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NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY

A KINETIC STUDY OF THE REDUCTION
OF MANGANESE DIOXIDE WITH METHANOL

by

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ABSTRACT

Manganese dioxide, in the form of pure pyrolusite, was readily reduced to the divalent, water soluble, manganese sulfates in a dilute aqueous solution of sulfuric acid and methanol at high temperatures and pressures. Other reducing agents such as formaldehyde and formic acid were also qualitatively tested. An equation was derived for the true rate per unit area and used in reducing the experimental data to a single general rate equation containing such variables of the investigation as the concentrations of acid and alcohol, and the temperature. Agitation as a variable was not studied. The reaction rate per unit area was found to decrease slowly with time. This effect is thought to be caused by carbon dioxide poisoning the surface sites of the MnO_2 . The activation energy for the overall reaction is 6,077 calories per mole.

INTRODUCTION

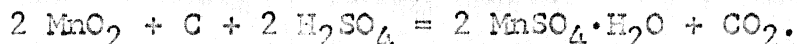
Purposes of the Investigation

The two major purposes of this thesis were (1) to investigate the possibilities of reducing MnO_2 to water soluble manganese sulfates while using cheap organic reducing agents in a dilute sulfuric acid medium, and with only one high temperature and pressure autoclaving step, and (2) to reduce the experimental data of the investigation to a general rate equation.

Review of Previous Work

A review of the literature reveals only one previous metallurgical investigation using organic reducing agents for the reduction of manganese dioxide to the divalent state and the simultaneous formation of soluble manganese sulfates. This particular study was completed by the U. S. Bureau of Mines¹ in 1959. Their treatment was: Fine grinding a low-grade manganese dioxide ore, followed by mixing the wet ore with an excess of concentrated sulfuric acid and adding a carbon reducing agent such as sawdust, lignin sulfonates, sugar, oils, and coal. This mixture was stirred at room temperature for about one hour, and then allowed to set until nearly all the MnO_2 was reduced.

The reaction given for the process was:



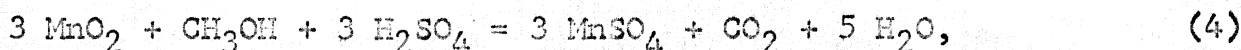
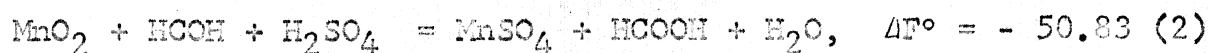
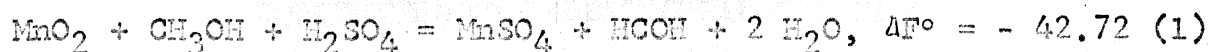
The major disadvantages from a commercial standpoint were (1) high acid consumption, and (2) the reaction rate was found to be very slow at room temperature when diluted sulfuric acid was substituted for concentrated sulfuric acid.

Outline of Initial Work

This thesis investigation started by using pine sawdust in an autoclave with dilute sulfuric acid. It was not possible to reduce minus 400 mesh MnO_2 even with experimental conditions such as 250°C . for one hour. A major problem encountered was the excessive corrosion of the metal parts of the autoclave by hot, dilute sulfuric acid.

An all-glass oil bath was constructed for testing various liquid organic reducing agents in sealed glass tubes to temperatures of $200\text{--}250^\circ\text{C}$. The liquid organic reducing agents tested were benzene, toluene, kerosene, carbon tetrachloride and methanol. Methanol was the first successful reducing agent tested using dilute sulfuric acid.

The reduction of MnO_2 and the subsequent oxidation of methanol is represented by the following sequence of reactions:



$$\Delta F^\circ = - 154.18$$

Reaction (4) is the overall reaction for the reduction of MnO_2 with methanol.

Separate experiments using the sealed glass tubes with methanol, formaldehyde and formic acid indicated that reaction (1), the oxidation of methanol to formaldehyde, was the rate controlling reaction, or slowest of the above sequence. Also, it was found that reaction (2) was slightly slower than reaction (3). Since methanol is cheaper than either formaldehyde or formic acid and will reduce three moles of MnO_2 per mole of methanol, a quantitative kinetic study was first begun with the reduction of MnO_2 with methanol to determine what effect temperature and various concentrations of sulfuric acid and methanol had on the overall reaction rate.

EQUIPMENT AND EXPERIMENTAL TECHNIQUE

To effectively study the reduction of MnO_2 with methanol, it was necessary that experiments be conducted on a larger scale than was possible with the sealed glass tubes.

Figure 1 is a detailed illustration of the autoclave used for this investigation. This autoclave has a 300 ml capacity, and was manufactured by Autoclave Engineers. Modifications to this autoclave were necessary in order to prevent excessive corrosion by dilute sulfuric acid. Tests with hot dilute sulfuric acid proved that the sampling tube and valve, and thermocouple well would be severely corroded even if they were made of Hastelloy B. For this reason the manufacturer's sampling tube and thermocouple well were cut off so that they never came directly in contact with any of the solutions inside the autoclave.

It was fortuitously discovered that the sulfuric acid was never part of the vapor phase inside the autoclave in sufficient amounts to cause corrosion, even at 250°C .

A stainless steel glass stirring chuck was made and substituted for the manufacturer's turbine stirrer. A small stainless steel cup was made and attached to the chuck, such that it was above the solution level inside the autoclave. A weighed sample of MnO_2 was loosely wrapped in a one-inch square of aluminum foil and placed in the sample cup. The stirring mechanism was then rotated, so that the aluminum

- 1 Stirring mechanism
- 2 Purging valve
- 3 Thermocouple well
- 4 Sample cup
- 5 Glass stirring rod in chuck
- 6 Pressure release valve
- 7 Gas port
- 8 Metal pressure gasket
- 9 Pressure chamber
- 10 Glass liner
- 11 Heating well
- 12 Thermocouple
- 13 Stirring motor

