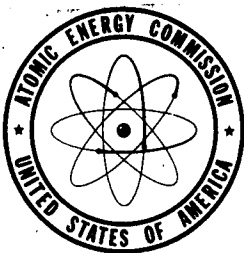*O*

UNITED STATES ATOMIC ENERGY COMMISSION

THE RADIATION CHEMISTRY OF HOMOGENEOUS REACTOR SYSTEMS. III. HOMOGENEOUS CATALYSIS OF THE HYDROGEN-OXYGEN REACTION

By
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THE RADIATION CHEMISTRY OF HOMOGENEOUS REACTOR SYSTEMS

III. HOMOGENEOUS CATALYSIS OF THE HYDROGEN-OXYGEN REACTION*

H. F. McDuffie, E. L. Compere, H. H. Stone,
L. F. Woo, and C. H. Secoy

SUMMARY

Hydrogen and oxygen, dissolved in aqueous solutions at elevated temperatures, have been found to react smoothly to form water when dissolved copper salts are present in the solution as homogeneous catalysts. This reaction is important to the development of aqueous homogeneous reactors in that it provides a possible means for suppressing the formation of hydrogen-oxygen gas bubbles from the decomposition of water by fission fragments. The kinetics of the reaction have been investigated over wide ranges of controllable variables, including environmental conditions of interest to the reactor program. (The rate determining step appears to be the reaction of dissolved hydrogen with the dissolved copper catalyst, and the activation energy appears to be around 24 kilocalories per mole.) Preliminary examination of a large number of inorganic compounds has not disclosed any homogeneous catalyst superior to copper for this reaction.

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*(Editors' note: This is the third part of a series of articles covering the intensive research and development conducted during the past two and one-half years at the Oak Ridge National Laboratory on the effects of reactor irradiation upon aqueous reactor solutions. The first part, entitled "Radiation-induced Decomposition," by J. W. Boyle, J. A. Chormley, C. J. Hochanadel, W. F. Kieffer, and T. J. Sworski, appeared in the March 1953 issue of Reactor Science and Technology (TID-2008). The second part, entitled "The Decomposition of Peroxide in Aqueous Homogeneous-Reactor Systems," by M. D. Silverman, G. M. Watson, and H. F. McDuffie, appeared in the September 1953 issue of Reactor Science and Technology (TID-2010). The editors plan to publish additional articles in this series in forthcoming issues. This study was carried out at ORNL as part of the chemistry program for the Homogeneous Reactor Project under the general supervision of C. H. Secoy as Project Chemist and H. F. McDuffie as leader of the Project Radiation Chemistry Group.)

INTRODUCTION

Disposal of the 2:1 mixture of hydrogen and oxygen, created by radiation decomposition of water in fissioning aqueous solutions (Paper I this series, Reactor Science and Technology, March 1953, TID-2008) presents a substantial technical and engineering problem in connection with the development of aqueous homogeneous reactors. The magnitude of the problem may be illustrated by reference to the operation of the HRE at 1000 KW, where the gas evolution has been estimated at 10.5 cfm (stp)[1]. As the gas comes from the core, mixed with saturated steam at $250^{\circ}C$ plus a small amount of excess oxygen, the composition of the mixture is well within the explosive range. In the operation of the HRE as originally designed, the gas is lowered to atmospheric pressure, burned in a flame recombiner, cleaned up by a catalytic bed recombiner, and the condensed water returned by pumps to the system. It is the purpose of this paper to discuss the characteristics of an internal homogeneous catalyst for the hydrogen-oxygen reaction which provides an alternative method for disposition of the hydrogen and oxygen.

THE REACTION

Solutions containing dissolved copper salts have been found to catalyse the recombination between hydrogen and oxygen to form (or re-form) water. The rate determining step appears to be reaction of the catalyst with dissolved hydrogen (with rapid regeneration by subsequent reaction with oxygen), and the applicable kinetic equation appears to be $-d[H_2]/dt = [H_2]^1 [Cu]^1 k_{Cu}$. Since the concentration of dissolved copper is maintained constant by regeneration, the reaction becomes effectively first order instead of second order and the equation may be written

$$-d[H_2]/dt = [H_2]^1 k_{sol}$$

where k_{sol}, the solution rate constant ($\equiv [Cu]^1 k_{Cu}$), is characteristic for the particular solution under study.

EXPERIMENTAL TECHNIQUE

Experiments are commonly carried out in the laboratory using hydrogen and oxygen supplied from ordinary gas cylinders (the next paper in this series will describe experiments in which the hydrogen and oxygen are generated in situ by the radiation decomposition of fissioning solutions). Small stainless steel or titanium autoclaves ("bombs") (Fig. 1) of 10-30 ml capacity are loaded with a known amount of catalyst solution to be tested, attached to a charging and pressure recording apparatus, placed in an aluminum block furnace equipped for rocking agitation, charged with a convenient mixture of oxygen and hydrogen (usually 300 and 600 psi), and then heated rapidly to the test temperature at which point rocking is begun and the pressure recorded as a function of time. Figure 2 presents the experimental arrangement. The experimental data are temperature, solution weight, bomb volume, solution composition, and pressure vs. time. A typical set of such data is presented as Table 1.
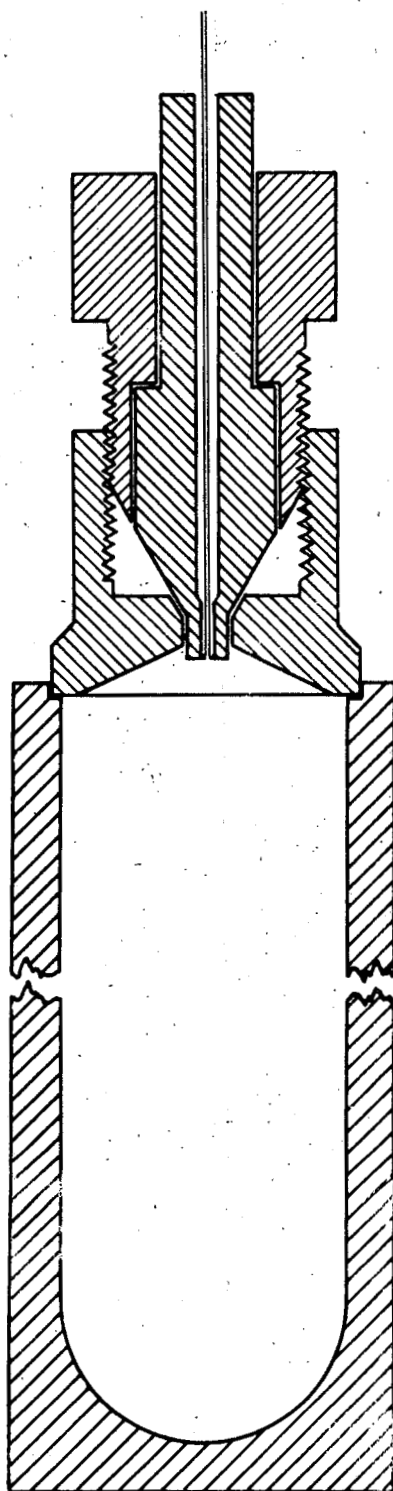
Fig. 1 - High Pressure Bomb and Connector.

I.C. THERMOCOUPLE

ALUMINUM HEATER BLOCK

RESISTANCE HEATER

347 SS CAPILLARY TUBING .035" OD ,.020" ID

TO GAS CHARGING AND EXHAUST MANIFOLD

ASBESTOS INSULATION

MAGNESIA INSULATION

BALDWIN SR-4 PRESSURE CELL

ELECTRICAL SIGNAL

BROWN ELECTROPULSE TEMPERATURE CONTROLLER

MERCURY RELAY BOX

PLATE HOLDING FURNACE TO ROCKING ARM

BROWN STRIP CHART PRESSURE RECORDER

ROCKING MOTOR

20 AMP VARIAC

Fig. 2 - Experimental Arrangement for Studying the Kinetics of the Hydrogen-Oxygen Recombination Reaction.

TABLE 1

Typical Laboratory Recombination Data

Run No.:   B-63

Bomb No.:   641

Soln. Comp.:   0.0010 M $CuSO_4$ and 26.2 g U/1 (as UO_2SO_4)
                at room temperature.

Wt. Soln.:   10.1 gm

Volume of bomb: 23.792 cc

Time (10 min. intervals)	Pressure (scale divisions)*	Δ P/20 min. (S.D.)
1	72.6	-
2	69.2	6.3
3	66.3	5.6
4	63.6	5.2
5	61.1	4.8
6	58.8	4.4
7	56.7	4.1
8	54.7	3.8
9	52.9	3.5
10	51.2	3.2
11	49.7	3.0
12	48.2	2.8
13	46.9	2.6
14	45.6	2.5
15	44.4	2.2
16	43.4	-2.0
17	42.4	1.9
18	41.5	1.7
19	40.7	1.7
20	39.8	-

* 1 S.D. = 25 psi

INTERPRETATION OF DATA

A plot of these data in the differential form of dP/dt vs. P is shown in Figure 3. The slope of the line is called k_{π}. The pressure axis intercept indicates the pressure of inerts plus steam remaining after all the hydrogen is oxidized. In this case the value for k_{π} was 0.468 hr^{-1}, and the residual pressure was 30.5 scale divisions or 762.5 psi. Experiments are usually carried out with a slight excess of oxygen.

In order to convert these data into values for k_{sol} and k_{Cu} it is necessary to take into account the fact that the hydrogen is distributed between two phases, with the reaction taking place only in the liquid phase while the pressure is measured for the vapor phase. A similar problem involving a liquid-liquid system with reaction occurring in one liquid phase only was studied by Lowenherz[2a], and by Goldschmidt and Messerschmidt[2b] whose conclusions were similar to those reported below.

Values for the solubility of hydrogen in water at high temperatures have been presented[3] from which were calculated the distribution coefficients as shown in Table 2.

It is important to emphasize that all values for k_{Cu} ultimately depend on knowledge of the solubility of hydrogen in the solution under test. Any changes in the estimation of this solubility will require changes in the assignment of the rate constant values. All the work reported in this paper is based on the values given in Table 2; thus it is assumed that these values are correct and that solubilities in uranyl sulfate solutions are the same as in water (the correctness of these assumptions is being investigated at the present time and, as will be shown later, it appears there is evidence that the reported solubilities are too low).

