogen under any feasible conditions at which it would catalytically oxidize carbon monoxide, there appears to be the possibility of a cheap and simple method for the removal of carbon monoxide from the above mentioned mixture.

There is a good deal of evidence in the literature that as a rule easily reducible oxides are reduced at lower temperatures by carbon monoxide than by hydrogen. Thus, Campbell[3] found for a specially prepared copper oxide, and Wright and Luff[4] for different varieties of the various oxides of copper, iron, manganese, lead, nickel, and cobalt, initial temperatures of reduction averaging about 60° lower for carbon monoxide than for hydrogen. Fay, Southerland and Ferguson[5] obtained similar results with the oxides listed in the following table.

TABLE I

INITIAL TEMPERATURES OF REDUCTION

Oxide	With CO °C.	With H₂ °C.	Oxide	With CO °C.	With H₂ °C.
Au₂O₃	0	0	HgO red	90	125
Ag₂O	0	0	CdO	140	125
Hg₂O	0	80	CrO₃	95–100	140–150
HgO yellow	0	50			

[2] Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, 12, 213 (1920).

[3] Campbell, *Am. Chem. J.*, 17, 688 (1895).

[4] Wright and Luff, *J. Chem. Soc.*, 33, 1, 504 (1878).

[5] Fay, Southerland and Ferguson, *Poly. Engineering*, 10, 72 (1910).

It seemed not unlikely, therefore, that Hopcalite would also require a higher temperature to react with hydrogen than with carbon monoxide, and that a range of temperatures would exist in which carbon monoxide might be completely and rapidly oxidized, while hydrogen would be unaffected. We have therefore studied the behavior of Hopcalite toward both dry and moist mixtures of hydrogen and air, of carbon monoxide and air, and of hydrogen and carbon monoxide and air.

Behavior of Hopcalite toward a Dry Mixture of Hydrogen and Air

We first tried the behavior of Hopcalite at room temperature toward a dry mixture of 90% hydrogen and 10% air.[6] The Hopcalite was contained in a glass tube of 3 sq. cm. cross section in a layer 5 cm. deep. The glass tube was surrounded by a larger glass tube wound with a spiral of Nichrome ribbon which could be electrically heated. A thermometer was fitted into the inner tube with its bulb just above the catalyst. The affluent gas mixture passing up through the narrow annular space between the two tubes was preheated, and then passed downward through the catalyst. The gas mixture was prepared by mixing hydrogen from a pressure cylinder in the proper proportions with air from a gasometer by means of flowmeters, and drawing this mixture through a third flowmeter, through bead drying towers containing sulfuric acid, and thence leading it into the catalyst tube. A rate of flow of 1500 cc. per minute was adopted, corresponding to a space velocity of 6000 per hour.[7] Under these conditions after a half hour's running no warming of the Hopcalite occurred, and hence no considerable oxidation of hydrogen could have taken place. When, however, the temperature of the affluent gases was raised to about 60° or 70° rapid oxidation of the hydrogen set in, and the catalyst became incandescent. Since

[6] The Hopcalite catalyst used in this investigation was prepared in the small experimental plant at the American University [for full details see Merrill and Scalione, THIS JOURNAL, 43, 1982 (1921)]. It was a 2-component mixture consisting of 60% of MnO_2 and 40% of CuO, primarily designed for a carbon monoxide absorbent or catalyst for gas-mask canisters. All precipitations were carried out in iron containers; but the precipitates were washed in wooden tanks by decantation, ordinary tap water being used.

The preparation of each component of the Hopcalite mixture was as follows. The manganese dioxide was prepared from manganous sulfate and potassium permanganate in strong sulfuric acid solution, the first step being the formation of $Mn(SO_4)_2$. On dilution the $Mn(SO_4)_2$ is hydrolyzed to MnO_2 giving a very finely divided precipitate which is extremely satisfactory as a component in this catalytic absorbent. The MnO_2 was activated by mixing with it 40% of cupric oxide prepared from basic copper carbonate. After the thorough mixing of these two thoroughly washed pulps in a kneader and compression of the mixture under 6000 lbs. per sq. inch, the pressed cake was dried at 120-130°, crushed to the desired mesh (in these experiments 10–16), screened, and redried for 3 hours at 200°.

[7] *I. e.*, 6000 liters per liter of catalyst per hour.

Hopcalite oxidizes carbon monoxide catalytically under these conditions, at temperatures of 0° and lower,[2] this experiment indicates that it should be possible to oxidize carbon monoxide preferentially in the presence of a large excess of hydrogen at room temperature, provided there is no induction effect of the burning carbon monoxide on the hydrogen.

Behavior of Hopcalite toward a Dry Mixture of Hydrogen, Carbon Monoxide and Air

To test the above conclusions, a mixture of 89.5% of hydrogen, 0.5% of carbon monoxide and 10% of air was dried and passed through the catalyst at a space velocity of 6000 per hour, and provision made to detect any water formed or carbon monoxide remaining unburned. The procedure was as follows.

Hydrogen prepared from zinc and hydrochloric acid, and purified from arsine and phosphine, was mixed in a large gasometer with the required proportions of air and of carbon monoxide prepared from formic acid. From this the gas mixture passed through 2 bead towers charged with sulfuric acid, through a flowmeter, and then into an unjacketed glass tube of 1 sq. cm. cross section containing the catalyst. Issuing from this. it passed through a weighed U-tube containing phosphorus pentoxide, through bead towers containing a solution of potassium hydroxide, and then through 2 Gomberg bulbs charged with a solution of barium hydroxide to indicate the completeness of the removal of the carbon dioxide. The gases were now led through a quartz tube filled with copper turnings and heated electrically to 300°, in order to oxidize any carbon monoxide not burned in the catalyst; through 2 more Gomberg bulbs containing barium hydroxide solution, and finally through the rotary oil pump to waste. A rate of flow of 500 cc. per minute corresponding to a space velocity of 6000 per hour was maintained. The experiment was continued for 1 hour, but no increase in weight of the phosphorus pentoxide tube occurred, nor was there any test for carbon dioxide in the final Gomberg bulb. The experiment was repeated several times with other samples of Hopcalite, with identical results. This demonstrates that the carbon monoxide is completely burned under these conditions, and that no more than a trace of hydrogen can have been oxidized.[8]

The same experiment was now tried with a gas mixture of similar composition except that it contained 1% of carbon monoxide. The reaction proceeded smoothly for 7 minutes, whereupon the Hopcalite became incandescent. Considerable moisture deposited on the walls of the catalyst tube and collected in the phosphorus pentoxide tube. The experiment was repeated several times with different samples of Hopcalite with the same result.