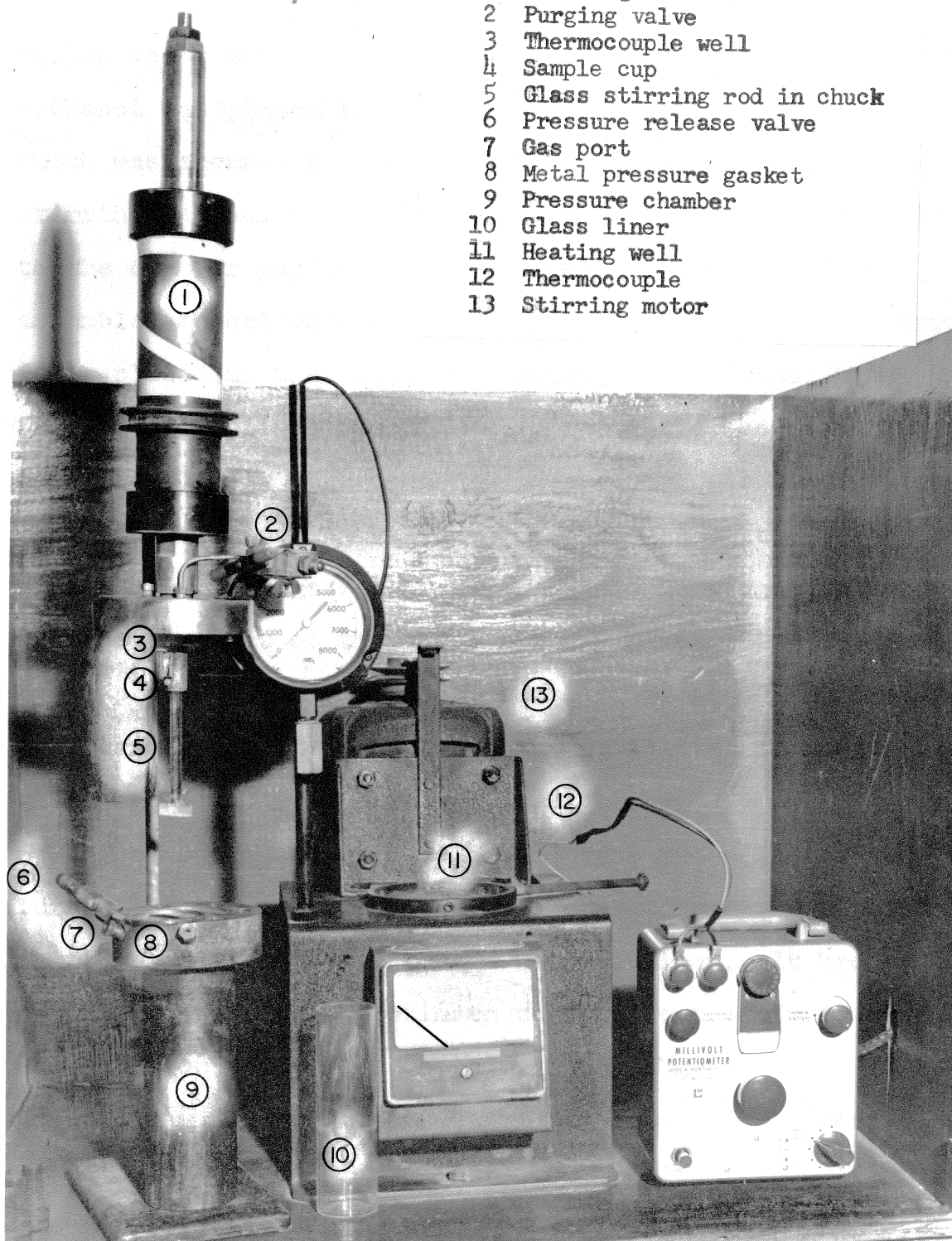


Fig. 1 The 300 ml. autoclave

packet was wedged between the thermocouple well and the chuck. A 300 ml pyrex glass liner containing 100 ml of distilled water with pre-selected amounts of sulfuric acid and methanol was placed into the pressure chamber of the autoclave, which was secured in a large vise. The autoclave cover and stirring mechanism with the packet of MnO_2 was then bolted to the chamber portion of the autoclave. The completely assembled autoclave was then removed from the vise and carefully placed in the autoclave heating well. Next, the (modified sampling) purging valve and a side port on the pressure chamber were opened, and a copper gas line was connected to the purging valve and a nitrogen bottle. For two minutes nitrogen gas at 60 psi was used to purge the autoclave from boiling out of the glass liner and corroding the stainless steel pressure chamber, a pressure of 60 psi of nitrogen was arbitrarily selected, and used as the initial pressure for all the experiments of this investigation.

Once the autoclave was heated to a pre-selected temperature, the stirring mechanism was actuated and the aluminum sample packet dropped into the hot solutions. It had been determined that an approximate ten per cent sulfuric acid solution would dissolve the aluminum packet in about 10 to 20 seconds. After the autoclave had been agitated for a pre-selected period of time, it was removed from its heating well and quenched in a water bath. Usually, the quenching cycle was begun one minute before the pre-selected time interval.

had expired. It was estimated that for all practical purposes, the reaction had stopped inside the autoclave after one minute of quenching.

After cooling, the autoclave was removed from the water bath and placed in the vise. The purging valve was opened to release the 60 psi nitrogen gas. Next, the cover and stirring mechanism were unbolted from the pressure chamber of the autoclave. The pyrex glass liner containing the solution was removed from the pressure chamber, the solution poured into a graduated cylinder, the total amount of liquids recorded, and two 20 ml samples pipetted for chemical analysis of the MnO_2 dissolved.

This procedure for compiling experimental data was time-consuming, considering that two to three runs were necessary to average one value of per cent dissolved for one point on a rate curve such as Figure 2. Apparently, at this time, there is no simpler method available for measuring the amount of MnO_2 dissolved at high temperatures and pressures when leaching with hot dilute sulfuric acid solution.

EXPERIMENTAL RESULTS

Sufficient experimental data was compiled to derive a general rate expression, containing the variables such as temperature and concentrations of sulfuric acid and methanol.

The methanol, sulfuric acid, and MnO_2 were the reagent grades, obtained from J. T. Baker Chemical Company. The MnO_2 was determined by x-ray analysis to be pure pyrolusite. Distilled water was used in all the experiments.

All experiments were run in a 300 ml autoclave at a constant agitation speed of 1500 rpm and an initial pressure of 60 psi nitrogen gas.

Five pounds of reagent grade MnO_2 was wet-screened, and the -100 +150 mesh size fraction used in this investigation. This size fraction weighed about one pound, more than enough to complete this study. A microscopic examination revealed that wet-screening had removed, for all practical purposes, all MnO_2 particles of other than -100 +150 mesh size particles, and that the particles were roughly spherical in shape and had a very hard, impervious appearance. Chemical analysis of the wet-screened MnO_2 particles gave a result of 99.91 per cent MnO_2 . The NUMEC Instruments and Controls Corp. made an N_2 adsorption surface area determination on 50 grams of the sized MnO_2 , giving a surface area of $6,150 \text{ cm}^2/\text{gm}$.

The experiments were run at 115, 135, and 155°C., with sulfuric acid concentrations varying from 1.86×10^{-1} to 55.95×10^{-1} mole/liter, and methanol concentrations varying from 2.47×10^{-1} to 9.89×10^{-1} mole/liter. All experiments were run with exactly $\frac{1}{2}$ gram samples of MnO_2 .

Two, and sometime three, experiments were run for each specific time interval and their results averaged for the per cent dissolved of MnO_2 . The average deviation of all the averages of the per cents dissolved was $\pm 1.10\%$. The time intervals used throughout this investigation were 20, 40, and 60 minutes. One experiment was made at 64 minutes. Time intervals shorter than 20 minutes always gave erratic results.

A potentiometric³ method of analysis was used to determine the amount of MnO_2 dissolved. A complete outline of the method of analysis was used because it was rapid, and it was accurate to three significant figures.

Table I is a summary of the data obtained in this investigation. K is the rate per unit area as a function of time, and K_0 is the initial rate per unit area.

Figure 2 is a typical plot of per cent MnO_2 dissolved versus time for this investigation. The curves of such a plot are designated "rate curves." Because the total surface area of the MnO_2 particles is constantly decreasing as the particles dissolve, the plots of MnO_2 dissolved versus time are not straight line plots. This means that in order to determine the rate per unit area of the reaction at any time,