RUN B-63
1 scale division = 25 P.S.I

$$k_\pi = \frac{6 \times 3}{68.9 - 30.4} = \frac{18}{38.5} = 0.468 \, hr^{-1}$$
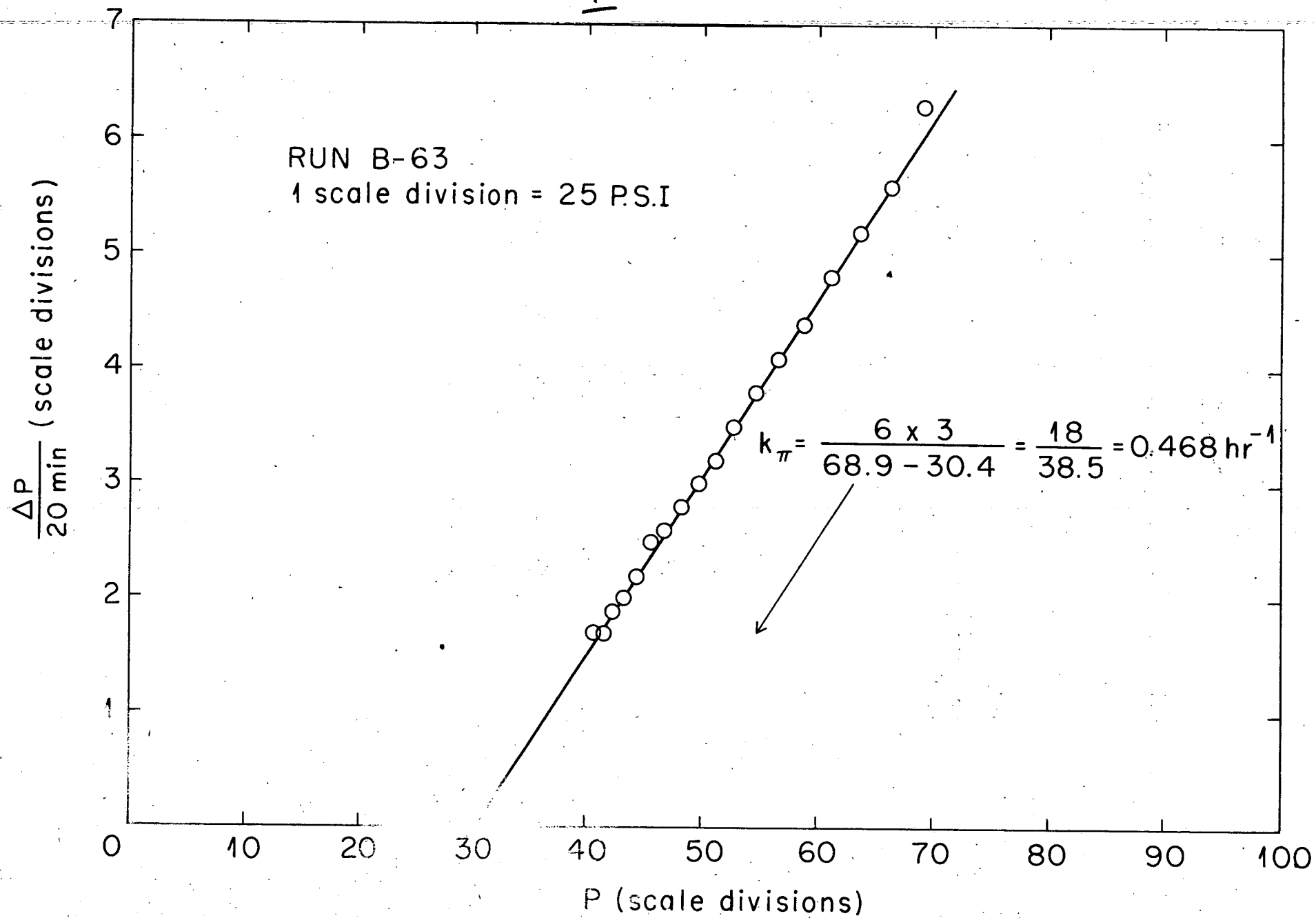
Fig. 3 - Treatment of Typical Experimental Data.

TABLE 2

Solubility of Hydrogen in Water at Elevated Temperatures

$$\propto \equiv \frac{P_{H_2} \text{(psi)}}{[H_2] \text{(moles/liter)}}$$

T°C	$\propto$
149	17,560
174	16,720
199	14,640
224	11,000
250	7,300 (Interpolated)
260	6,720
316	5,000
343	2,680

To develop the geometry factor (F_g) necessary to correct the observed rate (k_π) for the effect of the relative volumes of vapor and liquid phases and the distribution of hydrogen between these phases, the following argument is used:

Let N_t = total moles of hydrogen in the system.

N_g = total moles of hydrogen in the gas phase

N_1 = total moles of hydrogen in the liquid phase

P = pressure of hydrogen, psi

V_g = volume of gas phase, liters

V_1 = volume of liquid phase, liters

R = gas constant in appropriate units

(1.206 psi x liters x $^\circ K^{-1}$ x moles^{-1})

T = temperature, $^\circ K$

Then

$$N_t = N_g + N_1 = \frac{P\,V_g}{RT} + [H_2] V_1 = \frac{P\,V_g}{RT} + \frac{P}{\alpha} V_1 = P\left[\frac{V_g}{RT} + \frac{V_1}{\alpha}\right],$$

and $\dfrac{d\,N_t}{dt} = \dfrac{dP}{dt}\left[\dfrac{V_g}{RT} + \dfrac{V_1}{\alpha}\right]$, relating the rate of change in pressure over the system to the rate of change in the total number of moles of hydrogen in the system. Since hydrogen escapes from the system only by reaction in the liquid phase to form water, another expression for dN_t/dt can be obtained:

$$\frac{-dN_t}{dt} = -V_1 \frac{d[H_2]}{dt} = V_1 [H_2] k_{sol} = V_1 \frac{P}{\alpha} k_{sol}$$

Eliminating dN/dt between these two expressions we arrive at:

$$\frac{dP}{dt}\left[\frac{V_g}{RT} + \frac{V_1}{\alpha}\right] = \frac{V_1 P}{\alpha} k_{sol}, \text{ which rearranges to}$$

$$\frac{dP}{dt} \cdot \frac{1}{P}\left[\frac{V_g}{V_1} \cdot \frac{\alpha}{RT} + 1\right] = k_{sol}$$

Since hydrogen and oxygen always combine in a ratio of 2:1, we may replace the pressure of hydrogen by 2/3 the total pressure (minus steam and excess

inerts) and the change in hydrogen pressure by 2/3 the total change in pressure. Since the solubilities of oxygen and hydrogen are approximately equal in the temperature range of interest it is unnecessary to correct for the presence of oxygen. Thus dP/Pdt is the same as the experimentally determined k_{π}, and the equation may be further simplified to:

$$k_{\pi} \left[\frac{V_g}{V_l} \cdot \frac{\alpha}{RT} + 1 \right] = k_{sol}$$

The expression, $\left[\frac{V_g}{V_l} \cdot \frac{\alpha}{RT} + 1 \right]$, is called $1/F_g$. F_g may conveniently be thought of as the fraction of the total hydrogen of the system which is present in the liquid phase at any time.

As the ratio V_g/V_l approaches zero (no gas phase) the value of F_g approaches 1.0, and at this limit the observed value for k_{π} would approach the true value for k_{sol}. The correctness of this factor has been evaluated[4] by experiments in which the dependence of k_{π} upon the ratio V_g/V_l was determined for a single solution.

The relationship $\frac{1}{k_{\pi}} = \frac{1}{k_{sol}} + \frac{V_g}{V_l} \cdot \frac{\alpha}{RT} \cdot \frac{1}{k_{sol}}$ should give a linear plot of $1/k_{\pi}$ vs V_g/V_l with a slope of α/RTk_{sol} and an intercept of $1/k_{sol}$. From these it should be possible to arrive at independent estimates of $1/k_{sol}$ and α/k_{sol}.

Table 3 lists values of k_{π} corresponding to different values of V_g/V_l for a single solution composition, and Figure 4 shows a plot of $1/k_{\pi}$ vs V_g/V_l. A least squares line through these points fits the equation, $\frac{1}{k_{\pi}} = 0.2046 + 0.687 \, V_g/V_l$, from which it follows that $k_{sol} = 4.89$, $\alpha/k_{sol} = 433.$, and $\alpha = 2118$. The value of the ratio α/k_{sol} is believed considerably more reliable than the values for α or $1/k_{sol}$ since the percentage change in $1/k_{sol}$ is so great for a small error in the data. However, the ratio is the term of greatest practical usefulness since $-d\left[H_2\right]/dt = P_{H_2} \cdot \frac{k_{sol}}{\alpha}$. Thus, if the published values for α

TABLE 3

Effect of Gas-to-Liquid Ratio upon Recombination Rate
at 250°C in a 10^{-3} M $CuSO_4$ and 5×10^{-3} M H_2SO_4 Solution

$\dfrac{V_g}{V_l}$	k_π hr^{-1}	$\dfrac{1}{k_\pi}$	$\dfrac{14.2}{k_\pi}$	$\dfrac{14.2}{k_\pi} - 1$
0.367	2.25	0.444	6.3	5.3
0.522	1.98	0.505	7.17	6.17
0.836	1.34	0.746	10.6	9.6
1.056	1.025	0.975	13.85	12.85
1.057	1.06	0.942	13.4	12.4
1.427	0.893	1.12	15.9	14.9
1.809	0.694	1.44	20.45	19.5
1.831	0.654	1.53	21.73	20.7
2.818	0.465	2.15	30.5	29.5
2.781	0.455	2.21	31.4	30.4
2.826	0.490	2.04	29.0	28.0
3.633	0.398	2.51	35.6	34.6
3.649	0.385	2.60	36.8	35.8
4.956	0.282	3.55	50.4	49.4
5.02	0.276	3.62	51.4	50.4
5.98	0.227	4.41	62.6	61.6
6.01	0.227	4.41	62.6	61.6

Fig. 4 - Effect of Gas-to-Liquid Ratio Upon Recombination Rate.