These experiments indicate that with 1% carbon monoxide the heat of reaction is so considerable that oxidation of the hydrogen begins and a rapid incandescence follows.

[8] It does not demonstrate that *no* hydrogen burned, for we know that the Hopcalite is decidedly hygroscopic, and traces of moisture, if formed, might have been retained in it. However, since no decrease in its efficiency occurred, no more than a few cg. of water could have been formed with the small amount of catalyst used, and this would correspond to a ratio of less than 1:100 between the amount of hydrogen and carbon monoxide burned.

Behavior of Hopcalite toward a Moist Mixture of Hydrogen and Air

The actual gases to be purified in the manufacture of hydrogen from water-gas are saturated with water at a temperature of perhaps 30°, and it is desirable to remove the carbon monoxide from this mixture if possible without drying. The behavior of Hopcalite toward moist mixtures of hydrogen and air was therefore tried.

In order to detect the first trace of action with greater certainty than in the former experiments a different type of catalyst tube was employed. It consisted of 3 concentric metal tubes. The inner one of about 2 sq. cm. cross section served as a cooling tube, and water could be circulated through it. The intermediate tube was of about 5 sq. cm. cross section, and the catalyst was contained in a layer 5 cm. deep in the annular space between it and the inner tube. In the catalyst were placed 4 thermocouples at different depths. As they were sensitive to less than 1° the slightest oxidation of hydrogen would be disclosed. The outer tube had a cross section of about 9 sq. cm. and was wound with Nichrome ribbon which could be heated electrically. The gas mixture was humidified by passing through 2 bead towers in series into which water was kept slowly dropping, inserted in the place of the final drying towers. These 2 towers and the catalyst tube were placed in a large electrically heated, stirred, and regulated air thermostat which maintained a temperature of $40° \pm 0.1°$, and was provided with ample shields and deflectors to eliminate any irregularities of temperature due to radiation from the incandescent lamp heater. By this means an aqueous tension of 50 mm. of mercury was imparted to the affluent gas. This gas entered the catalyst tube at the top of the annular space, and as this was rather long, was thereby somewhat preheated.

Several determinations with this apparatus at a space velocity of 6000 per hour and with mixtures of 90% hydrogen with 10% air and 1% hydrogen in 99% air showed that with this amount of water vapor present no considerable oxidation of the hydrogen occurred until a temperature of 125° was reached in the catalyst.
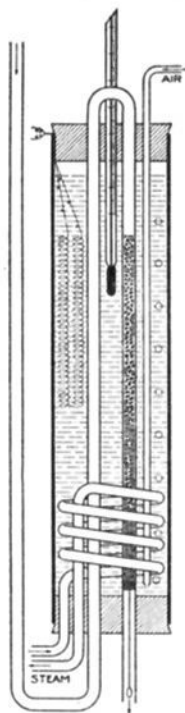
Behavior of Hopcalite toward a Moist Mixture of Carbon Monoxide and Air

Careful experiments were now made to ascertain the temperature required for complete combustion of carbon monoxide in nitrogen, in the presence of oxygen and similar amounts of water vapor. A still more carefully designed reaction tube shown in Fig. 1 was used for this purpose.

It consisted of 2 copper tubes 7 by 400 mm. running vertically through a water-bath. The gas passed up through one of them which was empty and served as a preheater, and down through the other which was filled for a distance of about 30 cm. along its middle with 15 cc. of catalyst. The water was heated nearly to the desired temperature by means of a small coil of copper steam-pipe, and the finer regulation obtained by an electrically heated coil of Nichrome wire immersed in the bath. The bath was stirred by means of air. The same humidity towers and air thermostat as described above were used. The two gas mixtures studied contained, before humidification, 0.5% of carbon monoxide, 2.5% of air, 97% of nitrogen; and 1.0% carbon monoxide, 5% of air, 94% of nitrogen; affording in each case twice the theoretical

Fig. 1.

amount of oxygen required for the combustion of the carbon monoxide. A space velocity of 6000 per hour was maintained.

TABLE II

PERCENTAGE EFFICIENCY OF HOPCALITE IN OXIDIZING CARBON MONOXIDE IN GAS MIXTURES CONTAINING H_2O AT A PRESSURE OF 50 MM. OF MERCURY

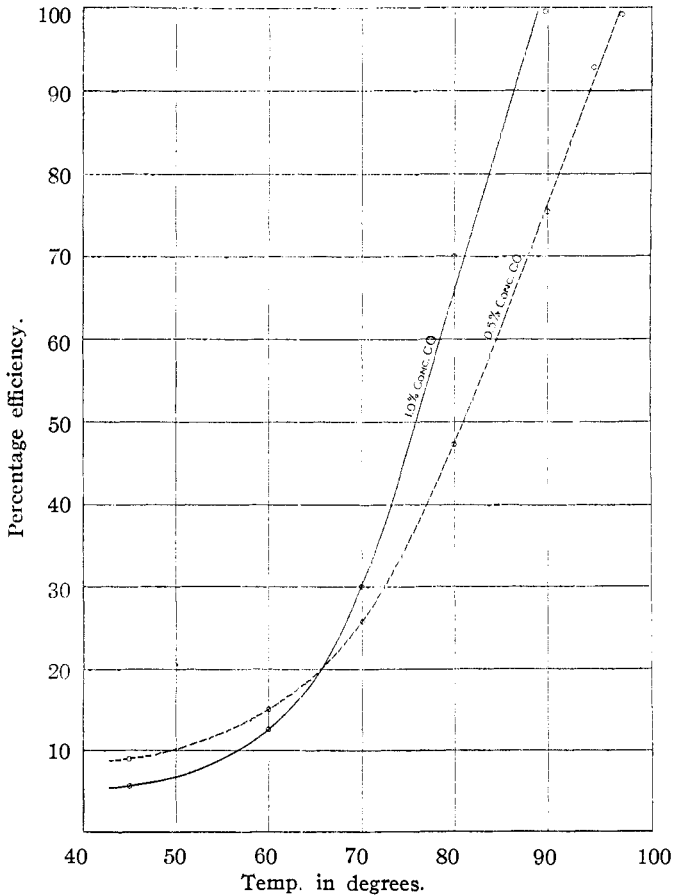| 0.5% of CO, 0.5% of O_2, 99% of N_2		1% of CO, 1% of O_2, 98% of N_2	
Temperature °C.	Efficiency %	Temperature °C.	Efficiency %
45	9.0	45	5.5
60	15.0	60	12.5
70	25.6	70	30.0
80	47.0	80	70.0
90	76.0	90	100.0
95	92.8	..	...
98	99.1	..	...