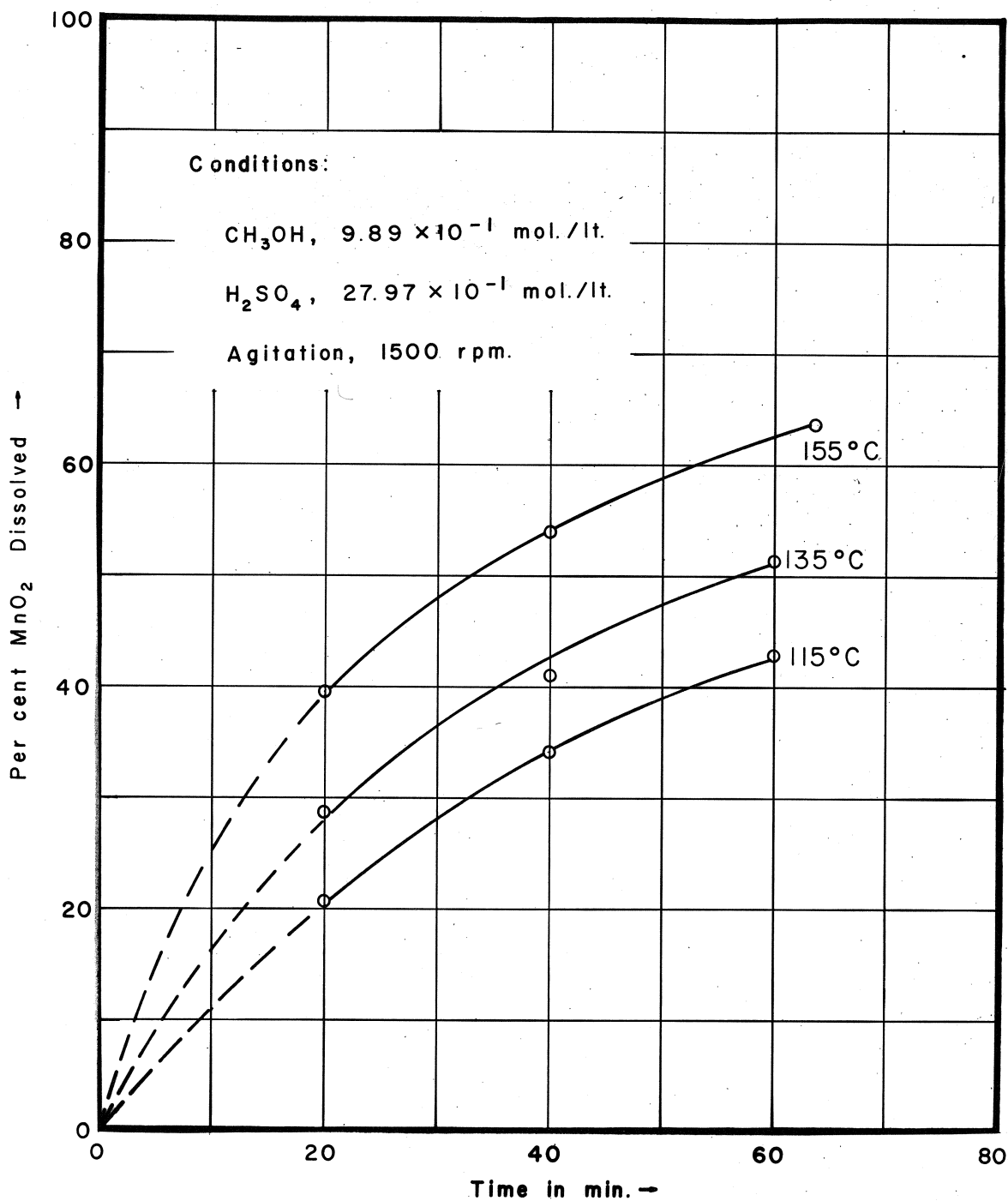


Fig. 2 Typical rate curves

TABLE I

Summary of Results

Temp. °C.	Time min.	% MnO ₂ leached	H ₂ SO ₄ mol/l. x 10 ⁻¹	CH ₃ OH	K x 10 ⁻⁶ gms/cm ² /min	K ₀ x 10 ⁻⁶
115	20	20.80	27.97	9.89	1.824	
115	40	34.23	27.97	9.89	1.589	1.97
115	60	42.92	27.97	9.89	1.385	
135	20	28.88	9.32	9.89	2.622	
135	40	42.00	9.32	9.89	2.025	3.05
135	60	48.67	9.32	9.89	1.622	
135	20	21.29	18.65	9.89	1.973	
135	40	30.11	18.65	9.89	1.373	2.12
135	60	36.39	18.65	9.89	1.139	
135	20	25.08	55.95	9.89	2.241	
135	40	35.83	55.95	9.89	1.675	2.62
135	60	41.51	55.95	9.89	1.330	
135	20	38.21	18.65	9.89	3.617	
135	40	49.20	18.65	9.89	2.464	4.98
135	60	54.24	18.65	9.89	1.866	
135	20	25.08	18.65	9.89	2.241	
135	40	35.83	18.65	9.89	1.675	2.62
135	60	41.51	18.65	9.89	1.330	
135	20	23.87	18.65	7.42	2.124	
135	40	32.00	18.65	7.42	1.472	2.43
135	60	37.80	18.65	7.42	1.190	
135	20	21.91	18.65	4.94	1.929	
135	40	29.11	18.65	4.94	1.322	2.12
135	60	33.37	18.65	4.94	1.031	
135	20	16.10	18.65	2.47	1.398	
135	40	23.99	18.65	2.47	1.067	1.72
135	60	28.04	18.65	2.47	0.847	
155	20	39.36	27.97	9.89	3.751	
155	40	54.07	27.97	9.89	2.790	4.36
155	64	63.79	27.97	9.89	2.190	
155	20	25.02	9.32	9.89	2.239	
155	40	32.12	9.32	9.89	1.476	2.70
155	60	36.39	9.32	9.89	1.139	
155	20	32.63	18.65	9.89	3.007	
155	40	45.76	18.65	9.89	2.252	3.60
155	60	51.75	18.65	9.89	1.755	

one has to obtain the slope of a tangent to the rate curves at various time intervals and divide each slope by the total remaining surface area of the MnO_2 particles at that particular time. This would be a very difficult task. However, a mathematical study on the rate of dissolving solid particles, in general, proved that all that was actually necessary for determining the rates per unit area is to know accurately the initial true surface area of the particles to be dissolved.

THEORETICAL CONSIDERATIONS

The General Rate Equation

According to the Absolute Reaction Rate Theory,⁴ the rate per unit area of any heterogeneous chemical reaction can be represented by a general equation such as

$$K = k[A]^a \cdots [I]^i T \exp\left(\frac{-\Delta F^*}{RT}\right) \quad (1)$$

where:

K = rate per unit area,

k = reaction constant, containing Boltzmann's and Plank's constants, concentration of active surface sites, transmission coefficient, partition functions, and the necessary conversion factors,

$[A] \cdots [I]$ = product of the concentrations of the reagents necessary for the reaction, usually expressed as moles per liter or atmospheres,

T = absolute temperature at which the rate is being measured,

ΔF^* = activation energy,

R = perfect gas constant,

$a \cdots i$ = power constants; their summation is the reaction order.

In order to determine the activation energy and the individual power constants it is necessary to know the rate per unit area as a function of time. Once the activation energy is calculated and the power constants determined, substitution of these values with a rate per unit area and its corresponding values of reagent concentrations and temperature allows the determination of the reaction constant of equation (1).

Derivation of the Mathematical Equivalent of the True Rate per Unit Area

The following derivation reveals an easy method for determining the true rate per unit area, K , when dissolving fine particles.

For this derivation the assumptions made concerning the fine particles to be dissolved are that their initial number, average shape, and roughness factor will not change during dissolution.

The rate of dissolving solids as a function of surface area can be expressed by the relation known as Wenzel's Law,⁵ which states that the rate of reaction between solids and liquids (or solids and gases) is proportional to the total area in contact with the dissolving medium. This relation can be expressed as

$$R = K A \quad (2)$$

where:

R = overall rate of dissolution (gms/sec),

K = proportionality constant or rate per unit area (gms/cm²-sec),

A = total surface area in contact with the dissolving medium at any time (cm²).

When leaching or dissolving an aggregate of fine particles we have that

$$R = -dW/dt = K A = K R_w A_g = K R_w n a d^2 \quad (3)$$

where:

$-dW/dt$ = the differential representing the change in mass of the particles being dissolved as a function of time,

$$R_w = \text{roughness factor}^6 = \frac{\text{true surface area measured by the } N_2 \text{ adsorption method}}{\text{surface area measured by geometric means}} \quad (4)$$

A_g = total surface area at any time measured by geometric means. Also,

$$A_g = n a d^2 \quad (5)$$

where:

n = total number of particles at any time to be dissolved,

a = shape factor, for example, equal to 6 for perfect cubes,

d = the average diameter of all the particles to be dissolved, at any time.

The roughness factor can be written as

$$R_w = \frac{A_t W}{n a d^2} \quad (6)$$

where:

W = total weight of particles undissolved at any time,

A_t = true area at any time of the fine particles, measured by the N_2 adsorption method and reported as cm^2/gms .

Since the N_2 adsorption surface area measurements are usually reported as area per unit weight, it is necessary to multiply " A_t " by the total weight of undissolved particles, W , in order that the numerator of equation (6) have only the value of the true area.

The total volume of the fine particles at any time is

$$V = n b d^3 \quad (7)$$

where:

b = shape factor, for example, equal to 1 for perfect cubes.

It follows that

$$W = D V = D n b d^3 \quad (8)$$

where:

D = the true density of the fine particles.

Differentiating equation (8) and setting equal to equation (3), we have

$$- dW/dt = D 3 n b d^2 dd/dt = K R_w n a d^2. \quad (9)$$

Therefore;

$$dd/dt = - \frac{K R_w a}{3 b D}. \quad (10)$$

Integrating equation (10) from d_0 , the initial diameter at time zero, to d at time t , we have

$$d = - \frac{K R_w a t}{3 b D} + d_0. \quad (11)$$

Substituting equation (11) into equation (9), we have

$$dW/dt = - K R_w n a \left(- \frac{K R_w a t}{3 b D} + d_0 \right)^2. \quad (12)$$

Integrating equation (12) from W_0 , the initial total weight of fine particles at time zero, to W at time t , we have

$$(W - W_0) = n b D \left(- \frac{K R_w a t}{3 b D} + d_0 \right)^3 - n b D d_0^3. \quad (13)$$

Solving for K , the rate per unit area, from equation (13), we have

$$K = \frac{3 b D}{R_w a t} \left[d_0 - \left(d_0^3 + \frac{(W - W_0)}{n b D} \right)^{1/3} \right]. \quad (14)$$

The quantity $(W - W_0)$ represents the amount dissolved at time t .

Since

$$D = W/V = \frac{W}{n b d^3}, \text{ it is also equal to } \frac{W_0}{n b d_0^3}. \quad (15)$$

The substitution of $D = \frac{W_0}{n b d_0^3}$ into equation (14) will allow considerable simplification of this equation since this equation already has d_0 in place of d . Also, because the per cent dissolved of the fine particles can be calculated after chemical analysis of the leach solution the substitution of

$$\frac{(W - W_0)}{W_0} = - \frac{\% \text{ dissolved}}{100} \quad (16)$$

will allow further simplification of equation (14).

Finally the substitution of

$$R_w n a d_0^2 = A_{t_0}, \quad (17)$$

derived from equation (6), where:

A_{t_0} = true surface area of the particles at time zero or before dissolution begins, measured by the N_2 adsorption method and reported as area per unit weight,

will give us the result we desire.

The substitution of equations (15), (16) and (17) into equation (14) results in

$$K = \frac{3}{A_{t_0} t} \left[1 - \left(1 - \frac{\% \text{ dissolved}}{100} \right)^{1/3} \right]. \quad (18)$$

Equation (18) is a mathematical equivalent of the true rate per unit area for the dissolution of fine particles.