LEAST SQUARES LINE

$$\frac{1}{k_\pi} = 0.2046 + 0.6867 \frac{V_g}{V_l}$$
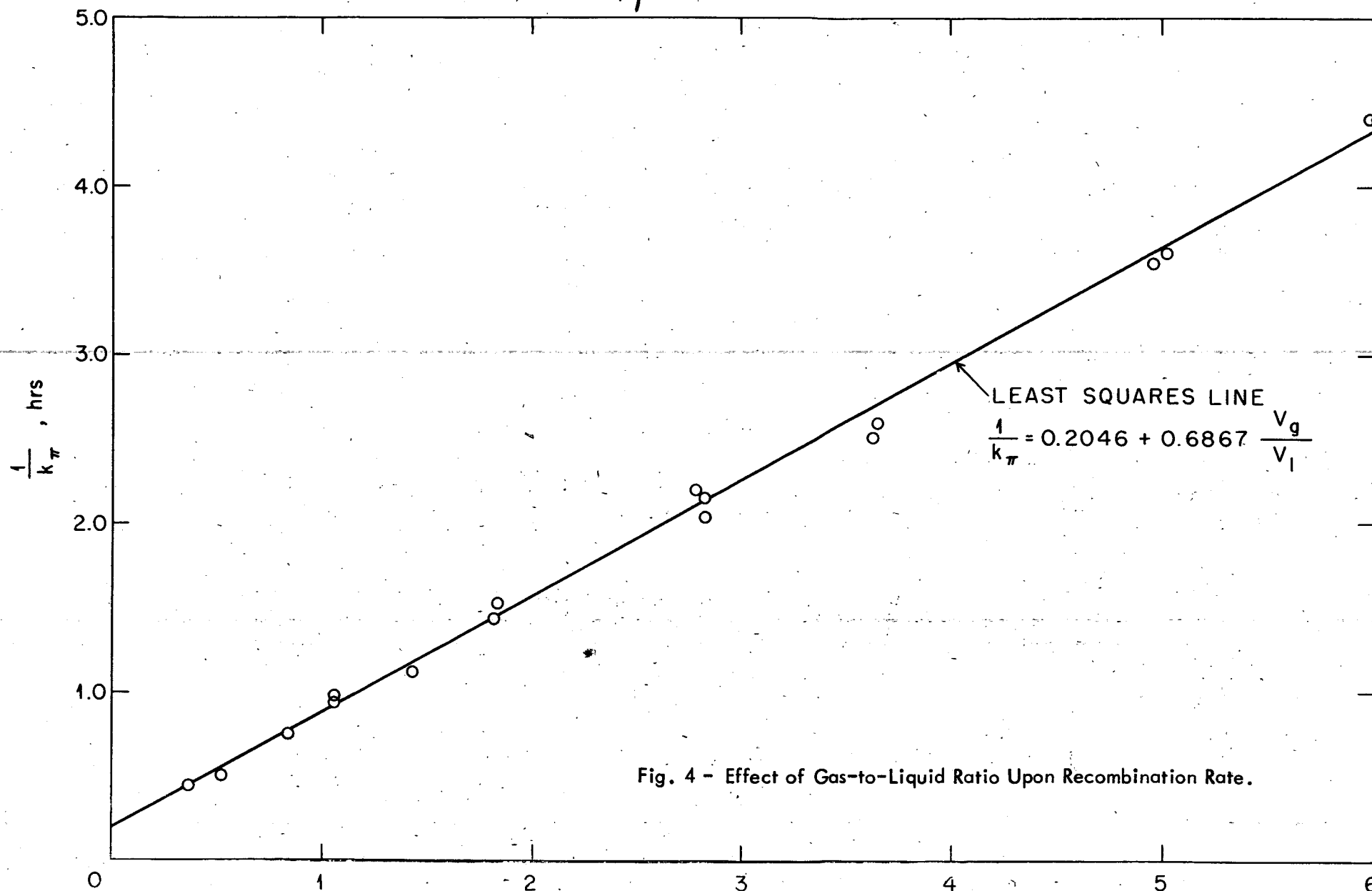
are used and are in error, the resulting experimental values for k_{sol} (and k_{Cu}) will be in error, but in almost exactly compensating amounts. Figure 5 shows how a plot of

$$\frac{k_{sol}}{k_{\pi}} - 1 \quad vs \quad \frac{V_g}{V_1},$$

using 14.2 for k_{sol} (derived from the published value $\alpha = 7300$) and the experimental data for k_{π}, compares with the theoretical slope for α/RT with $\alpha = 7300$. It will be noted that the agreement is best at values of V_g/V_1 near 1.0, the value used in the experiments from which the 14.2 was obtained.

Interpretation of data for uranyl sulfate solutions at high concentrations may require knowledge of the density of the solutions in order to obtain correct values for V_g/V_1 with which to calculate F_g. Marshall[5] has presented formulas for the density of uranyl sulfate solutions which are said to be accurate within the temperature range of interest (120-280°C). His equation #13, with weight percent uranyl sulfate converted to grams uranium per liter (at room temperature), may be replaced by the following equation

$$d_{soln} = .001296 \, g_u + d_{H_2 O_t}$$

where g_u = grams uranium per liter of solution at room temperature.

An additional correction factor may be required to take into account the amount of water which is transferred to the vapor phase when the solution is heated to the reaction temperature:

Let $\dfrac{V_g}{V_1} = \dfrac{1}{y}$ (the corrected ratio)

$\dfrac{V_g}{V_1}$ uncorr. = ratio which would exist in absence of water

vaporization

d_v = saturated steam density at temperature

(0.019976 gm/cc @ 250°C)

d_1 = density of water (0.799 at 250°C)

$x = \dfrac{d_v}{d_1}$ (= 0.025 at 250°C)
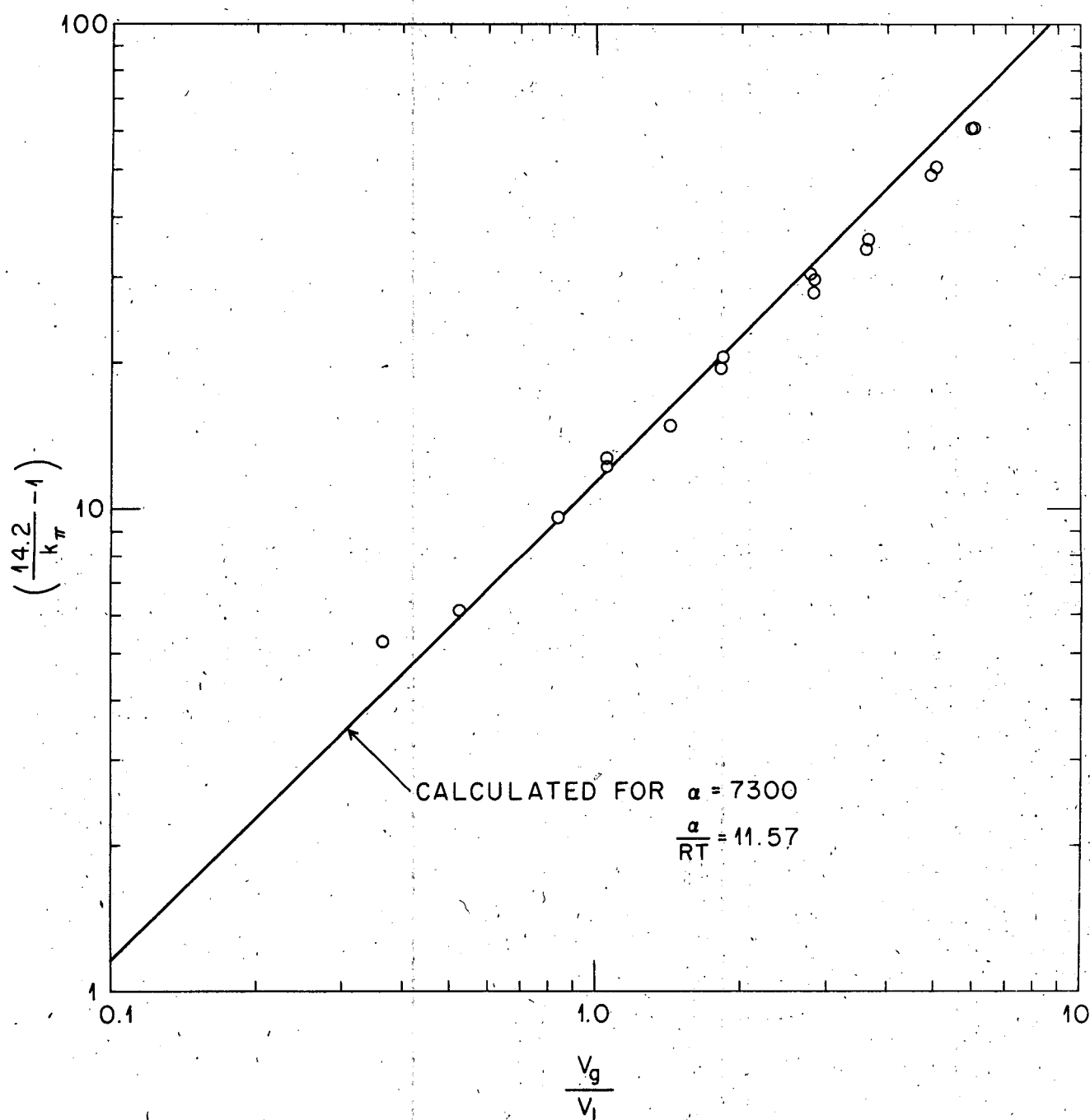
$1-x = 0.975$ (at 250°C)

Fig. 5 – Effect of Gas-to-Liquid Ratio Upon Recombination Rate; Comparison of Experimental Data with Line Based on Published Values for Hydrogen Solubility.

One cc of the saturated vapor will contain water equivalent to x cc of liquid, and the volume of the liquid in contact with 1 cc of the saturated vapor will thus be decreased by x cc from what it would have been in the absence of any loss of water to the vapor phase. Hence, the relationship which corrects for the release of water to the vapor phase is:

$$(V_g/V_1)_{uncorr} = \frac{1 - x}{y + x} = 0.975/(y + 0.025) \quad \text{(at } 250^\circ C)$$

where $1/y$ is the corrected ratio.

Application of the foregoing correction factors to the data of run B-63 leads to a corrected value for $1/F_g$ of 13.0, which gives a value of 6.1 for k_{sol}. Since, on heating, the solution expanded and simultaneously lost water to the vapor phase its volume changed from 9.79 cc at room temperature to 11.66 cc ($V_g/V_1 = 1.04$) at $250^\circ C$. Thus the copper concentration changed from 0.0010 M to 0.00084 M. Dividing 6.1 by 0.00084 gives a k_{Cu}, the molar bimolecular rate constant for copper in this particular environment, of 7.26×10^3 (with units of 1/concentration x 1/time; 1/moles/liter/hr).