Fig. 2.—Temperature-efficiency curve.

Determinations were made by adjusting the bath to a constant temperature, passing the gas mixture through the catalyst, and determining the unburned carbon monoxide by means of the calorimetric method.[9] Sufficient time was allowed to insure the establishment of equilibrium conditions of constant efficiency. The results are collected in Table II, and are shown graphically in Fig. 2.

These results were confirmed by many additional measurements. They indicate that at a temperature of 90–100° in air complete oxidation of carbon monoxide is obtained even in the presence of water vapor equivalent to 50 mm. of mercury pressure, and with a relatively small excess of oxygen (100%); and that, therefore, a margin of about 20° exists between this temperature and that at which hydrogen begins to be oxidized under similar conditions.

Behavior of Hopcalite Toward a Moist Mixture of Carbon Monoxide and Hydrogen Containing a Little Oxygen

It remained to find out whether this margin of 20° between the temperatures of oxidation of the separate gases would persist in a mixture of the two gases, or in other words, whether or not the oxidation of the carbon monoxide exerted any induction effect upon the oxidation of the hydrogen.

To do this, and at the same time to show that no serious deterioration of the catalyst occurs on prolonged running even at efficiencies less than 100%, a prolonged continuous test was carried out on a gaseous mixture containing a little carbon monoxide and oxygen and a large amount of hydrogen.

Determination of Carbon Monoxide in the Presence of Hydrogen.—The above mentioned calorimetric method so useful for the analysis of carbon monoxide in air could not be used here on account of the relatively large amount of hydrogen present. A complete combustion of the gas, on the other hand presented numerous difficulties. We attempted to apply the iodine pentoxide method which has been recommended for this purpose,[10] but without success. We found that at 150–160° iodine pentoxide oxidizes about 15% of the hydrogen in a 1 or 10% hydrogen-air mixture, and 26% of the hydrogen in a 10% hydrogen, 0.9% carbon monoxide, and 89.1% air mixture. At 96–100° only about 2.6% of the hydrogen of a 10% hydrogen-air mixture was oxidized, but with 1% carbon monoxide over 90.5% and 96.5% was oxidized at this temperature in two determinations. This greater activity of our iodine pentoxide may have been due to its preparation by the chloric acid method.[11]

Finally, since we had already demonstrated that Hopcalite oxidizes carbon monoxide completely at room temperature in dry hydrogen containing a little oxygen, we simply dried the effluent gas, passed it through a layer of this substance, and collected the carbon dioxide in standard alkali. There were, however, two difficulties which required consideration. In the first place, it was found that Hopcalite retains adsorbed carbon dioxide tenaciously at room temperature. The adsorbed carbon dioxide is given off slowly at 100°, and more rapidly at 140° (boiling xylene), while at 205° (boiling nitro-

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[9] Lamb and Larson, This Journal, 41, 1908 (1919).

[10] Nicloux, Compt. rend., 126, 746 (1898). Kinnicut and Sanford, This Journal, 22, 14 (1900). Graham and Winhill, J. Chem. Soc., 105, 1996 (1914). Graham, J. Soc. Chem. Ind., 38, [2] 10 (1919).

[11] Lamb, Bray and Geldard, This Journal, 42, 1636 (1920).

benzene) carbon dioxide of constitution is apparently given off slowly from the basic carbonates in the Hopcalite, for prolonged heating to 240° failed to eliminate it completely. After use, therefore, the Hopcalite was first swept out at room temperature with air, and then heated, and the sweeping continued. The length of time necessary for complete removal varies with the amount of carbon dioxide adsorbed, the quantity of Hopcalite used and the velocity of the air current, but in our experiments 45 minutes was found to be adequate. The second difficulty was the complete absorption of the carbon dioxide in the dilute alkali from such relatively dilute mixtures (0.5 to 0.02% of carbon monoxide) at rapid rates of flow. This was successfully accomplished by using 3 small absorption bulbs of the injector type arranged in series, and heated to about 80° in a bath of water. A centrifugal stirrer-injector would probably be even more efficient. From the point of view of the difficulty of absorption the retention of the carbon dioxide by the Hopcalite is an advantage, for particularly at low concentrations it is practically all adsorbed, and can then be driven out by a slow current of air at a considerably higher concentration. The procedure adopted, therefore, is as follows. The sample of gas, varying in volume from 2 liters when about 0.5% of carbon monoxide is present to 10 liters when less than 0.02% of carbon monoxide is present, is mixed with about $1/3$ of its volume of purified air, unless it already contains a considerable excess of oxygen. It is then passed through bead towers moistened with potassium hydroxide solution, another bead tower moistened with sulfuric acid, thence into the oxidation apparatus, and finally through the absorption bulbs, at a rate of about 300–500 cc. per minute. Pure air is then passed through the apparatus until the gas therein has been displaced. Finally the xylene is heated to boiling, and a current of pure air, quite slow at first but finally increasing in amount to about 300 cc. per minute, is passed throught the apparatus for about 45 minutes. The absorption bulbs are then disconnected, washed out with water free from carbon dioxide, and the liquid titrated with dilute standard acid (about 0.02 N), using phenolphthalein as indicator. Blank determinations are also run and the correction, seldom amounting to as much as 0.001%, is applied.