Equation (18) has the advantage over equation (2) because the rate per unit area does not depend upon knowing the surface area as a function of time. All that is required is a knowledge of the initial surface area per unit weight of the fine particles to be dissolved and the

per cent dissolved at time t . This calculated true rate per unit area is also known as the absolute rate per unit area.⁴

Appendix II contains tabulated values of per cent dissolved versus the quantity in the square brackets for equation (18).

With the aid of equation (18) to calculate K , the true rates per unit area, the experimental data of this investigation can now easily be reduced to a general rate equation of the form of equation (1).

Formulation of The General Rate Equation

With a value for the initial surface area, A_{t_0} , equal to $6,150 \text{ cm}^2/\text{gm}$, and equation (18), values of K were determined as a function of time, and tabulated in Table I.

Figure 3 is a typical plot of the calculated rates per unit area versus time, using the data corresponding to the rate curves of Figure 2. It is apparent from Figure 3 that the rate per unit area is decreasing as time increases. The author believes that dissolved carbon dioxide, formed as a reaction product, is being adsorbed⁷ on the active surface sites of the undissolved MnO_2 , thereby reducing the initial concentration of these active surface sites. If this hypothesis is correct, then the reaction constant, k , of equation (1) will not remain constant with time since k contains, among other things, the concentration of MnO_2 active surface sites.

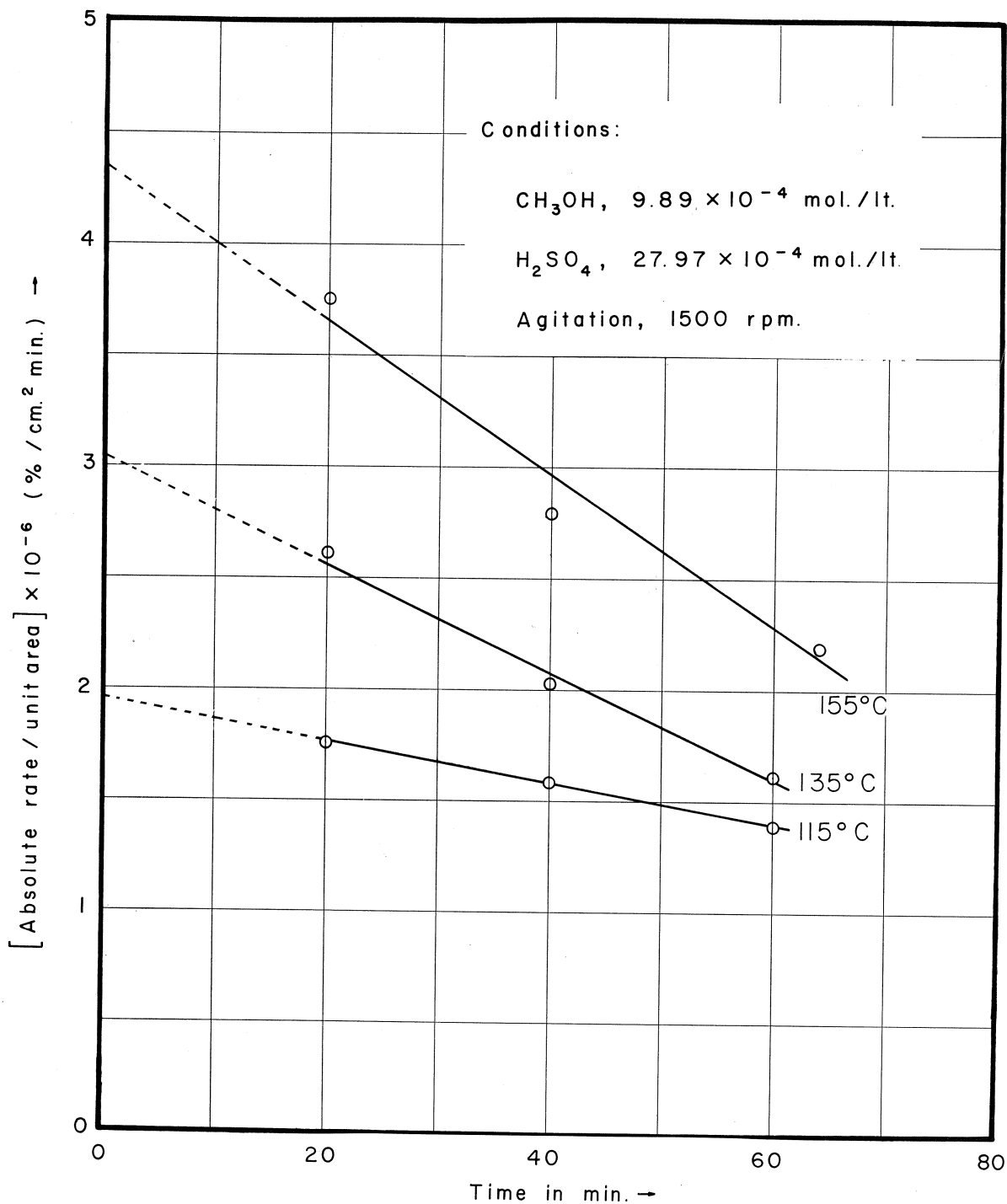


Fig. 3 Rate per unit area versus time

The author does not believe that the concentrations of sulfuric acid or methanol are changing by an amount large enough to cause the large decrease in the rate per unit area with time. For example, a sulfuric acid concentration of 9.32×10^{-1} mole/liter corresponds to about 16 times as much sulfuric acid as is actually needed to completely reduce the one-half gram of MnO_2 , and 4.94×10^{-1} mole/liter of methanol is about 13 times in excess. The latter acid and alcohol concentrations represent the least amounts used in this investigation.

Extrapolating K from plots similar to Figure 3 to time zero, one obtains the initial rate per unit area, K_0 . Table I contains both the rates per unit area as a function of time, and the initial rates per unit area at time zero, for each rate curve that was necessary for the evaluation of a general rate equation. Using the data from Table I, Figure 4, a log-log plot of the initial rates per unit area versus their corresponding concentrations was plotted. This plot is used for evaluating the power constants, $a \dots i$, of equation (1). Figure 4 is a combination plot for both the sulfuric acid and the methanol. The values of the slopes from this plot for the sulfuric acid and methanol were 0.475 and 0.305 respectively. The slight curvature of the experimental points for the sulfuric acid required an approximated straight line. This slight curvature is probably due to a non-linear change in the activity coefficient of the sulfuric acid as its concentration is increased.

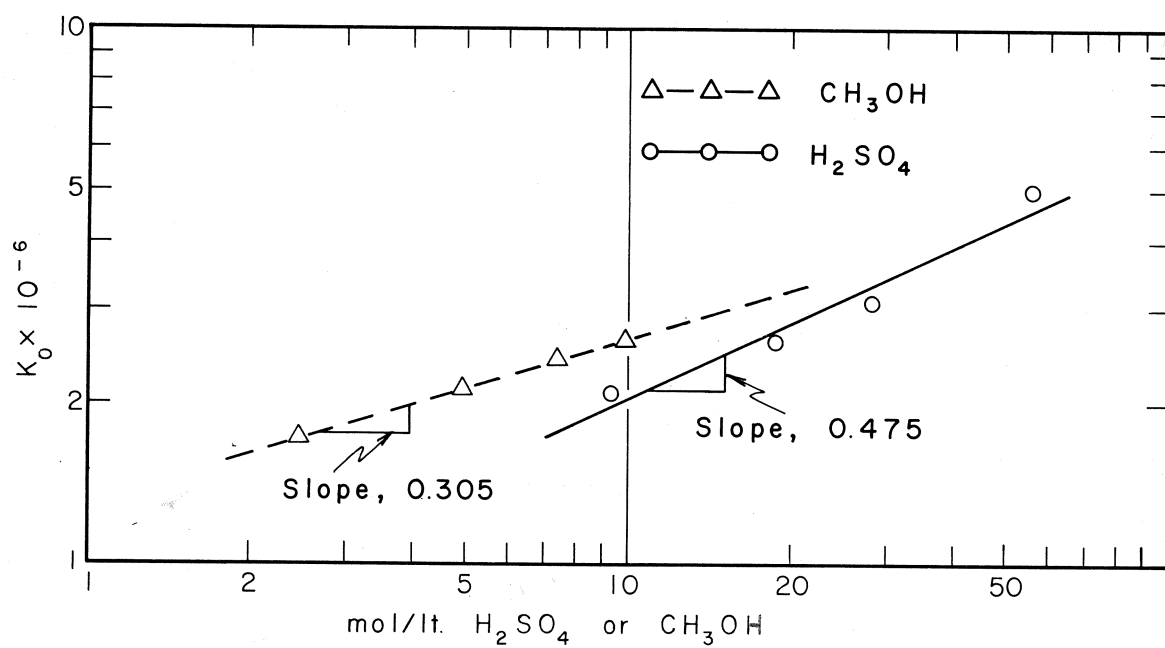


Fig. 4 Log-Log plot for determination of the power constants

The power constants are reasonably temperature independent.⁸ This is to be expected since these constants actually represent the reaction orders. Heterogeneous chemical reactions are usually thought to involve one molecule in solution reacting with one molecule on one active surface site. In this case a value of 1.0 should be the power constant corresponding to the concentration of active surface sites, or in the case of equation (1), the reaction constant, k , would have a power constant value of 1.0 since the concentration of active surface sites has been included in the reaction constant. Including the concentration of active surface sites into the reaction constant was initially done for simplification. This is because it is usually accepted that the concentration of active surface sites remains constant throughout dissolution. This investigation has shown that the reaction constant actually decreases with time, and this presents an interesting possibility; if the hypothesis concerning the adsorption of CO_2 on an active surface site is true, then a log-log plot of the rate per unit area versus the change in the reaction constant, k , may be expected to have a slope of 1.0. However, before this hypothesis could be tested it was first necessary to determine the activation energy. The activation energy, ΔF^* can be determined from the slope of a plot of K_0/T versus $1/T$.⁴ The negative slope of this plot is equal to $-\Delta F^*/R$, hence ΔF^* is of positive value. Figure 5 is the Arrhenius plot