Corrections for density and loss of water to the vapor phase have been made only for the runs in Tables 3, 4, 6 and 10. Normally the solution is treated as if it were water at the temperature in question with no loss to the vapor phase. Figure 6 presents plots of $1/F_g$ vs the percent cold fill of the bomb for various temperatures; these plots are normally used in estimating the approximate value of $1/F_g$ to be multiplied by the observed value of k_{π}. Concentrations of copper at room temperature are corrected to lower concentrations at elevated temperatures, based on the specific volume of water, before calculating values of k_{Cu}. A number of additional factors, such as external dead volume, effect of pressure on vapor pressure, effect of pressure on the volume of the metal system, effect of temperature on the volume of the bomb, effect of one gas on solubility of another, etc., have been considered with reference
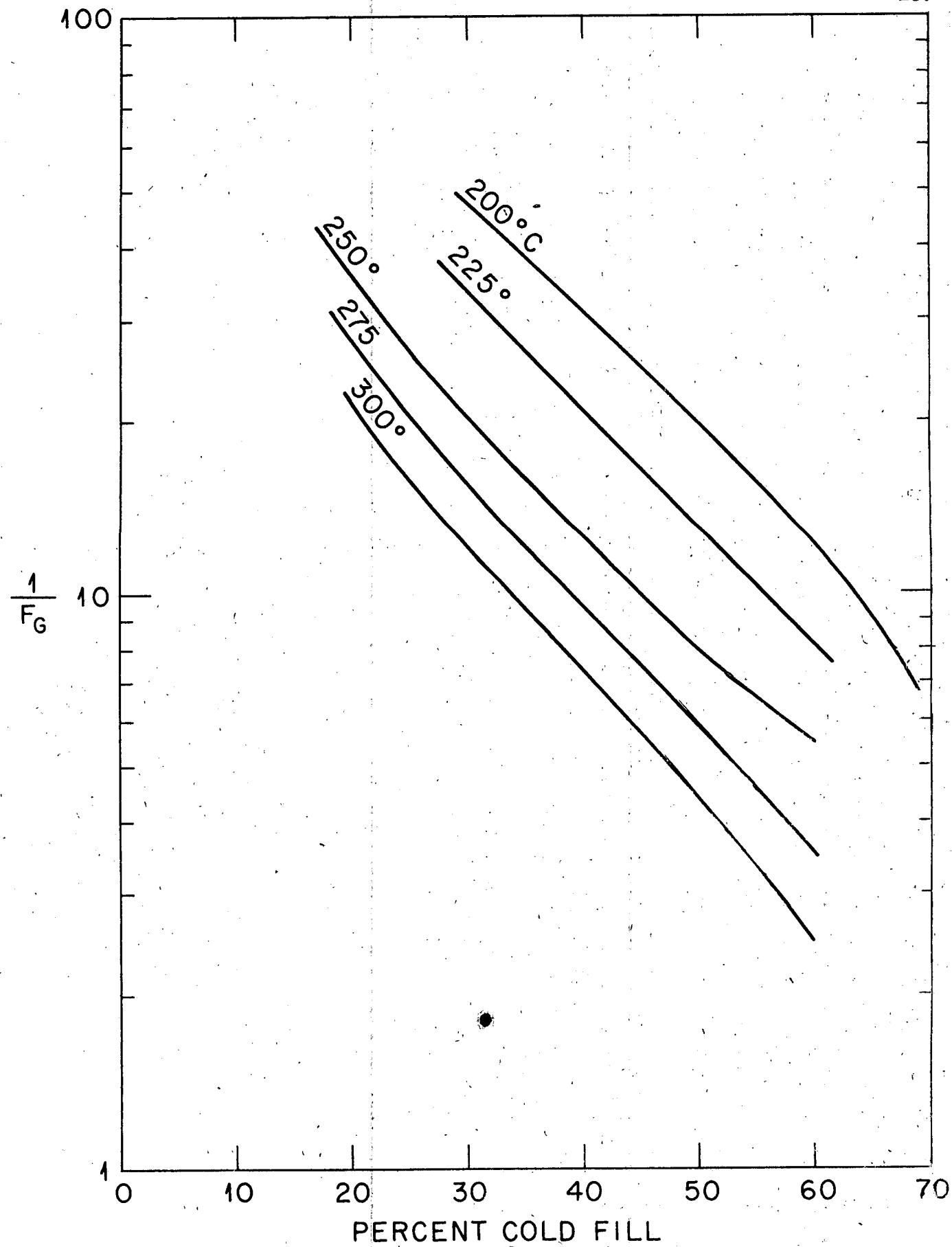
Fig. 6 - Geometry Factors at Elevated Temperatures.

to the interpretation of reaction rate data. Of these, the external dead volume is most important; in the present work it has been minimized by filling the pressure cells with water and by using short lengths of small diameter (0.020 inches I.D.) capillary tubing to connect the high temperature system to the charging valve and pressure measuring cell.

EFFECTS OF DIFFUSION AND AGITATION

In all the previous discussion it has been assumed that the hydrogen in the liquid and vapor phases is in good equilibrium. During the course of early experimental work relating V_g/V_1 to the observed k_π, using non-agitated cylindrical bombs mounted vertically, it became evident that the results did not agree with expectations. It was suspected that diffusion of hydrogen might be acting as a limiting factor. Placing the bombs in a horizontal position (which increased the free surface area of the liquid and decreased the depth of the liquid) resulted in much faster rates of reaction which were more in line with expectations. Adding the rocking agitation feature discussed in the section on Experimental Technique has eliminated subsequent troubles with hydrogen diffusion. An analysis of the diffusion problem in vertical cylindrical bombs with no agitation or convection has shown that, after a transient approach, a steady state of hydrogen concentration vs depth in the liquid is established[6]. From an equilibrium concentration at the surface the dissolved hydrogen decreases by the factor $1/e$ in a distance $(D/k_{sol})^{1/2}$, D being the diffusion coefficient for hydrogen in water at the temperature in question and having a value of 1.34×10^{-4} cm^2/sec. at 250°C. For a representative value of k_{sol} of 11.0/hr or 0.00306/sec., the exponential length is seen to be 2.1 mm. Thus, in unagitated bombs containing such a solution most of the reaction would be taking place in the 1 cm layer immediately below the gas-liquid interface. As will be discussed

in the next paper of the series, diffusion does not present a problem when the hydrogen is being produced homogeneously throughout the solution (e.g. decomposition of water by a fissioning aqueous homogeneous reactor solution) and when this solution is exposed to the equilibrium or steady-state pressure of hydrogen.

DEPENDENCE ON HYDROGEN CONCENTRATION

The first order dependence on hydrogen concentration has been established by several methods. The slope of the dP/dt vs P line obtained experimentally (k_{π}) does not change as the reaction progresses to completion; thus, for a variety of pressures of hydrogen the rate remains proportional to the hydrogen pressure. Changing the amount of excess oxygen supplied initially does not change the value of k_{π} but only affects the position of the pressure axis intercept. Starting at different pressures of hydrogen likewise does not change the value of k_{π}. Furthermore, the use of varying gas to liquid ratios gives rise to a constant value for k_{sol} which could only be true if the model, chosen for the reaction, is correct. The in-pile experiments to be reported in the next paper of this series carry this demonstrated first order dependence on hydrogen pressure up to nearly 5000 psi.

DEPENDENCE ON COPPER CONCENTRATION

Using varying concentrations of copper (added as cupric sulfate) in a uranyl sulfate solution containing 40 gms U/l (at room temperature), the reaction at 250°C has been shown to be apparently first order in copper. Tables 4 and 10 and Figure 7 present these data.

Using varying concentrations of copper sulfate in sulfuric acid (0.005 M H_2SO_4 at room temperature) the reaction also appears to be first order in copper at 250°. Table 5 and Figure 8 present the data.

TABLE 4

Effect of Copper Sulfate Concentration upon Recombination Rate at 250°C in 0.166 Molar Uranyl Sulfate Solution

Run No.	Bomb No.	Bomb Vol. cc	Soln. Wt. gms	Soln. Dens. at 250°C gms/cc	V_1 250° Uncorr.	% Hot Fill Uncorr.	V_g/V_1 Corr.	$1/F_g$	k_π hr⁻¹	k_{sol} hr⁻¹	Vol. Soln. Room Temp.	Vol. Soln. 250° Corr.	[Cu] 250°
B-202	637	24.14	12.169	.851	14.3	59.2	0.743	9.6	0.078	0.748	11.56	13.85	.0001252
3-203	638	23.98	10.134	.851	11.9	49.65	1.097	13.7	0.094	1.288	9.63	11.44	.0002102
B-204	639	24.20	10.171	.851	11.95	49.4	1.106	13.8	0.1855	2.56	9.67	11.50	.00042
B-205	637	24.14	11.056	.851	13.0	53.8	0.924	11.7	0.105	1.228	10.52	12.55	.0002096
B-206	638	23.98	10.097	.851	11.87	49.5	1.097	13.7	0.182	2.494	9.6	11.44	.0004195
B-207	639	24.20	12.034	.851	14.14	58.4	0.764	9.85	0.0866	0.854	11.43	13.72	.000125
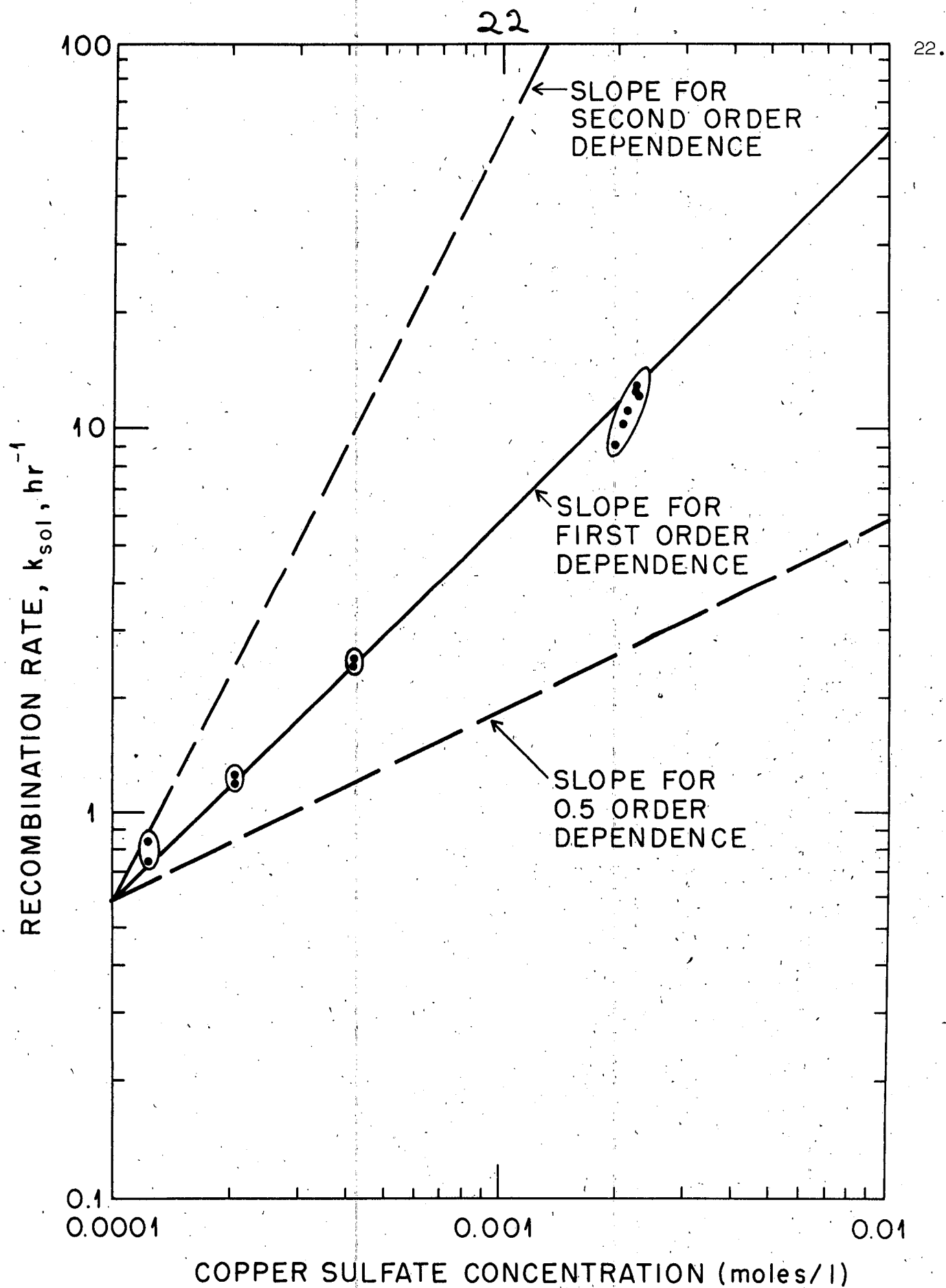
Fig. 7 – Effect of Copper Sulfate Concentration Upon Recombination Rate
at 250°C in 0.166 M Uranyl Sulfate Solutions.