Results obtained on known mixtures, varying between 9.5% and 0.005% of carbon dioxide, gave a satisfactory concordance. Thus, with the very dilute mixtures given in the following table the inaccuracy amounts to but 0.0015 and 0.0006%, respectively.

TABLE III

ANALYSIS OF CARBON MONOXIDE-HYDROGEN MIXTURE

Concentrations of carbon monoxide

Taken %	Found %	Corrected %	Error %
0.0110	0.0102	0.0095	−0.0015
0.0055	0.0056	0.0049	−0.0006

Continuous Test.—The composition of the gaseous mixture was 74.25% of hydrogen, 24.75% of nitrogen, 0.5% of carbon monoxide, and 0.5% of oxygen. To prepare this mixture the carbon monoxide and oxygen were first mixed in equal volumes and stored in 20-liter glass aspirator bottles, and then fed into the mixing chamber through a flowmeter at the rate of 5 cc. per minute. A very pure mixture of hydrogen and nitrogen in the proportion of 3:1 at a pressure of 100 atmospheres was kindly furnished us by the Arlington Laboratory of the Nitrate Division of Ordnance, U. S. A. It had been prepared by cracking ammonia gas at a high temperature, and was further purified by passage through a deep layer of Hopcalite, through a tower containing chromic acid maintained at

80°, and finally through another containing 50% sodium hydroxide solution. Thence it entered a constant-pressure tube where a continuous slight escape of the excess gas took place, and then entered a mixing chamber where it mingled with the carbon monoxide-air mixture, the resulting mixture being sucked through a second flowmeter, the humidity towers and finally through the catalyst tube and the analytical train. The catalyst tube consisted of a copper tube 7 mm. wide and 400 mm. long to which a spiral coil of small copper tubing was soldered to serve as a preheater. The Hopcalite occupied about 10 cm. length of the copper tube, and was supported by a small roll of copper gauze. The tube and preheater were immersed in a paraffin thermostat electrically heated and regulated to maintain a temperature of 101.8° ± 0.2°.

With these arrangements the gas mixture was now drawn through the apparatus at a rate of 500 cc. per minute, corresponding to a space velocity of 6000 per hour with the 5 cc. of catalyst employed, and the effluent gas analyzed at frequent intervals for carbon monoxide by the method outlined above. With this small volume of catalyst a fairly constant efficiency of 93% was maintained for a continuous operation of 200 hours. During this period the catalyst purified 6000 liters of gas, or over a million times its own volume, and removed nearly 10 times its own weight of carbon monoxide without deterioration.

During the succeeding 48 hours the efficiency slowly dropped to 74%, when the run was discontinued and the catalyst tube opened. It was found that the top (initial) layer of catalyst had darkened in color and a further examination showed that paraffin had leaked in through 2 pinholes just below the level of the paraffin bath. This was adequate to explain the drop in efficiency in the concluding 48 hours.

Experiments somewhat similar to the above were carried out with a mixture containing 1% of carbon monoxide, 10% of air, 29% of nitrogen, and 60% of hydrogen, but after a short period of operation incandescence of the catalyst took place, indicating, as in the case of dry hydrogen, that the heat of reaction is not dissipated in our apparatus rapidly enough to prevent reaction with the hydrogen.

The Influence of Various Factors on the Efficiency of the Hopcalite and the Temperature Rise in the Catalyst

Having shown that 0.5% carbon monoxide can be successfully removed even from a very moist mixture of hydrogen and nitrogen, it remained to investigate the influence of important factors such as space velocity at different temperatures, catalytic poisons, and the concentration of the oxygen, on the catalytic combustion of the carbon monoxide. Moreover, since the rate of dissipation of the heat of reaction from the catalyst limits the concentration of carbon monoxide which can be tolerated by

the catalyst in the presence of hydrogen, we have on the one hand considered means for combating this effect and on the other have studied the actual temperatures produced in tubes of different diameters at a variety of space velocities.

Temperature and Space Velocity.—The variation with the temperature of the efficiency of the catalytic oxidation of 0.5% and 1% carbon monoxide in a mixture of moist oxygen and nitrogen at a space velocity of 6000 per hour had already been studied as described above (pp. 742–744). We now made similar measurements at space velocities up to 30,000 and in tubes 4 to 7 mm. in diameter, with otherwise the same apparatus. The results are collected in Table IV, and are shown graphically in Figs. 3 and 4. The temperatures were those of the well-stirred water-bath; the temperatures within the catalyst were undoubtedly somewhat higher.

TABLE IV

EFFECT OF SPACE VELOCITY, TEMPERATURE, ETC., ON THE EFFICIENCY OF OXIDATION OF CARBON MONOXIDE BY HOPCALITE

20% of oxygen, 79.5% of nitrogen and 0.5% of carbon monoxide used in all experiments except those marked (a) in which 79% of nitrogen and 1.0% of carbon monoxide were used.

Temp. bath °C.	CO oxidized %	Temp. bath °C.	CO oxidized %	Temp. bath °C.	CO oxidized %
Space velocity 6000		Space velocity 18000		Space velocity 27000	
50 mm. of H₂O. Tube 5.5 mm.		No H₂O. Tube 4 mm.		50 mm. of H₂O. Tube 4 mm.	
71	59	29	64	85	51
80	90	40	86	95	80
87	99	50	94	99	90
Space velocity 13000		61	99	105	95
50 mm. of H₂O. Tube 4 mm.		70	100	110	98
72	41	Space velocity 18000		113	100
80	61	50 mm. of H₂O. Tube 4 mm.		Space velocity 30000	
85	79	80	41	50 mm. of H₂O. Tube 5.5 mm.	
90	88.5	85	54	77	33
95	94.5	85	58[b]	80	37
99	98	90	69	84	50
Space velocity 15000		95	86	90	60
50 mm. of H₂O. Tube 5.5 mm.		99	95	99	83
80	57	105	99	99	81[a]
80	61[a]	107	100	Space velocity 30000	
		85	58	No H₂O. Tube 4 mm.	
				54	61
				65	80
				72	88
				85	98.5
				90	99.5