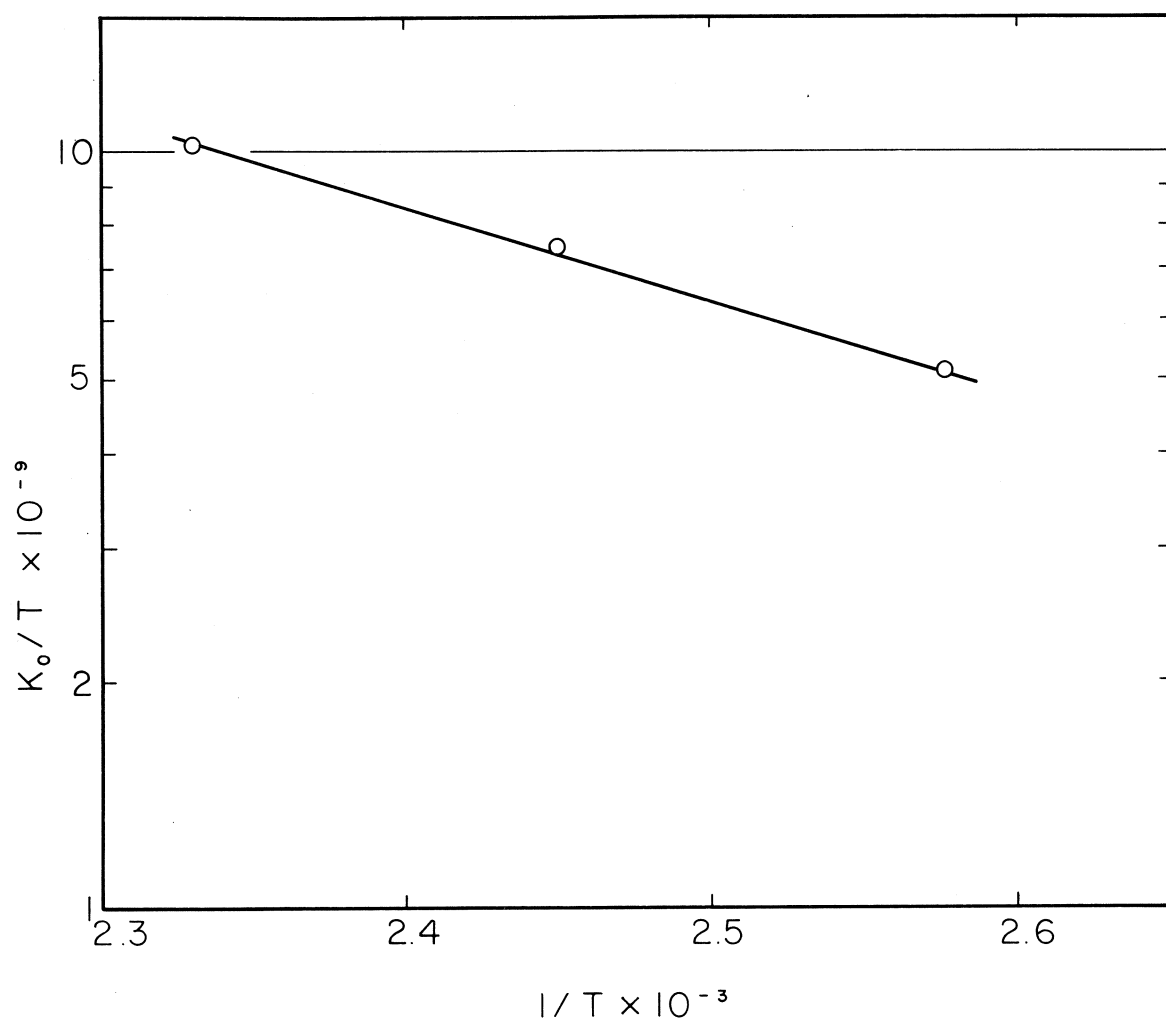


Fig. 5 Arrhenius plot for determination of activation energy

used for determining the activation energy for this investigation. This value was found to be 6,077 calories per mole.

Using the latter value for the activation energy, and the power constants corresponding to the sulfuric acid and methanol concentrations, values for the reaction constant, k , as a function of time, were calculated using a general rate equation of the form of equation (1).

Table II is a tabulation of the results of these calculations. Using the values of the reaction constants of Table II, Figure 6 was plotted versus their corresponding rates per unit area.

We see from Figure 6 that the slopes have a value of 1.0, proving the hypothesis that the concentration of active surface sites is changing with time and that one molecule from solution is reacting on one active surface site.

Connecting the points of equal times in Figure 6, an interesting result develops. It becomes apparent that for the conditions of these tests that these equal time lines converge in a general area, which has been designated the equilibrium region. Within this equilibrium region the rate per unit area appears to remain a constant value with increasing time, that is to say, that whatever was causing the decrease of the active surface sites with time (the actual adsorption of dissolved carbon dioxide has not been proved), has reached equilibrium with the rate at which the MnO_2 was being dissolved within

December 24, 1966

Martin Speare, Librarian
N. M. Institute of Mining and Tech.
Campus Station
Socorro, N. M.

Dear Martin:

A recent examination of my thesis, with the aid of Kennecott's IBM computer, revealed several glaring typing errors, which I have corrected in the enclosed Errata. Please insert the Errata in your copy.

Thank you. Hope to see you soon. Until then,

Sincerely yours,

Rudy Jacobson
Rudy Jacobson

Enc.

ERRATA

For the correction of the Master of Science thesis on " A Kinetic Study of the Reduction of Manganese Dioxide With Methanol ", completed June 1965 at the New Mexico Institute of Mining and Technology, by Rudolph H. Jacobson Jr.

Page 25: Table II should read as follows:

Temp. °C.	Time min.	CH ₃ OH	H ₂ SO ₄	$K \times 10^{-6}$	$k \times 10^{-6}$
		$\frac{\text{mol/l.} \times 10^{-1}}{\text{gm/cm}^2/\text{min}}$			k units(?)
115	0	9.89	27.97	1.97	8.517
115	20	9.89	27.97	1.824	7.886
115	40	9.89	27.97	1.589	6.87
115	60	9.89	27.97	1.385	5.988
135	0	9.89	27.97	3.05	8.509
135	20	9.89	27.97	2.622	7.316
135	40	9.89	27.97	2.025	5.649
135	60	9.89	27.97	1.622	4.525
155	0	9.89	27.97	4.36	8.15
155	20	9.89	27.97	3.751	7.019
155	40	9.89	27.97	2.790	5.221
155	60	9.89	27.97	2.36*	4.416

* Approximate value for 60 minutes

Page 26: The abscissa of Fig. 6 should read $k \times 10^{-5}$ not $k \times 10^{-6}$.

Page 27: Line 27 should read - 5.54×10^{-8} not - 5.54×10^{-9} .

Page 28: (a) Line 4, - 5.54×10^{-9} should read - 5.54×10^{-8} .
(b) Line 13, 8.13×10^{-7} should read 8.39×10^{-6} .

(c) Line 18, [$8.13 \times 10^{-7} - 5.54 \times 10^{-9} t$] should read
[$8.39 \times 10^{-6} - 5.54 \times 10^{-8} t$].

Page 26, Fig. 6: Using the new values of Table II, above, Fig. 6 will be slightly skewed to the right. However, the " Equilibrium region " remains the same, and the slopes of the constant temperature lines all have a value of 1.0.

Page 29, Fig. 7: The "Equation formulated" curve fits the actual curve more closely using the above correction for equation (20), page 28.