TABLE 5

Effect of Copper Sulfate Concentration Upon Recombination Rate
at 250°C in 0.005 Molar Sulfuric Acid Solutions

Run No.	Cu Concn. Moles/l.	k_{sol} hr^{-1}
B-214	0.00010	17.2 *
B-222	0.00010	1.76
B-223	0.00010	1.38
B-215	0.00025	26.7 *
B-219	0.00025	8.28 *
B-221	0.00025	3.97
B-225	0.00025	3.09
B-226	0.00025	2.89
B-216	0.00060	36.3 *
B-218	0.00060	7.66
B-220	0.00060	7.08
B-224	0.00060	7.65
B-217	0.0010	11.6
B-227	0.00010	1.45 **
B-228	0.00010	1.39 ***

*   Data excluded because of contamination from previous runs

**   Sulfuric acid concentration 0.0010 M

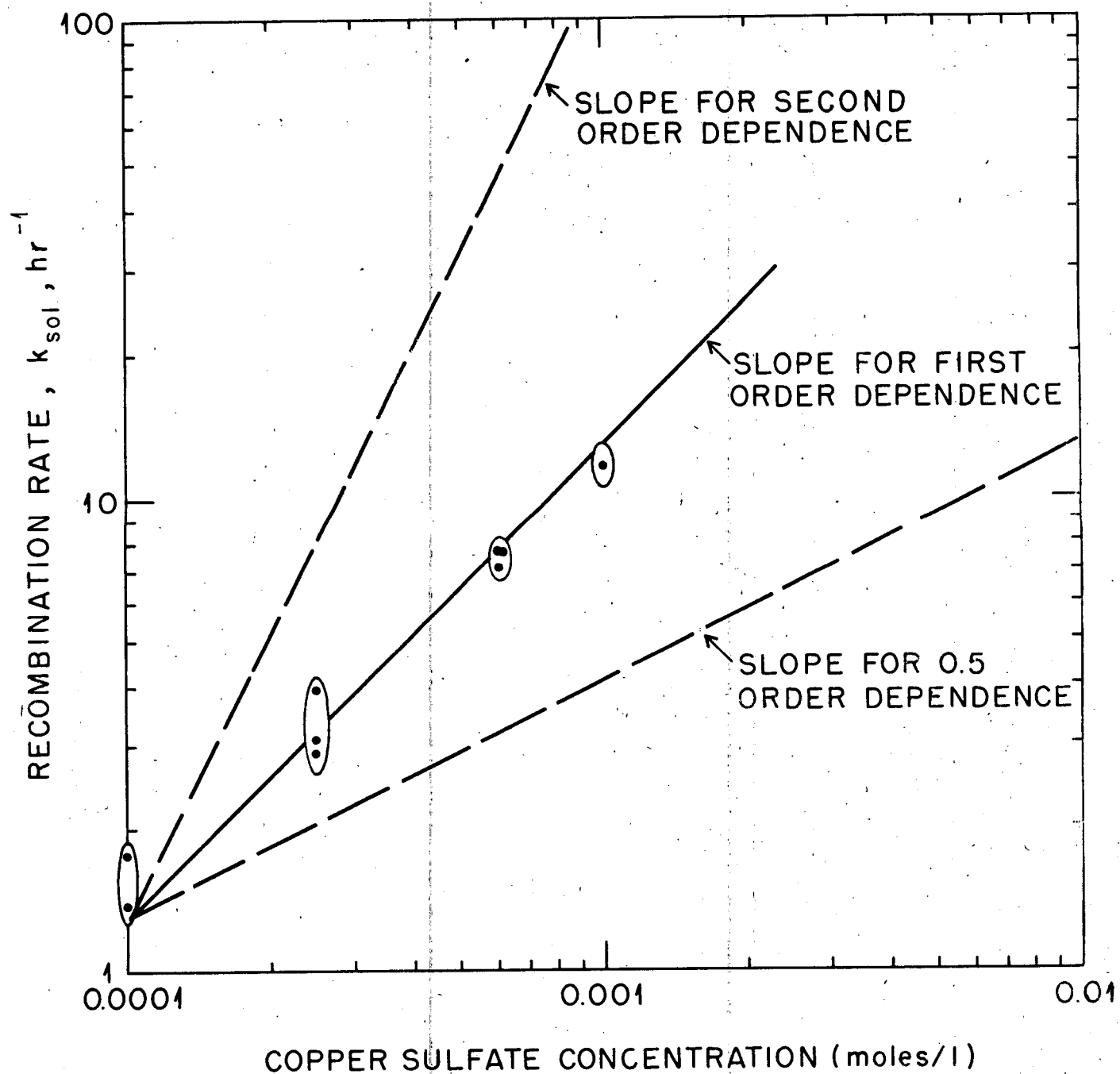***   Sulfuric acid concentration 0.0030 M

Fig. 8 – Effect of Copper Sulfate Concentration Upon Recombination Rate at 250°C in 0.005 M Sulfuric Acid Solution.

EFFECT OF URANYL SULFATE CONCENTRATION

Using solutions which were initially all 0.0010 M in copper but which contained varying concentrations of uranium as uranyl sulfate, the effect of the uranyl sulfate upon the value of k_{Cu} was determined as shown in Table 6 and Figure 9. The scatter in the data at uranium concentrations below nine grams per liter is associated with phase instability and hydrolytic precipitation. The addition of excess acid (25 and 50 mole precent, based on the uranyl sulfate) overcomes this phase stability and permits measurements of the recombination rate to be made at low uranium concentrations. Table 7 presents data covering the temperature range 250-295°C, and the concentration range of 2.5-10 gm U/l for solutions containing 25-50 mole percent excess sulfuric acids and 0.0010-0.0050 M $CuSO_4$. The data at 250°C give further support to the first order dependence on copper concentration discussed above.

DEPENDENCE ON SULFATE CONCENTRATION AND ACIDITY

The pronounced dependence of the reaction upon the environment in which the copper finds itself is illustrated by Table 8 and Figure 10 which show the effect of various concentrations of sulfuric acid upon the recombination behavior of solutions of 0.0010 M $CuSO_4$. Studies are now in progress in which the dependence of the reaction rate upon acidity, sulfate concentration, and copper concentration is being determined over wide ranges of these variables.

ACTIVITY OF CUPRIC PERCHLORATE PLUS PERCHLORIC ACID

Perhaps the simplest hypothesis which could be advanced to explain the recombination of hydrogen and oxygen in the presence of dissolved cupric compounds would involve a reaction of dissolved hydrogen with the cupric ion. Accordingly it was very desirable to determine the activity of copper under conditions which would tend to minimize any complexing of the cupric ion by anions of the

TABLE 6

Effect of Uranyl Sulfate Concentration upon Recombination Rate in 10^{-3} M Copper Sulfate Solution at 250°C

Run No.	Bomb No.	Bomb Vol. cc	Conc. U at Room Temp. gm.U/l	Soln. Wt. gms	Soln. Dens. at 250°C gms/cc	V_1 250° Uncorr.	% Hot Fill Uncorr.	V_g/V_1 Corr.	$1/F_g$	k_π hr⁻¹	k_{sol} hr⁻¹	Vol. Soln. Room Temp.	Vol. Soln. 250° Corr.	[Cu] 250°	k_{Cu} 10^{-3}	$(gm.U/l)^{\frac{1}{2}}$
B-72	641	23.79	1.0	9.7	.800	12.12	50.94	1.05	13.1	0.455	5.96	9.7	11.60	.00084	7.10	1.0
B-75	641	23.79	1.0	9.5		11.88	49.93	1.08	13.50	0.533	7.20	9.6	11.44	.00084	8.57	
B-79	642	23.90	1.0	13.37		16.73	70.00	0.457	6.29	0.88	5.54	13.37	16.40	.00082	6.76	
B-88	642	23.90	1.0	6.055		7.57	31.67	2.35	28.19	0.31	8.74	6.06	7.13	.00085	10.28	
B-93	641	23.79	1.0	11.723		14.67	61.66	0.672	8.78	0.68	5.97	11.74	14.23	.00083	7.19	
B-80	640	23.73	2.25	9.457	.802	11.79	49.68	1.09	13.61	0.64	8.71	9.41	11.35	.00083	10.49	1.5
B-87	641	23.79		12.004		14.98	62.96	0.633	8.32	0.71	5.91	11.94	14.57	.00082	7.21	
B-94	642	23.90		4.842		6.04	25.27	3.27	38.83	0.16	6.21	4.85	5.60	.00087	7.14	
B-62	640	23.73	2.62	9.4	.802	11.73	49.43	1.11	13.84	0.555	7.68	9.35	11.25	.00083	9.25	1.62
B-66	641	23.79		9.4		11.73	49.30	1.12	13.90	0.500	6.95	9.35	11.22	.00083	8.37	
B-81	641	23.79	4.0	9.527	.804	11.86	49.83	1.08	13.7	0.60	8.22	9.46	11.44	.00083	9.90	2.0
B-86	640	23.73		6.150		7.65	32.23	2.28	27.5	0.33	9.08	6.11	7.23	.00085	10.68	
B-96	641	23.79		11.664		14.52	61.03	0.688	8.94	0.625	5.59	11.64	14.09	.00083	6.73	
B-82	642	23.90	6.25	9.425	.807	11.69	48.91	1.13	14.1	0.60	8.46	9.34	11.22	.00083	10.19	2.5
B-90	641	23.79		5.903		7.32	30.76	2.44	29.3	0.25	7.33	5.85	6.92	.00085	8.62	
B-97	642	23.90		12.170		15.10	63.17	0.625	8.25	0.875	7.22	12.11	14.71	.00082	8.80	
B-83	640	23.73	9.0	9.683	.811	11.95	50.35	1.07	13.4	0.525	7.04	9.56	11.46	.00083	8.48	3.0
B-91	642	23.90		11.72		14.47	60.54	0.705	9.15	0.75	6.86	11.57	14.02	.00083	8.26	
B-71	640	23.73	10.0	9.9	.813	12.18	51.32	1.03	12.9	0.60	7.74	9.8	11.69	.00084	9.21	3.16
B-76	642	23.90		9.5		11.69	48.91	1.13	14.1	0.587	8.28	9.4	11.22	.00084	9.86	
B-63	641	23.79	26.2	10.1	.834	12.12	50.94	1.04	13.1	0.468	6.13	9.79	11.66	.00084	7.30	5.1
B-67	642	23.90		9.9		11.88	49.70	1.10	13.7	0.444	6.08	9.57	11.38	.00084	7.24	