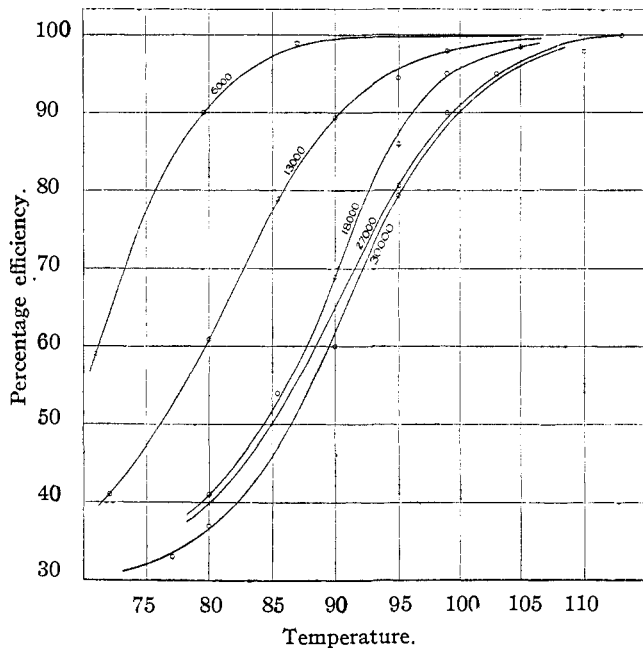[a] 79% of nitrogen and 1.0% of carbon monoxide.
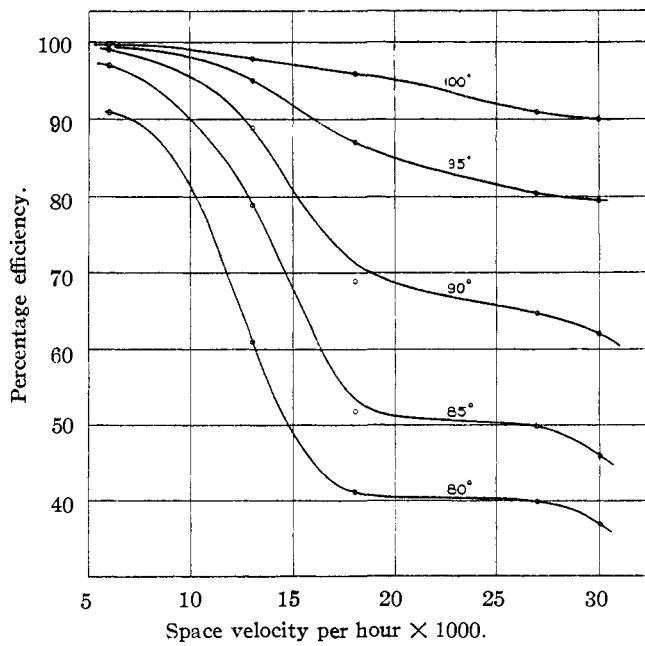[b] Tube 5.5 mm.

Fig. 3.

Fig. 4.

From these tables and figures it is evident that increasing the space velocity lessens the efficiency very greatly at 80° and relatively slightly at 99°; or, stated differently, to obtain high percentage efficiency at a high space velocity requires a relatively high temperature. If one sets 100° as the highest permissible temperature and 90% as the required efficiency, a space velocity as high as 27,000 can be attained.

Concentration of Carbon Monoxide.—Comparisons of the efficiency of combustion of 0.5 and 1.0% mixtures of carbon monoxide with air containing water vapor at 50 mm. mercury pressure were made under identical conditions, using copper tubes 5.5 mm. in diameter, with otherwise the same apparatus, the results of which are given in the following table.

TABLE V

EFFICIENCY OF COMBUSTION WITH DIFFERENT CONCENTRATIONS OF CARBON MONOXIDE

Temperature	Space velocity per hour	Efficiency	
°C.		For 0.5% of CO %	For 1.0 % of CO %
80	15,000	57	61
85	18,000	58	58
95	18,000	86	83

These results indicate that when adequate provision is made for the dissipation of the heat there is little, if any, gain in the percentage efficiency with different concentrations of carbon monoxide. An examination of Fig. 2 confirms this. There, in 7mm. tubes the heat dissipation was adequate at the lower temperatures and efficiencies, so that under these conditions the curves for 0.5% and 0.1% carbon monoxide are nearly identical; but at higher temperatures, where the efficiencies were much higher the heat evolution was greater, and the temperature therefore higher with 1% than with 0.5% carbon monoxide, and the two curves therefore diverge.

Concentration of Oxygen.—The combustion of one volume of carbon monoxide requires but half a volume of oxygen. In a technical utilization of this process it would be important to operate with as small an excess of oxygen as possible, as this excess must later be removed at the cost of an equivalent amount of hydrogen. A comparison of the results given in Tables II and III, where in the first case the concentration of the oxygen is 0.5% and in the second 20%, shows that the higher concentration has, at a space velocity of 6000, increased the efficiency by an amount roughly equivalent to a temperature rise of 15°. In practice, therefore, a balance would have to be struck between, on the one hand, the increased efficiency or correspondingly increased space velocity and, on the other, the cost of the extra hydrogen thus consumed.

Carbon Dioxide.—In the manufacture of hydrogen from water-gas the carbon dioxide is quite fully and easily removed by water-scrubbing,

and indeed the carbon dioxide thus removed may represent a useful by-product. Nevertheless, if this scrubbing could be omitted, or conducted in a less thorough and less expensive manner, an economy might be effected. It is of some interest, therefore, to study the effect of carbon dioxide on the efficiency of the catalytic oxidation. There is of course no possibility of a realization of the water-gas equilibrium at this temperature, but since, as pointed out above, carbon dioxide is very strongly adsorbed by Hopcalite, its introduction into the influent gases might be expected to effect a lowering of the efficiency. We have not tested this at all adequately, but using a dry gas mixture consisting of 0.5% of carbon monoxide, 20% of carbon dioxide, 10% of air, 60% of hydrogen and 9.5% of nitrogen at room temperature and a space velocity of 6000, there is no leakage of carbon monoxide when tested with the Hoolamite detector (0.03%).[12] This indicates that the effect of admixed carbon dioxide is slight.