Page 31, Conclusion: Line 13, 9.89×10^{-1} mole/liter and.... should read 9.89×10^{-1} mole/liter CH₃OH and.....

R.H. Jacobson, Jr. 12/24/66

R. H. Jacobson Jr.

TABLE II

Determination of the Reaction Constant, k , as a
Function of Time

Temp. °C.	Time min.	H ₂ SO ₄ mol/l. $\times 10^{-1}$	CH ₃ OH	$\frac{K \times 10^{-6}}{\text{gm/cm}^2/\text{min}}$	$\frac{k \times 10^{-7}}{k \text{ units}(?)}$
115	0	9.89	27.97	1.97	8.48
115	20	9.89	27.97	1.824	7.80
115	40	9.89	27.97	1.589	6.80
115	60	9.89	27.97	1.385	5.92
135	0	9.89	27.97	3.05	8.35
135	20	9.89	27.97	2.622	7.18
135	40	9.89	27.97	2.025	5.62
135	60	9.89	27.97	1.622	4.43
155	0	9.89	27.97	4.36	7.51
155	20	9.89	27.97	3.751	6.22
155	40	9.89	27.97	2.790	4.85
155	60	9.89	27.97	2.36*	4.10

* Approximate value for 60 minutes.

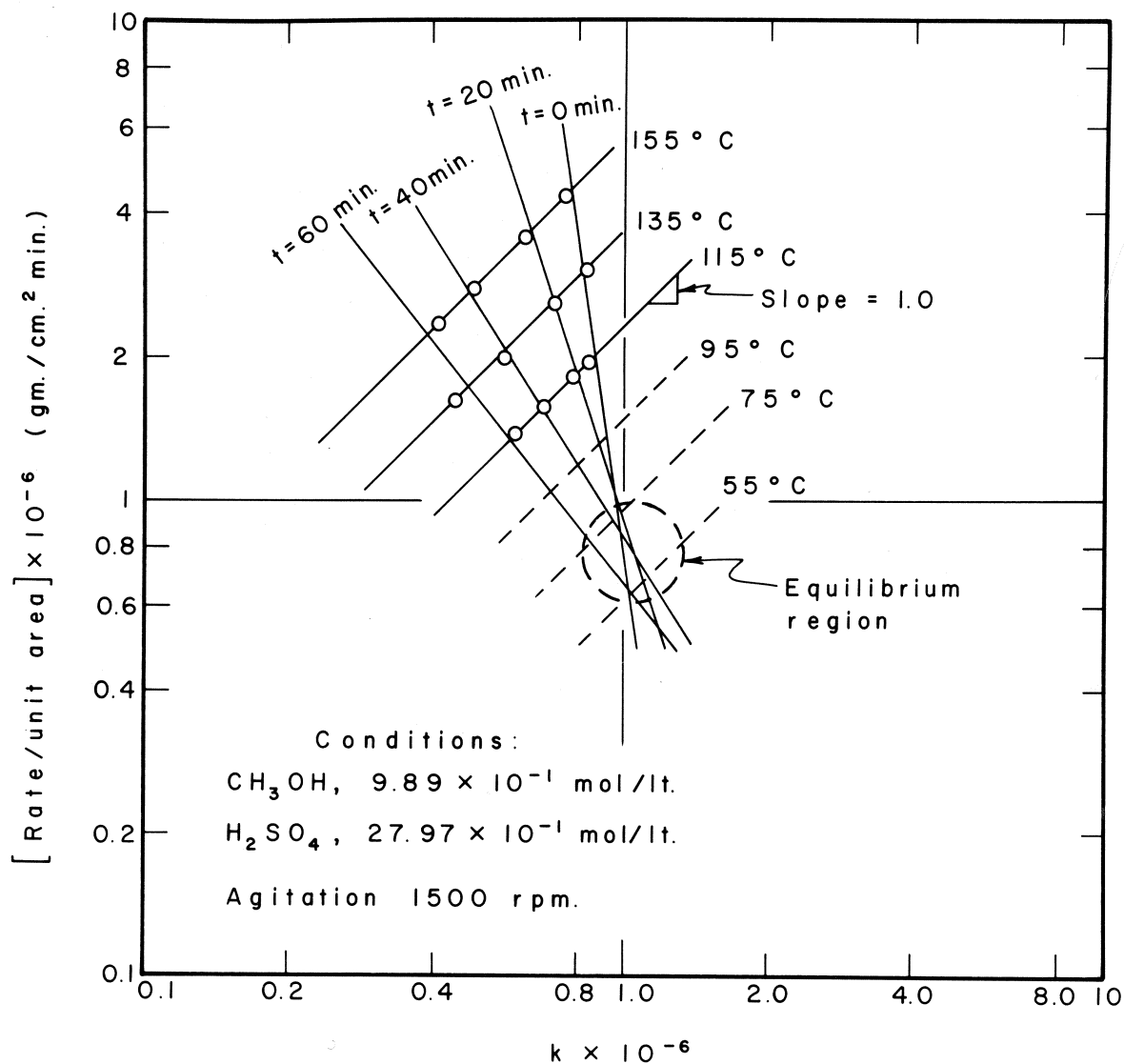


Fig. 6 "k" versus rate per unit area

the equilibrium region.

Since the lines connecting points of equal temperature appeared to be equal distance apart for 20 degree temperature intervals, other constant temperature lines were extrapolated for the same parallel separation as 155°C. to 135°C., and 135°C. to 115°C. Within the equilibrium region, a temperature of 70°C. appeared to coincide with a constant rate per unit area of 0.8×10^{-6} gm/cm²-min. This value for the rate per unit area was substituted into equation (18), and a per cent dissolved for a time interval of 60 minutes was calculated as 26.5%.

Two experiments were run in the modified 300 ml autoclave for 60 minutes at a temperature of 70°C. $\pm$ 2°C. An average of 26.1% $\pm$ 2.03% was obtained for the MnO₂ dissolved, as compared to the calculated value of 26.5%, indicated that the rate per unit area does remain relatively constant within the equilibrium region.

In order to formulate a general rate equation for the reduction of MnO₂ with methanol, an empirical expression for the variation of the reaction constant as a function of time was formulated. This was achieved by an approximation since not enough data was compiled to illustrate the effect of every conceivable variable on the reaction constant. It was found that for the conditions of the tests in Figure 6 that a plot of k versus time resulted in near parallel negative sloped for 115, 135, and 155°C. The average of these three slopes was -5.54×10^{-9} $\frac{k \text{ units.}}{\text{min.}}$

If k were to have been the same value at time zero for each of the three temperature intervals plotted, then k as a function of time could have been represented as

$$k = k_0 - 5.54 \times 10^{-9} t, \quad (19)$$

where:

t = time in minutes,

k_0 = reaction constant at time zero.

However, it is obvious that k_0 is not a constant for each of the three temperature intervals plotted since the zero constant time line of Figure 6 is not quite vertical. However, the values of k_0 on the zero time line are almost constant, therefore, an average k_0 (for the three temperature intervals plotted in Figure 6) of 8.13×10^{-7} k units is used as an approximation.

Using the approximate value of k_0 in equation (19), a general rate equation of the form of equation (1) is formulated to express the results of this investigation as

$$K = [8.13 \times 10^{-7} - 5.54 \times 10^{-9} t]^{1.0} [\text{CH}_3\text{OH}]^{0.305} \dots \\ [\text{H}_2\text{SO}_4]^{0.475} T \exp\left(\frac{-6,077}{RT}\right), \quad (20)$$

where the values of the concentrations of sulfuric acid and methanol are in moles per liter and the temperature in degrees Kelvin.

Equation (20) is restricted to a solution agitation of 1500 rpm or an exact equivalent, that was used in this investigation. Also, the equation applies only to the dissolution of pure pyrolusite of one-half gram amounts in 100 ml.