TABLE 6 (Continued)

| Run No.	Bomb No.	Bomb Vol. cc	Conc. U at Room Temp. gm.U/l	Soln. Wt. gms	Soln. Dens. at 250°C gms/cc	V_l 250° Uncorr.	% Hot Fill Uncorr.	V_g/V_l Corr.	$1/F_g$	$k_{\pi-1}$ hr^{-1}	k_{sol} hr^{-1}	Vol. Soln. Room Temp.	Vol. Soln. 250° Corr.	[Cu] 250°	k_{Cu} 10^{-3}	(gm.U/1)$^{\frac{1}{2}}$
B-68	640	23.73	83	11.0	.907	12.14	51.15	1.03	13.0	0.32	4.16	9.91	11.69	.00085	4.89	8.2
B-69	642	23.90	142.5	11.2	.984	11.38	47.61	1.18	14.8	0.207	3.06	9.43	10.96	.00086	3.56	11.9
B-70	641	23.79	205	11.9	1.065	11.18	46.99	1.22	15.2	0.207	3.15	9.38	10.72	.00088	3.58	14.3
B-64	642	23.90	262	12.6	1.139	11.06	46.27	1.24	15.5	0.166	2.57	9.37	10.67	.00088	2.92	16.2
B-65	640	23.73		12.5		10.97	46.22	1.25	15.6	0.182	2.84	9.29	10.55	.00088	3.23	
B-106	640	23.73		6.373		5.60	23.59	3.62	42.88	0.070	3.00	4.72	5.14	.00092	3.26	
B-107	641	23.79		11.681		10.26	43.12	1.42	17.43	0.23	4.01	8.65	9.83	.00088	4.56	
B-108	642	23.90		19.999		17.56	73.47	0.382	5.42	0.45	2.44	14.8	17.29	.00086	2.84	
B-119	641	23.79		5.457		4.79	20.14	4.53	53.41	0.070	3.74	4.04	4.30	.00094	3.98	
B-120	642	23.90		19.211		16.87	70.58	0.445	6.15	0.427	2.63	14.23	16.54	.00086	3.06	
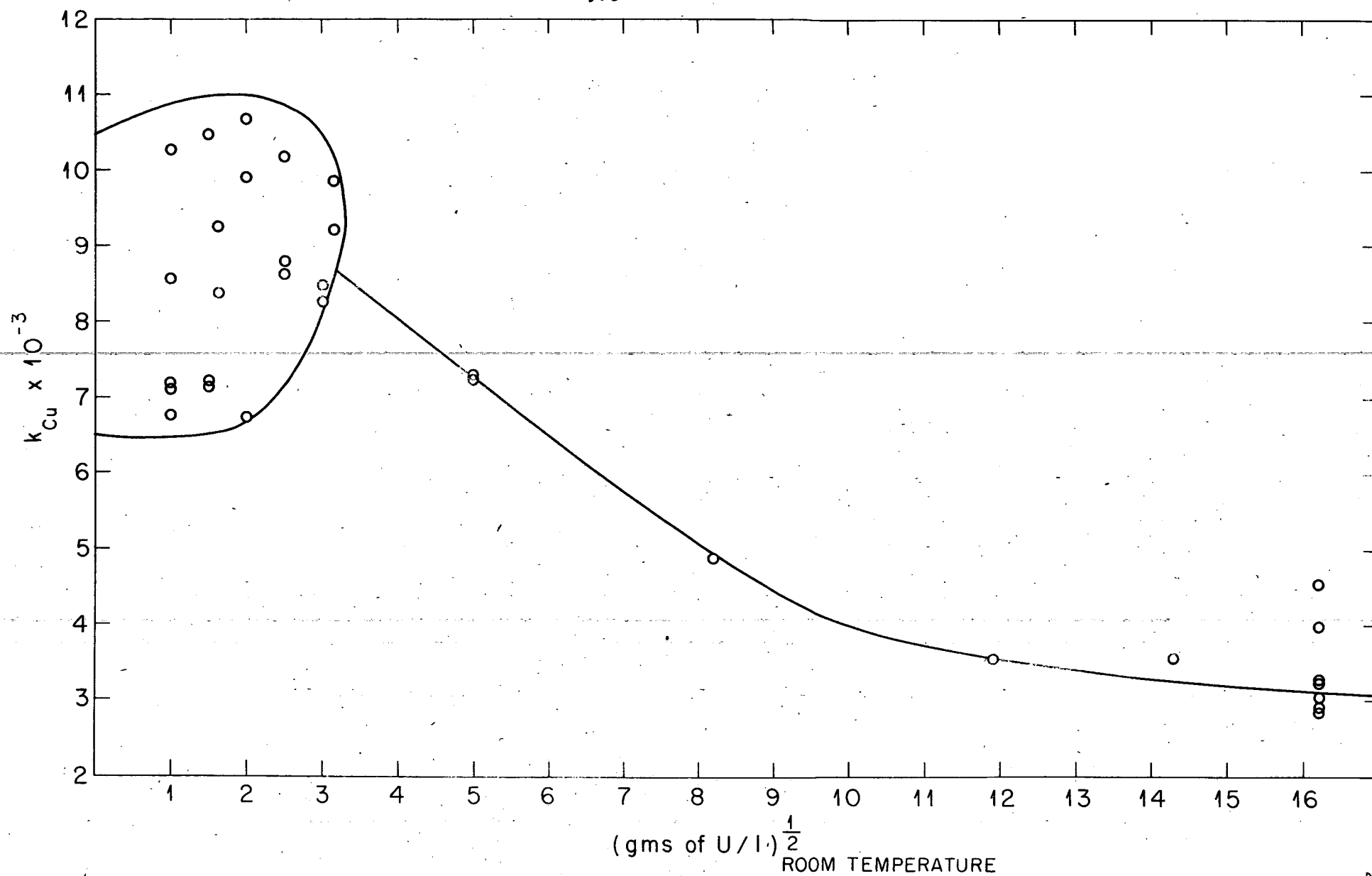
Fig. 9 – Effect of Uranyl Sulfate Concentration Upon Hydrogen-Oxygen Recombination in
0.001 M Copper Sulfate Solution at 250°C.

TABLE 7

Effects of Uranium Concentration, Copper Concentration, Excess Sulfuric Acid, and Temperature upon Recombination Rate

Mole % Excess Acid	T°C	U Conc. gm./l.	0.0010 M* Cu			0.0050 M* Cu		
			Expt. No.	$k_{sol.}$ hr^{-1}	k_{Cu} X 10^{-3}	Expt. No.	$k_{sol.}$ hr^{-1}	k_{Cu} X 10^{-3}
25	250	2.5	B-239	7.51	9.38	B-274	36.5	9.13
		2.5	243	8.37	10.46	278	38.55	9.64 **
		2.5	247	7.21	9.01			
		5	240	9.31	11.65	275	36.5	9.13 **
		5	244	6.16	7.70	279	34.52	8.63
		5	245	6.22	7.78			
		10	241	5.29	6.62	276	30.2	7.56
		10	242	4.76	5.95	277	30.65	7.67
		10	246	----	leak			
50	250	2.5	248	6.73	8.41			
		2.5	252	7.28	9.10			
		5.	249	5.57	6.96			
		5.	253	4.98	6.23			
		10	250	4.86	6.08			
		10	251	4.93	6.16			
25	275	2.5				280	65.4	17.22
		2.5				283	121.6	32.0 **
		2.5				287	90	23.7
		5				281	82.2	21.7
		5				284	98.5	26.0
		5				288	79.2	20.9
		10				282	68.1	17.95
		10				285	91.0	24.0
		10				286	82	21.6
50	275	2.5	256	25.5-15.0	34-20?			
		2.5	257	18.4	24.2			
		5	254	16.6	21.8			
		5	258	15.2	20.0			
		10	255	13.4	17.6			
		10	259	24.6	32.4?			
25	295	2.5	268	32.6	45.1			
		2.5	272	42.4	58.6			
		5	269	35.1	48.5			
		5	273	38.2	52.8			
		10	270	33.5	46.3			
		10	271	34.5	47.7			

<div align="center">

TABLE 7

(Continued)

</div>

Mole % Excess Acid	T°C	U Conc. gm./l.	Expt. No.	k_{sol} hr^{-1}	k_{cu} X 10^{-3}	Expt. No.	k_{sol} hr^{-1}	k_{cu} X 10^{-3}
50	295	2.5	262	42.2	58.3			
		2.5	266	45.4	62.8			
		5	263	38.1	52.6			
		5	267	35.7	49.3			
		10	264	erratic	--			
		10	265	29.0	40.1			

*   Concentration at room temperature

** All in same bomb - may have become contaminated on walls
to give high results.

TABLE 8

Effect of Sulfuric Acid Concentration upon Recombination Rate over 0.0010 M Copper Sulfate at 250°C