Hydrogen Sulfide.—To test the effect of hydrogen sulfide, mixtures of 1% of carbon monoxide, 33% of carbon dioxide, and 64% of air with hydrogen sulfide were prepared by allowing the carbon dioxide to bubble through a concentrated solution of sodium sulfide. A strip of filter paper moistened with lead acetate placed in the effluent gases from the catalyst showed no change after several minutes, but immediately turned black when the gas mixture was by-passed around the Hopcalite. After 60 minutes' passage of this gas mixture the catalyst still oxidized the carbon monoxide completely at room temperature, and continued to do so for a half hour longer after the carbon dioxide, and hence the hydrogen sulfide, had been turned off. The next day, on further treatment with the same mixture containing hydrogen sulfide and carbon dioxide, the efficiency started at 100% but dropped after 45 minutes to 98%. Tested again on 1% carbon monoxide in air it gave a 99% efficiency which dropped after 2 hours to 95%. This indicates that the Hopcalite catalyst completely absorbs or destroys the hydrogen sulfide, and at first is not much impaired thereby, although continued exposure gradually destroys its activity. Examination of the catalyst at the end of the experiment confirmed this; the first 2 cc. of the Hopcalite had changed to a gray or black color. The hydrogen sulfide is presumably oxidized, and the resulting sulfur, or acids of sulfur, either react chemically with the Hopcalite, or form an adsorbed film which inhibits further action.

The Temperature Rise in the Catalyst.—The incandescence of the hydrogen, which invariably occurs when mixtures containing as much as 1% of carbon monoxide are catalytically oxidized by Hopcalite, is certainly a result of the too slow dissipation of the heat of combustion of the carbon monoxide. It is of, interest, therefore to inquire, first, what the maximum

[12] Ref. 2. Hoover, *J. Ind. Eng. Chem.*, **13**, 770 (1921).

temperature rise could be for, say, a 1% carbon monoxide mixture; second, what general relation should obtain between the composition of the gas mixture, the space velocity, and the temperature rise; and third, to test this relation experimentally. For reasons of convenience these experiments were carried out not with the hydrogen-nitrogen mixture used in the Haber process, but with a carbon monoxide-air mixture. The maximum temperature rise and the temperature distribution are different in the two mixtures, but the same general principles should apply to both.

The maximum temperature rise will evidently occur when no heat is dissipated except to the effluent gas. An affluent gas mixture of the composition 1% of carbon monoxide, 20.7% of oxygen, and 78.3% of nitrogen, after combustion will have very nearly the composition 1%, 20.3%, and 78.7%, respectively. The average heat capacity of this mixture per hundredth of a mol of carbon monoxide at temperatures between room temperature and 100° is 6.87 mayers; the heat of combustion of this amount of carbon monoxide is 68,300/100 cals., and the maximum temperature rise will thus be 683/6.87 or 99.4° for a 1% mixture. No such rise, of course, takes place in our apparatus, so that the narrow copper tubes immersed in the well-stirred liquid bath must have dissipated a very large fraction of the heat evolved.

The general relation which should obtain between the composition of the gas mixture, the space velocity and the characteristic heat-dissipating capacity of the catalyst and its container can be deduced as follows. The heat supplied by the combustion of the carbon monoxide, when a steady state has been reached, must be equal to the sum of the heat lost to the gas and the heat dissipated by the catalyst container. Or, calling Q the heat of combustion per mol of carbon monoxide; C_1 the heat capacity of the affluent gases per initial mol of carbon monoxide; S the space velocity; C_2 the dissipation capacity of the gram molecular volume of the catalyst in mayers per hour; p the percentage by volume of carbon monoxide present; and Δt the temperature rise,

$$pQS = \Delta t(SC_1 + C_2)$$

and therefore

$$\Delta t = \frac{pQS}{SC_1 + C_2} = \frac{\frac{pQS}{C_1}}{S + C_2/C_1}.$$

Or, since $Q = 68,300$ cals., and for small percentages of carbon monoxide C_1 does not differ greatly from 6.87 mayers

$$\Delta t = \frac{99.4 \, pS}{S + C_2/6.87},$$

which is the desired relation. For adiabatic conditions, that is, when no heat is dissipated except to the effluent gas, this reduces to $\Delta t = 99.4$

TABLE VI

TEMPERATURE RISE IN CATALYST

Bore of reaction tube mm.	5.5						7						10			
CO, %	0.5			1.0			0.5			1.0			0.5		1.0	
Space velocity per hour, thousands	7.5	15	30	7.5	15	30	7.5	15	30	7.5	15	30	7.5	15	7.5	15
Ratio of depths of layer																
$1/6$	2.0	3.4	2.8	4.0	6.2	5.8	4.0	6.8	8.2	7.2	12.6	19.2	5.6	9.6	10.4	21.0
$2/6$	1.0	2.8	4.0	1.6	4.6	7.6	3.0	6.8	10.0	4.4	12.0	22.4	3.1	8.8	5.2	14.2
$3/6$	0.2	1.0	3.0	0.6	1.8	5.4	1.2	3.2	7.2	1.6	5.0	10.2	1.4	5.0	2.2	6.6
$4/6$	0.2	0.6	1.6	0.4	0.8	2.8	0.2	1.2	2.2	0.4	1.4	2.8	0.8	3.0	1.0	3.6
$5/6$	0.2	0.4	0.8	0.2	0.4	1.2	0.2	0.6	1.2	0.4	0.8	1.4	0.6	1.0	0.8	1.2
Integrated Obs.	0.72	1.50	2.10	1.40	2.60	3.94	1.66	3.19	4.94	2.68	5.78	9.78	2.22	4.89	5.34	8.59
Average Calc.	0.66	1.31	2.27	1.33	2.62	4.13	1.52	2.94	5.00	3.02	5.87	9.31	2.41	4.60	4.82	9.19
$C_2/6.87 \times 1/1000$	506	479	608	{521	554	581	215	217	240	268	241	242	159	137	131	157
C_1/C_2 Mean	550,000 ± 8%						237,000 ± 6%						146,000 ± 8%			

In all of these cases the efficiency was approximately 100% except in the measurements at a space velocity of 30,000, where the efficiency was approximately 90%.

p as previously stated; that is, the temperature rise then amounts to 99.4° per cent. of carbon monoxide. For very rapid dissipation of heat this expression reduces to $\Delta t = \dfrac{(99.4)(6.87)}{C_2} pS$; that is, the temperature rise becomes very small, and proportional both to the percentage of carbon monoxide and to the space velocity.