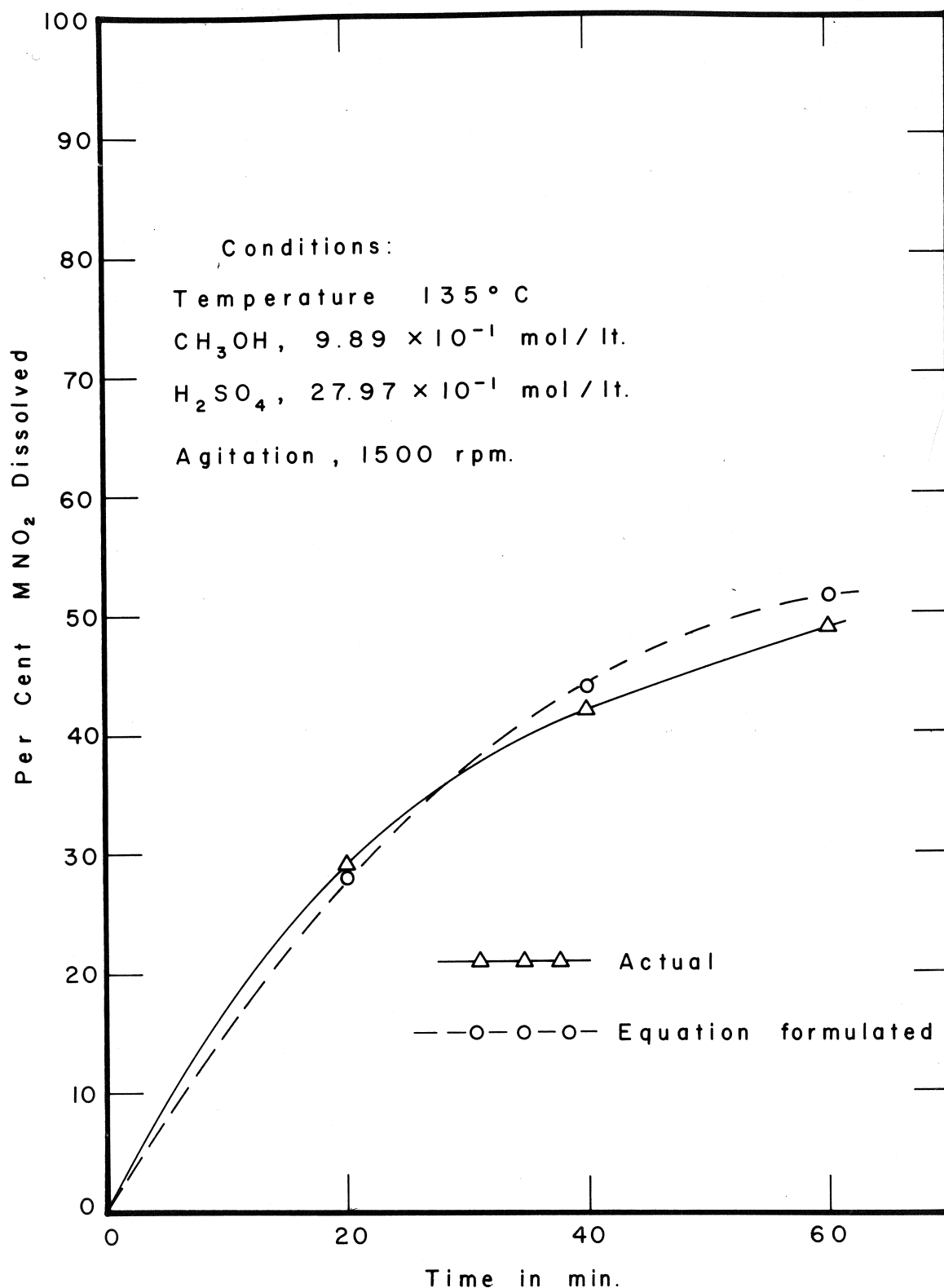


Fig. 7 Comparison of actual and "equation formulated" rate curves

of distilled water, with an initial surface area of 6,150 cm^2/gm , and large excess concentrations of alcohol and acid.

Figure 7 illustrates the comparison of an actual rate curve of this investigation and one calculated using equations (18) and (20). Considering the approximations necessary in order to formulate equation (20), the calculated curve of Figure 7 is a reasonably close fit to the curve determined experimentally.

CONCLUSION

A kinetic study of the reduction of MnO_2 with methanol has been made and the results reduced to an approximate general equation for the rate per unit area. Values of K can now be calculated with this rate equation for various temperatures, and concentrations, and these K values substituted into equation (18) in order to solve for the per cent dissolved at various time intervals. In this fashion, approximate rate curves can be constructed from the calculated data for preliminary processes evaluation. One must, however, keep in mind the restrictions placed on equation (20) for any process evaluations of an industrial nature.

A theoretical rate curve was calculated for $250^\circ\text{C}.$, 9.89×10^{-1} mole/liter and a sulfuric acid concentration roughly corresponding to the anolyte solution produced by the electrolytic production of manganese metal,⁹ that is, a pH 1.2 and 200 grams of ammonium sulfate per liter of water.

These calculations indicated a 93% dissolution in 40 minutes, but after 40 minutes the rate of dissolution diminished rapidly.

It is of interest that an equilibrium region exists, wherein the rate per unit area remains constant. Capitalizing on this fact, it was calculated that 98% dissolution would be possible in about $6\frac{1}{2}$ hours, using the conditions inside the equilibrium region of Figure 6.

The derivation of equation (18) in terms of an initial surface area measured by the N_2 or other reliable gas adsorption methods has several advantages. The first is that the surface area is measured by molecules. Harkins and Jura have stated the advantage of measuring the surface area with molecules in this manner: "When the purpose for which the area of a solid is determined, is associated with the actions of molecules upon the surface, it seems that molecules should be the instruments best adapted for the measurement of area."¹⁰

A second advantage is that the adsorption methods have been universally accepted as the best means for estimating the true surface area for fine particles and in the case of hard crystalline materials, it is believed that this method results in the true surface area. However, from the standpoint of diffusion controlled heterogeneous reactions, it can be argued that the area measured by the N_2 adsorption method is not the true area, and for other reasons also. To counter these arguments, the author believes that any method that gives a consistent surface area measurement is better than none at all. That is to say, if all persons investigating heterogeneous oxidation or reduction processes were, in the case of fine particles, to measure the initial surface area by the N_2 adsorption method, for example, then the results of these investigations could probably be duplicated or compared rather closely by other interested persons. This is because the N_2 adsorption method does give consistent results. Also, this adsorption method has the added advantage

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over air permeability methods because of its much wider range, from a few square meters per gram to more than 1000 square meters per gram.

Equation (18) resembles the widely accepted "McKewan equation"¹¹ when the roughness factor of equation (14) is assumed to be one. If such an assumption had been made for the MnO_2 used in this investigation, the rates per unit area would all be smaller by a factor of over 100! As it stands, the author believes that the rates per unit area reported in this investigation are probably the first true or absolute rates per unit area that have been made public information for a heterogeneous dissolution process.

Equation (20) contains an empirical time relation which approximates the change in the concentration of active surface sites as the dissolution time increases. The fact that any change in the concentration of active surface sites was detectable was because a relatively large amount of MnO_2 could only have been dissolved, for the conditions of this investigation, if fine particles were dissolved; and, if fine particles were dissolved, the true rates per unit area as a function of time could only be calculated with equation (18). For future leaching studies equation (18) should, therefore, prove very useful because it allows one to dissolve particles without resorting to the use of particular shapes. However, the fine particles should all be of one close size range.

The plot of Figure 6 is the first such plot reported that proves that the change in the concentration of active surface sites results in a slope of 1.0, or one molecule reacts on one surface site at a time.

The author has not tried to break down the value of k to determine the true concentration of active surface sites, nor has he attempted to explain every possible step for the chemical reactions which take place in this investigation.

It is the author's opinion that the reduction of MnO_2 with methanol and hot dilute sulfuric acid is not industrially practical until either a catalyst has been found that will speed up the reaction at near room temperature, or suitable materials are developed for high temperature-pressure autoclaves that will withstand corrosion by hot dilute sulfuric acid.

SUGGESTED TOPICS FOR FURTHER STUDY

The author has performed a few qualitative leaching experiments with the modified 300 ml autoclave using a hot dilute sulfuric acid medium with various reducing agents which indicated several areas for further study. They are:

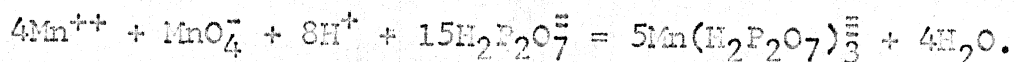
- 1 the reduction of MoS_2 with hydrogen gas
- 2 the direct reduction of calcopyrite to copper powders with hydrogen gas
- 3 the reduction of MnO_2 with various reducing gases such as methane, propane, and hydrogen
- 4 the development of a continuous analysing device such as now used at the University of British Columbia, Canada, in order to speed up high temperature-pressure leaching studies
- 5 the reduction of MnO_2 ores with the above mentioned reducing agents
- 7 the reduction of MoS_2 , MnO_2 , and CuFeS_2 with the above mentioned reducing agents in the presence of catalysts, such as platinum, etc.
- 8 further testing of equation (18) with the above mentioned kinetic studies, and a comparison study of the reduction of various iron ores with hydrogen gas
- 9 an investigation for developing materials that are corrosion-resistant to hot dilute sulfuric acid, such as induced voltages applied to copper-lined autoclaves, ceramics, or precious metals--iron alloys
- 10 reduction of manganese-silver ores with the above mentioned reducing agents in a hot dilute sulfuric acid medium

APPENDIX I

The Potentiometric Method for the Determination of Manganese³

The determination of manganese is based on the titration of the manganous ion with permanganate ion in a neutral pyrophosphate solution.