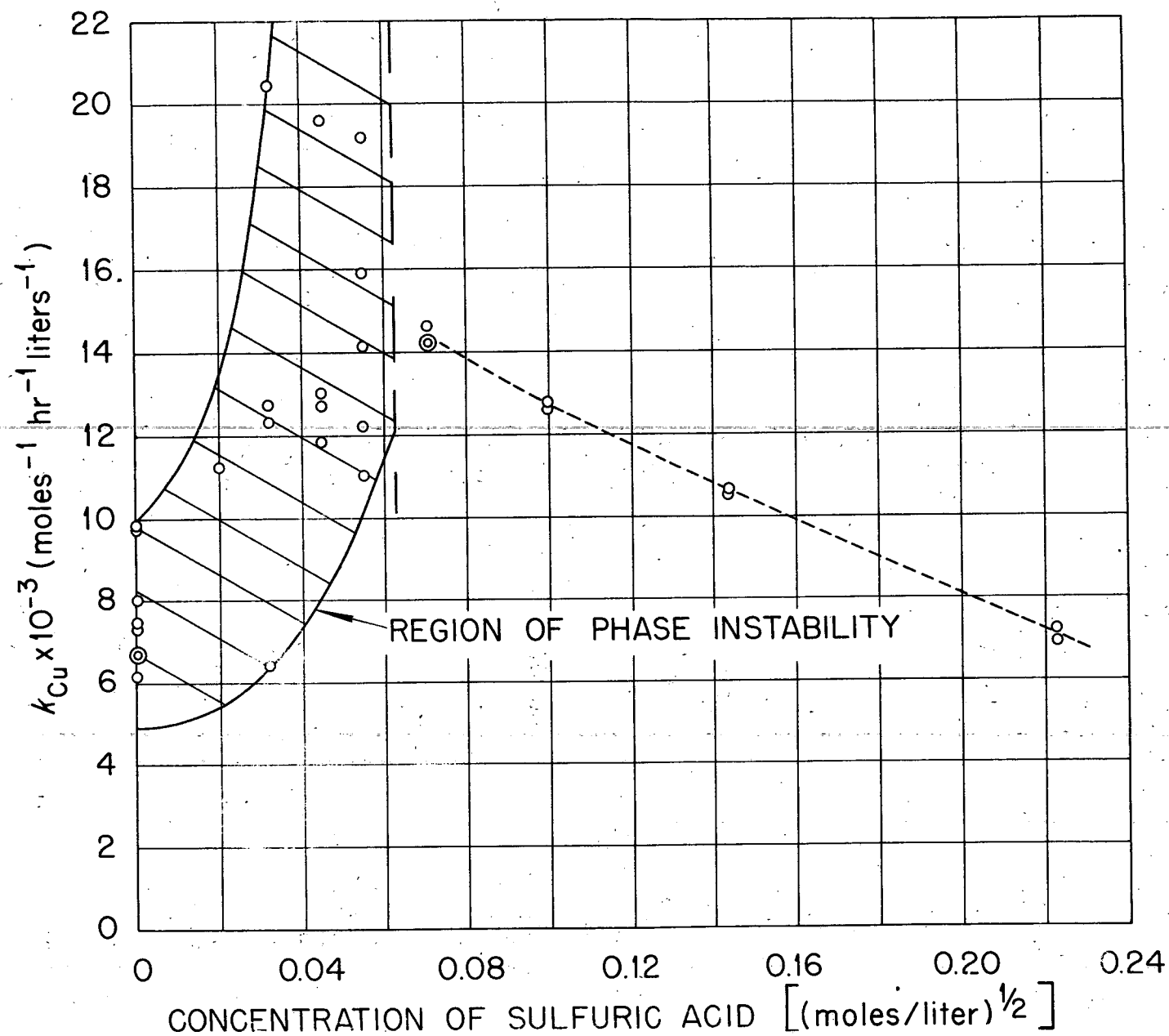| Run No.	Concentration H_2SO_4	$10^{-3} k_{Cu}$	$[H_2SO_4]^{1/2}$
B- 1	0.00 M	6.7	
18		6.7	
73		7.7	
74		9.8	
77		9.7	
85		6.1	
89		7.3	
99		8.0	
47	0.00040	11.2	.02
33	0.0010	20.6	.032
136		6.4	
140		12.7	
144		12.3	
34	0.0020	19.6	.045
137		12.7	
141		12.98	
142		11.8	
35	0.0030	19.2	.055
138		14.1	
139		12.2	
143		27.6	
145		11.0	
146		15.9	
130	0.0050	14.2	.071
135		14.2	
147		14.6	
131	0.010	12.6	0.10
134		12.7	
109	0.020	10.5	.141
114		10.6	
132	0.050	7.2	0.223
133		6.9	

Fig. 10 - Effect of Sulfuric Acid Concentration Upon Hydrogen-Oxygen Recombination in 0.001 M Copper Sulfate Solution at 250°C.

solution. The known usefulness of the perchlorate ion to this end for a variety of systems at room temperatures suggested that cupric perchlorate be tested. At 0.0010 Molar cupric perchlorate precipitation was found to occur at $250^{\circ}C$, but the presence of 0.005 Molar perchloric acid was found sufficient to maintain phase stability at this temperature. Recombination experiments were run with perchloric acid concentrations of 0.005, 0.010 and 0.050 M in the presence of 0.0010 M cupric perchlorate with the results shown in Table 9.

The constancy of k_{Cu} at 5000 suggests that this may be the value for the activity of uncomplexed cupric ion. The data further indicate that no complexing by perchlorate is taking place and that there is no direct participation of hydrogen ions in the reaction (except for the suppression of the hydrolytic precipitation).

All experiments with perchlorate have been limited to short times at high temperatures to avoid exessive corrosion of apparatus by traces of chloride ion released from decomposition of perchlorate.

TEMPERATURE COEFFICIENT OF THE REACTION

Table 10 presents data for the reaction rate at several different temperatures. The starting solutions were the same at room temperature, and therefore the compositions were not precisely the same at reaction temperature. Corrections for the small differences in composition have been applied to give the observed values for k_{Cu}. The experimentally observed activation energy for the $190-250^{\circ}$ values is 24,400 calories. Further data on this point from in-pile irradiation studies will be presented in the next paper of this series.

Data from Table 7 illustrate the temperature dependence of the reaction for somewhat different environmental conditions. Figure 11 shows how the temperature dependence is essentially unaffected by these variations in solution composition.

TABLE 9

Effect of Perchloric Acid Upon Recombination
Over 0.0010 M Cupric Perchlorate at 250°C

Run No.	Concentration Perchloric Acid	k_{Cu}
B-151	0.0050 M	4988
B-152	0.010	4975
B-153	0.050	5025

TABLE 10

Temperature Dependence of Recombination in 0.166 M Uranyl Sulfate Plus 0.0025 M Copper Sulfate Solutions

| Run No.	Temp. °C	Bomb No.	Bomb Volume cc	Soln. Wt. gms	Hot Soln. Density	Hot Soln. Volume Uncorr.	% Hot Fill Uncorr.	V_g/V_l Uncorr.	V_g/V_l Corr.	$1/F_g$	k_π	k_{sol}	Cold Soln. Vol.	Hot Soln. Vol. Corr.	Hot Cu Conc. M	k_{Cu} X10^{-3}	Avg. k_{Cu} X10^{-3}
A-236	190	613	30	14.49	.927	15.63	52.1	0.92	0.935	27.	0.0237	0.64	13.82	15.5	0.00223	0.287	
A-237		617		14.26		15.38	51.2	0.954	0.97	28	0.0206	0.576	13.61	15.22	.002235	0.258	.261
A-243		617		14.97		16.15	53.8	0.858	0.870	25.2	0.021	0.53	14.28	16.05	.002225	0.238	
A-233	220	610	30	14.36	.891	16.13	53.75	0.943	0.975	20.2	0.510	10.3	13.70	15.18	.00226	4.55 *	
A-234		611		14.12		15.85	52.8	0.894	0.922	19.16	0.172	3.29	13.47	15.60	.00216	1.52	
A-240		611		14.60		16.40	54.7	0.828	0.853	17.8	0.169	3.01	13.93	16.18	.00215	1.40	1.50
A-241		612		14.70		16.51	55.0	0.818	0.844	17.63	0.194	3.42	14.03	16.27	.002155	1.59	
A-216	250		30	4.80	.850	5.65	18.84	4.31	4.95	58.3	0.223	13.0	4.58	5.04	.00227	5.72	5.35
A-217				5.14		6.05	20.17	3.96	4.51	53.2	0.240	12.8	4.90	5.45	.002245	5.7	
A-221		610		4.736		5.57	18.56	4.385	5.0	58.8	0.212	12.46	4.52	5.0	.00226	5.51	
A-277		620		15.62		18.88	62.9	0.590	0.615	8.12	1.146	9.31	14.90	18.57	.00201	4.63	
A-297		612		15.04		17.70	59.0	0.695	0.728	9.42	1.203	11.33	14.35	17.37	.00211	5.36	
A-210		611		15.18		17.96	59.8	0.672	0.702	9.13	1.25	11.4	14.48	17.62	.00210	5.43	
A-213		617		15.55		18.30	61.0	0.640	0.670	8.76	1.20	10.5	14.84	17.95	.00207	5.07	
B-208	220	637	24.14	11.062	.891	12.415	51.43	0.944	0.975	20.21	0.1828	3.694	10.56	12.22	.00216	1.71	
B-209		638	23.98	10.233		11.485	47.89	1.088	1.13	23.26	0.159	3.698	9.76	11.26	.00217	1.70	1.67
B-210		639	24.20	9.347		10.490	43.35	1.307	1.36	27.79	0.126	3.501	8.92	10.25	.00218	1.61	