To study this question experimentally we have measured the temperature rise in a Hopcalite catalyst, operating against mixtures containing 1% and 0.5% of carbon monoxide in air, at different space velocities, and in copper tubes of various diameters.

The purification, measuring and drying apparatus was identical with that already described. The catalyst container was a U-shaped copper tube with a side-tube soldered to a hole at the bottom of the U. Through this side-tube a glass tube carrying a copper-constantin thermocouple was inserted with its junction as nearly as possible at the center of the U. The catalyst was filled into both arms of the U, and different positions of the thermocouple with respect to the catalyst were obtained by altering in successive experiments the amount of the catalyst on either side of the thermocouple. In this way observations were made at $1/6$, $2/6$, $3/6$, $4/6$ and $5/6$ of the distance from the inlet to the outlet surface of the catalyst bed. Three sizes of copper tubing, 5.5, 7.7 and 10 mm. in bore, were used; and the volume of catalyst was so adjusted that at corresponding space velocities, identical linear velocities were maintained. The catalyst tube was surrounded by an aqueous solution of calcium chloride kept accurately at 100°, and the affluent gases were preheated by passing through a coil of copper tubing immersed in the bath. The temperature rise in the tube during the oxidation of the carbon monoxide was measured by comparing the readings of the thermocouple while oxidation was taking place with those made when the moist air alone was passing through the catalyst. The results are collected in Table V. In every case the efficiency was 100% except in the measurements at 30,000 space velocity where it was approximately 90%.

To find how closely these results accord with the formula deduced above, it was first necessary to find an average value for the temperature rise (Δt) in each tube. We have done this by plotting the five thermocouple readings for each tube at the same space velocity and with the same concentration of carbon monoxide, and integrating graphically the area under each curve. The resulting values are given after the heading "Integrated Averages Observed" in Table VI.

Inserting these values of Δt and the corresponding values of the percentage (p) and the space velocity (S), we have computed $C_2/6.87$. In those runs at 30,000 space velocity where the efficiency was only 90% we have made a proportionate allowance therefor. The resulting values are given in the bottom lines of Table V. $C_2/6.87$ should be a constant for each diameter of tube, if the formula is correct. It can be seen that this is indeed the case, the average deviation of the individual values from the means being only 8%, or no more than corresponds to the experimental error. To show this more clearly we have calculated back to find what the average temperature rise should be from the average value of $C_2/6.87$

for each tube. These values are given in the line headed "Integrated Averages Computed." The agreement is very close.

The average values of $C_2/6.87$ for the tubes of different size would be expected to vary approximately inversely as the area of the tubes, or inversely as the squares of the bore. Actually the ratio of the C_1/C_2 values is $1:1.6:3.8$, while the inverse ratio of the squares of the bores is $1:1.6:3.3$. Since the formula

$$\Delta t = \frac{99.4\, pS}{S + C_2/6.87}$$

does indeed hold, and since under operating conditions it reduces practically to $\Delta t = KpS$, where K is a constant, it follows that for any permissible maximum value of Δt the product pS cannot exceed a certain limit, so that for a high percentage content of carbon monoxide only a small space velocity can be tolerated, and *vice versa*. This would indicate that a recirculation of the purified gas would be of no advantage, because for any decrease in p there would necessarily be an equivalent increase in S.

This formula does not, however, cover the whole situation. Δt is the *average* temperature rise, and this is not the most significant variable. The danger of combustion of the hydrogen is a function rather of the *maximum* rise in the catalyst mass, and this is by no means identical with or proportional to Δt. At low space velocities this maximum temperature rise always occurs at or very close to the front surface of the catalyst, but at high space velocities it is displaced toward the exit end of the tube.

To facilitate comparison, the maximum temperatures, ascertained by plotting the results in Table VI, are collected in Table VII.

TABLE VII
MAXIMUM TEMPERATURE RISE IN DEGREES

Bore of tube, mm.		5.5		7		10	
CO, %		0.5	1.0	0.5	1.0	0.5	1.0
Space velocity	7,500	2.4	4.8	4.2	7.4	5.8	10.6
	15,000	3.6	6.4	7.2	12.8	9.6	21.0
	30,000	4.4	8.6	11.0	24.8	..	..

It can be seen from Table VI that the maximum temperatures are quite closely proportional for the same tube and the same space velocity to the percentage of carbon monoxide. For the largest tube studied (10 mm.) they are also approximately proportional to the space velocity, but with the smallest tube the maximum temperature increases much more slowly than the space velocity, indeed approximately as the *square root* of the space velocity. It follows from this that, at least for small tubes, it would be advantageous to recirculate a fraction of the purified gas, mixing it with the raw gas. The physical interpretation of this effect, of course, is that by displacing the maximum temperature to the middle

of the catalyst a greater average temperature rise can be tolerated without danger of starting the oxidation of the hydrogen.

It can also be seen that the maximum temperature rise, like the average temperature rise, is approximately proportional to the square of the diameter of the tubes, and therefore approximately proportional to their area.

Optimum Operating Conditions.—On the basis of the above experimental results and discussion a number of postulates can be established relative to the optimum conditions for obtaining a complete, rapid, and economical preferential oxidation of the carbon monoxide, although many factors which are important in determining the optimum conditions for the technical operation of this process can only be ascertained from tests on full-size apparatus.   On the one hand it is important to operate at as near the top of the temperature differential as possible, because the carbon monoxide is thereby rapidly and completely burned, or conversely very high space velocities can be utilized without a serious drop in efficiency.   On the other hand, this temperature must be low enough to avoid any danger of combustion of the hydrogen at the higher temperature which will prevail within the catalyst, and of course to provide a margin of safety against accidental fluctuations in temperature.   The "heat dissipating capacity" of the catalyst and its container should, of course, be as great as possible, this being secured by the use of small bore metallic tubes or a multicellular metallic container with its horizontal partitions made of wire gauze, the whole cooled by a circulating liquid. By a suitable design a disproportionate cooling could be applied to the region of maximum temperature rise, and thereby a uniform temperature maintained throughout the catalyst, or the maximum temperature displaced to a point at or near the exit surface of the catalyst.   The simplest method of securing the latter arrangement is to adopt a two or multiple stage system, burning most of the carbon monoxide at a low temperature and relatively low efficiency (say 75%) in a first catalyst chamber, and then completing the combustion with the now much more dilute gas in a second chamber at a temperature not far from the top of the temperature differential.   In this way a high space velocity coupled with a high efficiency could be attained safely.   Several tests of this method were made, using 0.5 and 0.75% of carbon monoxide in mixtures consisting of 10% of air, 29.5% of nitrogen, and 60% of hydrogen, keeping the first catalyst tube at 82–87°, and the second at 90–99°, and a rapid and complete oxidation of the carbon monoxide was secured without difficulty.

In papers published since the completion of the above work Rideal and Taylor[13] and Rideal[14] have described catalysts consisting of specially activated copper oxide, as well as of iron oxide, with ceria and thoria as

[13] Rideal and Taylor, *Analyst*, **44**, 89 (1919).
[14] Rideal, *J. Chem. Soc.*, **115**, 993 (1919).

promoters, which preferentially oxidize carbon monoxide admixed with hydrogen at temperatures from 100° up to 300°. Data are given showing the relative amounts of carbon monoxide and of hydrogen oxidized in a 1:8 admixture with hydrogen at temperatures from 160° to 400°. The proportion of hydrogen oxidized increases very rapidly with rising temperature. Rideal calculates the relative amounts which should be oxidized on the basis of the Marcellin-Rice-Lewis radiation theory, and finds an approximate agreement, or at least a marked similarity in the shape of the experimental and theoretical curves at the higher temperatures.

At the lower temperatures, where only the copper oxide remains sufficiently active, the curves show a greater divergence, the copper oxide curve, extrapolated to 100°, indicating a ratio of hydrogen and carbon monoxide burned of about 0.15, while the theoretical equation gives a ratio of 0.004.

Applying this equation to our mixtures containing 0.5% of carbon monoxide and 89% of hydrogen, the ratio should be 0.0015 at 100°. Our experiments, in which any water which formed would have been collected and weighed, indicated no combustion of hydrogen greater than would correspond to this ratio, and do, therefore, afford some further confirmation of the equation.

Summary

1. It has been shown that Hopcalite, which oxidizes carbon monoxide in air rapidly and catalytically at room temperatures, does not affect hydrogen in air under similar conditions, and that by its means carbon monoxide can be completely and continuously removed from a dry mixture containing, for instance, 0.5% of carbon monoxide, 89.5% of hydrogen, and 10% of air without any noticeable action on the hydrogen. A similar mixture containing 1% of carbon monoxide, on the other hand, liberates so much heat that under these conditions oxidation of the hydrogen sets in, and the catalyst is soon heated to incandescence and is destroyed.

2. It has been shown that moist mixtures of carbon monoxide and air, and of hydrogen and air require much higher temperatures for oxidation. In the presence of water vapor at a pressure of 50 mm. of mercury, carbon monoxide in a 0.5% mixture with air is completely oxidized at a temperature of 90° or lower. Hydrogen, on the other hand, mixed with air, does not begin to be oxidized under these conditions until a temperature of 120–125° is reached. It is possible, therefore, to remove carbon monoxide completely and continuously from a mixture having, for instance, the composition 0.5% of carbon monoxide, 0.5% of oxygen, 24.75% of nitrogen, and 74.25% of hydrogen, and containing water vapor at a pressure of 50 mm. of mercury, without any considerable oxidation of the hydrogen. On the other hand, in a similar 1% carbon monoxide

mixture the hydrogen soon catches fire, and the catalyst becomes incandescent.

3.   The effects on the efficiency of the catalyst of temperature, space velocity, carbon dioxide, hydrogen sulfide, and the concentration of the carbon monoxide have been studied.

4.   Formulas for the temperature rise in the catalyst, the factor limiting the permissible concentration of the carbon monoxide, have been derived and have been experimentally verified at different space velocities, and in tubes of different diameters.

5.   On the basis of these results, the proper conditions for the technical application of this method of removing carbon monoxide from hydrogen have been outlined.

6.   Our results have been shown to be in agreement with the computations of Rideal, relative to the simultaneous oxidation of carbon monoxide and hydrogen.

7.   A method for the analysis of small amounts of carbon monoxide in the presence of hydrogen has been worked out.

CAMBRIDGE 38, MASSACHUSETTS

THE THERMAL DECOMPOSITION OF NITROGEN PENTOXIDE IN SOLUTION

BY ROGER H. LUECK

The problem of reaction velocity is one of paramount interest to chemists.   Attempts which have been made to explain the tremendous temperature coefficients of reaction velocities solely on the basis of the kinetic theory have not been verified by experimental data.   For a $10°$ rise in temperature, reaction velocities are known to increase from 200 to 400%, whereas the number of collisions between the molecules increases by not more than 2%.

Arrhenius[1] early investigated the problem and found that the dependence of the velocity constant on the temperature could be satisfactorily expressed by the formula

$$\frac{d \, ln \, k}{dT} = \frac{E}{RT^2} \tag{1}$$

where E is a quantity possessing the dimensions of energy, and which is found to vary but slightly with the temperature.   Arrhenius sought an explanation of the huge temperature coefficients in postulating the existence of an equilibrium between "active" and "passive" molecules

[1] Arrhenius, Z. physik. Chem., 4, 226 (1889).