* Excluded from average
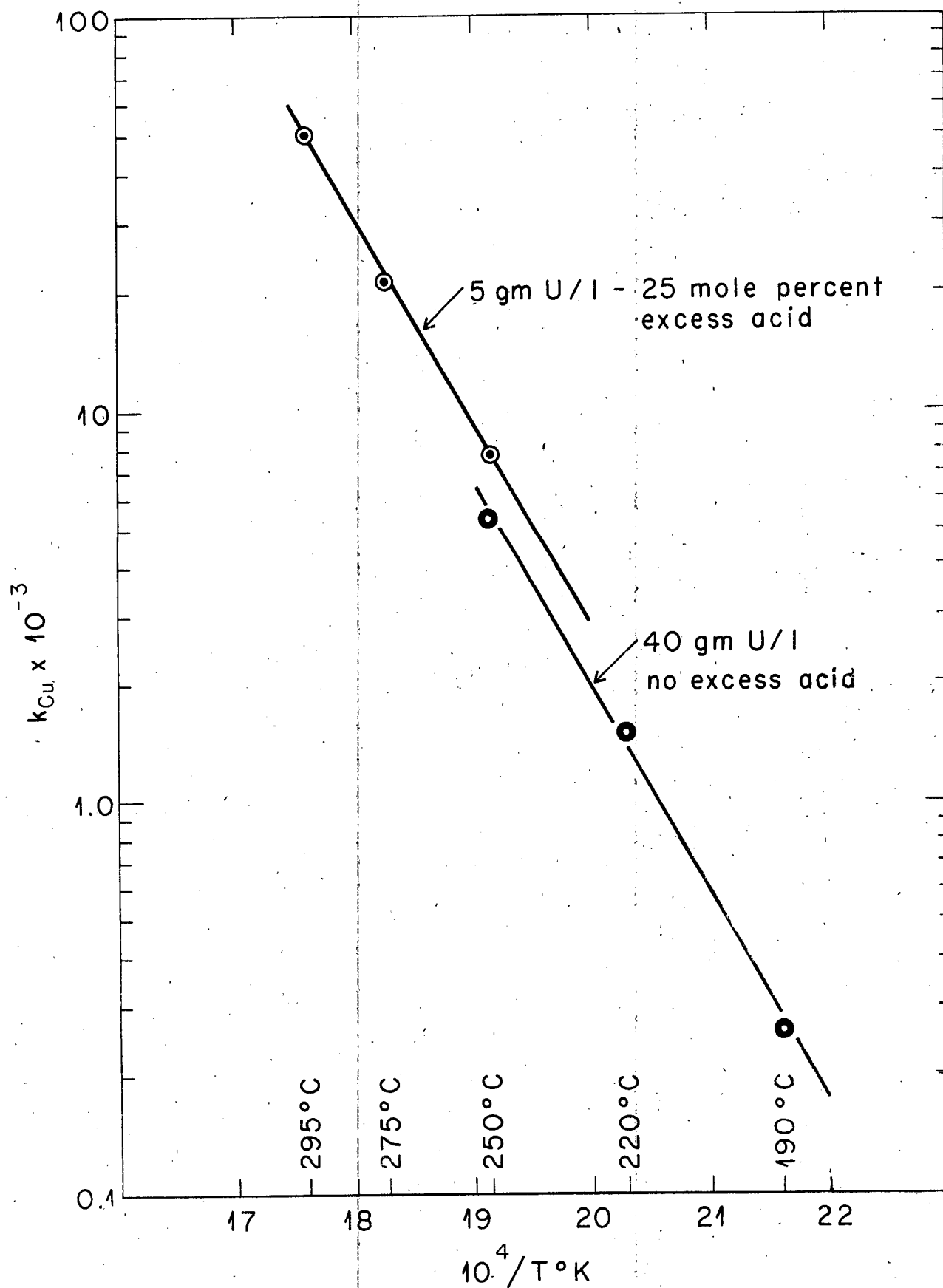
FIG. 11 – EFFECT OF TEMPERATURE ON THE RECOMBINATION RATE

RATE OF REACTION WITH DEUTERIUM

Since operating reactors of the homogeneous type may well use heavy water solutions instead of light water, the decomposition gases would be deuterium and oxygen instead of hydrogen and oxygen. The reaction of deuterium with the catalyst might be expected to be somewhat slower than the reaction of hydrogen. Accordingly three experiments, at different ratios of liquid to gas phase were conducted in which deuterium gas was substituted for hydrogen gas (ultimately the reaction will be checked using heavy water solutions and deuterium). The solution was one for which considerable data with hydrogen gas was available (0.005 M sulfuric acid and 0.001 M copper sulfate). The results are presented in Table 11. A least squares line for the relationship between V_g/V_l and $1/k$ gave the following values:

$$k_{sol} = 2.227$$
$$\alpha = 1693$$
$$\frac{\alpha}{k_{sol}} = 760$$

Comparison of the ratio α/k_{sol} with that for hydrogen, 433, indicates that the reaction is about 60% as fast with deuterium as with hydrogen. The solubility of deuterium is indicated as being slightly greater than that of hydrogen in light water, but the number of experiments is too small to permit any strong conclusion. At least the solubilities do not differ substantially.

OTHER POSSIBLE CATALYSTS

A large number of inorganic ions have been tested for possible recombination catalysis. None has been found to approach copper in activity. No significant activity at 250°C was found for Ni, Co, Zn, Cd, Pb, As, Li, Rb, Cl, K, Br, Mg, and SO_4 ions. Uranyl solutions have slight activity. Fe, Tl, Ce, Sn, Mn, V, and Ti were found to have slight activity in the presence of uranyl sulfate

TABLE 11

Recombination of Deuterium and Oxygen in Light Water Solutions
0.005 M Sulfuric Acid and 0.001 M Copper Sulfate
at 250°C

Run No.	V_g/V_1	$1/k_{\pi}$
B-233	6.05	7.751
B-234	0.60	1.075
B-235	1.87	2.906

solution. In one preliminary experiment an acidified pertechnitate solution showed moderate recombination activity, but interpretation was made difficult by the formation of a large amount of black precipitate during the run. Silver and iodine were found to exhibit substantial activity in the presence of uranyl sulfate (added as silver sulfate and potassium iodide, respectively). At the end of these experiments the iodide appeared as elemental iodine in the solution and the silver as a gray fog of apparently precipitated silver. The questions raised by these anomalies have not yet been answered, largely due to the marked superiority of copper for reactor use. The possibility has been considered that pairs of inorganic oxidation-reduction reactions might be found which would couple to give improved performance. None has yet been found.

HOMOGENEOUS CATALYSIS OF REACTIONS INVOLVING HYDROGEN

A few examples in the literature provide indications of reactions between molecular hydrogen and molecularly dispersed species in solution. These should be considered carefully for their relevance to any ultimate development of the mechanism of the recombination reaction. The use of hydrogen for the reduction of copper ions dates from the work of Ipatieff and Werchowsky[7] in which reduction to large microcrystals of the metal was accomplished. Other papers of Ipatieff[8,9] and, lately, the paper by Ipatieff, Corson, and Kurbatov[10] have established that under proper conditions Cu, Ni, Co, Pb, and Bi can all be reduced and precipitated. Within the last few years commercial processes for refining metallic ores, based partly on these techniques, have made their appearance[11]. Another interesting line of work involving reactions of molecular hydrogen with dissolved reagents, initiated by Calvin et. al., was discussed in a recent paper by Mills and Weller[12]. Working in non-aqueous systems using

nitrogen bases as the solvents and quinone as a hydrogen acceptor they found cuprous acetate to be a powerful homogeneous catalyst for the oxidation of molecular hydrogen. A dimerized complex was postulated as the active species, with the hydrogen molecule becoming simultaneously attached to two copper atoms in the activated complex. A similar approach of molecular hydrogen to a dimerized cobalt carbonyl is considered responsible for the catalytic activity of the "oxo" reaction as discussed in recent papers by Wender, Orchin, Storch, et al[13].

The temptation to look for a dimerized catalyst species containing two atoms of copper was very attractive in view of the positive findings in these other experimental approaches to homogeneous catalysis of reactions involving molecular hydrogen. However, our copper-concentration-dependence data fail to support any such hypothesis. The first order dependence on copper concentration in the presence of 0.16 M UO_2SO_4, found in our experiments, when analyzed in a manner similar to that described by Weller and Mills, would require either that the dimer complex be extremely strong, i.e, already largely in the dimer form at a copper concentration of 0.0001 Molar (which seems very unlikely even at 250°C), or that the active species be a monomer. Our data extend over a concentration range from 0.0001 to 0.002 M, a factor of 20, with in-pile concentrations up to 0.05 M (to be discussed in the next paper of the series) giving a total factor of 500 in concentration over which first order dependence appears to be observed. The influences of acidity and sulfate concentration, as mentioned above, are under study. At the present time the indications are that the activity of a solution of fixed copper concentration (10^{-3} M) with varying concentrations of sulfate and acid increases as the solution composition approaches regions in which hydrolytic precipitation of the copper

is observed*   Bleaney[14] has recently reported evidence that, in the solid
state, cupric acetate is characterized by the presence of pairs of copper ions.
It may be of interest that, despite any concentration dependence evidence
which would support the concept of a dimer, the activity of solutions appears
to rise as the conditions for precipitation (and formation of pairs of copper
ions) are approached. One might speculate as to whether copper ions would
tend to pair off in solution prior to the appearance of any solid phase.

Examination of activiation energies also fails to provide any significant
evidence. In the work discussed by Weller involving a cuprous acetate dimer
the activation energy at $100^{\circ}C$ was 15 kcal whereas the higher temperature
hydrogen-oxygen recombination appears to have an activation energy of 24 kcal.
In Weller's work the quinone is apparently acting only as a hydrogen acceptor
from the $(Cu-H)_2$ complex and does not oxidize the cuprous copper to cupric,
while oxygen gas at $250^{\circ}C$ is perfectly capable of keeping the copper in the
cupric state. Moreover, the solubility of cuprous salts at high temperatures is
not known. Consequently it might be possible that in Weller's studies the
cupric catalyzed reaction of higher activation energy was masked by the more
rapid cuprous catalyzed reaction (better catalysis because activation energy
is lower), while at higher temperatures the cuprous reaction is blocked by the
oxygen leaving the cupric - H_2 reaction to be noticed, the temperature being
high enough to bring the rate into measurable range for a 24 kcal activation
energy.

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*   In the presence of a large excess of ammonia, the copper has been
    maintained in solution at elevated temperatures and recombination of
    hydrogen and oxygen has been demonstrated.

Many interesting lines of research have been opened by the experimental work thus far on the program. Exploration of copper systems on the alkaline side using complexing agents of lower vapor pressure such as the aromatic nitrogen bases and bidentate reagents such as diamines, amino ketones, and hydroxy ketones may provide increased understanding of the reaction. More detailed studies on the acid side, using a variety of anionic constituents, may give indications of the strengths of complexes in aqueous solutions at elevated temperatures. For example, in the presence of enough perchloric acid to prevent hydrolytic percipitation copper and zirconium may be allowed to compete for a limited amount of sulfate (or bisulfate) and the reaction rate may provide indication as to the relative effectiveness of each in complexing sulfate. Studies of uranyl perchlorate at elevated temperatures will likewise provide indications as to the behavior of the uranyl ion through measurement of its slow recombination rate. A more detailed study of the many inorganic ions already surveyed will probably disclose environmental conditions under which somewhat higher recombination rates can be achieved (though perhaps not as high as those obtained with copper). As noted earlier some attempts have been made to find "couples" of reactions which might go more rapidly. When more detailed information for a wider number of cations and anions becomes available it will become much easier to assess the possibility of obtaining such a synergism. Experiments without an oxidizing agent or with one other than oxygen gas may permit more fundamental studies of the reaction mechanism by allowing the reduced form of the catalyst to become manifest (at present it is not known whether the first step involves the formation of the cuprous or the free copper state since the oxygen immediately regenerates the cupric form).

Experiments in non-aqeuous or mixed solvents at elevated temperatures may
also be of fundamental importance in bridging the gap between the homogeneously
catalyzed reactions of hydrogen reported in the literature and the homogeneous
recombination of hydrogen-oxygen which has been the subject of this investigation.

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