Reaction:



Mn^{++} is oxidized, and MnO_4^- is reduced to the pyrophosphate complex of +3 state. The $\text{Mn}(\text{H}_2\text{P}_2\text{O}_7)_3^{\equiv}$ complex has a clear cherry red color and interferes with the color change normally present with permanganate titrations.

This method of analysis is faster than the bismuthate method, and is more accurate because practically all the common elements associated with manganese ores or alloys do not interfere. The elements and ions which will not interfere even in large amounts are: Cl^- , Fe^{+++} , Co^{++} , Cu^+ , Ni^+ , Cr^{+++} , Mo^{+6} , W^{+6} , U^{+6} , Zn , Al , Mg , Cd , nitrate, sulfate, and perchlorate ion. Normally titration is performed at a pH of 6 to 7; however, if the vanadium ion is present greater than one fifth of the amount of Mn^{++} , interference is noted. This may be remedied by going to a pH of 3 to 3.5

Tests have shown that when manganese was present in ores to about 60%, the accuracy is to three significant figures and ± 0.2 on the 4th significant figure. For samples of less than 0.5% manganese, the accuracy was to two significant figures with ± 0.4 on the 3rd significant figure.

Apparatus: pH meter with the addition of a third, platinum, electrode.

Solutions: (1) Saturated sodium pyrophosphate solution (0.3 M). This solution should be changed about once a month, or the reaction slows down due to the hydrolysis of the pyrophosphate ion. It has been recommended to use only the purest grades of sodium pyrophosphate. (2) Permanganate solution of approximately 0.02 M, or approximately 3.2 grams of potassium permanganate per liter of distilled water. This solution was standardized weekly with a U. S. Bureau of Standards manganese dioxide ore.

General Procedure: 20 ml of leach solution was pipetted into a 600 ml beaker. Next, 150 to 200 ml of the saturated pyrophosphate solution was added to the beaker. The pH of this solution was adjusted between 6 and 7 for maximum break in the titration curve. There is very little endpoint break at pH of 8.0 and none above 8.7. The pH is best adjusted with dilute sulfuric acid and sodium hydroxide solutions. After the pH is adjusted, the platinum electrode is substituted for the glass electrode, and the solution titrated with the standard permanganate solution. The endpoint is indicated by a sharp break on the emf scale.

APPENDIX II

Tabulated values of the percent dissolved, to three places, versus the factor A, where A equals:

$$[1 - (1 - \% \text{ dissolved} / 100)^{1/3}]$$

<u>%</u>	<u>A</u>	<u>%</u>	<u>A</u>	<u>%</u>	<u>A</u>
00.1	0.0003334	05.1	0.0172975	10.1	0.0348683
00.2	0.0006671	05.2	0.0176428	10.2	0.0352263
00.3	0.0010010	05.3	0.0179883	10.3	0.0355846
00.4	0.0013351	05.4	0.0183341	10.4	0.0359431
00.5	0.0016695	05.5	0.0186801	10.5	0.0363019
00.6	0.0020040	05.6	0.0190264	10.6	0.0366609
00.7	0.0023388	05.7	0.0193729	10.7	0.0370203
00.8	0.0026738	05.8	0.0197196	10.8	0.0373798
00.9	0.0030090	05.9	0.0200666	10.9	0.0377397
01.0	0.0033445	06.0	0.0204139	11.0	0.0380998
01.1	0.0036802	06.1	0.0207614	11.1	0.0384602
01.2	0.0040161	06.2	0.0211091	11.2	0.0388209
01.3	0.0043522	06.3	0.0214571	11.3	0.0391818
01.4	0.0046886	06.4	0.0218054	11.4	0.0395430
01.5	0.0050252	06.5	0.0221538	11.5	0.0399045
01.6	0.0053620	06.6	0.0225026	11.6	0.0402663
01.7	0.0056991	06.7	0.0228515	11.7	0.0406283
01.8	0.0060364	06.8	0.0232008	11.8	0.0409906
01.9	0.0063729	06.9	0.0235507	11.9	0.0413532
02.0	0.0067116	07.0	0.0239000	12.0	0.0417160
02.1	0.0070496	07.1	0.0242500	12.1	0.0420792
02.2	0.0073878	07.2	0.0246002	12.2	0.0424426
02.3	0.0077262	07.3	0.0249507	12.3	0.0428062
02.4	0.0080649	07.4	0.0253014	12.4	0.0431702
02.5	0.0084038	07.5	0.0256524	12.5	0.0435344
02.6	0.0087429	07.6	0.0260037	12.6	0.0438989
02.7	0.0090822	07.7	0.0263552	12.7	0.0442637
02.8	0.0094218	07.8	0.0267069	12.8	0.0446288
02.9	0.0097616	07.9	0.0270589	12.9	0.0449941
03.0	0.0101017	08.0	0.0274112	13.0	0.0453597
03.1	0.0104420	08.1	0.0277637	13.1	0.0457256
03.2	0.0107825	08.2	0.0281165	13.2	0.0460918
03.3	0.0111233	08.3	0.0284695	13.3	0.0464583
03.4	0.0114643	08.4	0.0288288	13.4	0.0468250
03.5	0.0118055	08.5	0.0291763	13.5	0.0471921
03.6	0.0121470	08.6	0.0295301	13.6	0.0475594
03.7	0.0124887	08.7	0.0298842	13.7	0.0479270
03.8	0.0128306	08.8	0.0302385	13.8	0.0482948
03.9	0.0131728	08.9	0.0305931	13.9	0.0486630
04.0	0.0135152	09.0	0.0309479	14.0	0.0490315
04.1	0.0138578	09.1	0.0313030	14.1	0.0494002
04.2	0.0142007	09.2	0.0316583	14.2	0.0497692
04.3	0.0145438	09.3	0.0320140	14.3	0.0501385
04.4	0.0148872	09.4	0.0323698	14.4	0.0505081
04.5	0.0152308	09.5	0.0327260	14.5	0.0508780
04.6	0.0155746	09.6	0.0330824	14.6	0.0512482
04.7	0.0159187	09.7	0.0334390	14.7	0.0516186
04.8	0.0162631	09.8	0.0337960	14.8	0.0519894
04.9	0.0166076	09.9	0.0341532	14.9	0.0523604
05.0	0.0169524	10.0	0.0345106	15.0	0.0527318

<u>%</u>	<u>A</u>	<u>%</u>	<u>A</u>	<u>%</u>	<u>A</u>
15.1	0.0531034	20.1	0.0720692	25.1	0.0918437
15.2	0.0534753	20.2	0.0724565	25.2	0.0922480
15.3	0.0538475	20.3	0.0728441	25.3	0.0926527
15.4	0.0542200	20.4	0.0732320	25.4	0.0930578
15.5	0.0545928	20.5	0.0736403	25.5	0.0934632
15.6	0.0549659	20.6	0.0740089	25.6	0.0938690
15.7	0.0553393	20.7	0.0743978	25.7	0.0942752
15.8	0.0557130	20.8	0.0747870	25.8	0.0946817
15.9	0.0560869	20.9	0.0751766	25.9	0.0950886
16.0	0.0564612	21.0	0.0755665	26.0	0.0954958
16.1	0.0568358	21.1	0.0759567	26.1	0.0959034
16.2	0.0572106	21.2	0.0763472	26.2	0.0963114
16.3	0.0575858	21.3	0.0767381	26.3	0.0967198
16.4	0.0579613	21.4	0.0771293	26.4	0.0971285
16.5	0.0583370	21.5	0.0775209	26.5	0.0975376
16.6	0.0587131	21.6	0.0779127	26.6	0.0979471
16.7	0.0590895	21.7	0.0783050	26.7	0.0983569
16.8	0.0594661	21.8	0.0786975	26.8	0.0987671
16.9	0.0598431	21.9	0.0790904	26.9	0.0991777
17.0	0.0602204	22.0	0.0794836	27.0	0.0995887
17.1	0.0605979	22.1	0.0798771	27.1	0.1000000
17.2	0.0609758	22.2	0.0802710	27.2	0.1004117
17.3	0.0613540	22.3	0.0806653	27.3	0.1008238
17.4	0.0617325	22.4	0.0810598	27.4	0.1012363
17.5	0.0621113	22.5	0.0814547	27.5	0.1016491
17.6	0.0624904	22.6	0.0818500	27.6	0.1020623
17.7	0.0628698	22.7	0.0822456	27.7	0.1024759
17.8	0.0632495	22.8	0.0826415	27.8	0.1028899
17.9	0.0636295	22.9	0.0830377	27.9	0.1033043
18.0	0.0640098	23.0	0.0834344	28.0	0.1037191
18.1	0.0643905	23.1	0.0838313	28.1	0.1041342
18.2	0.0647714	23.2	0.0842286	28.2	0.1045497
18.3	0.0651527	23.3	0.0846262	28.3	0.1049656
18.4	0.0655343	23.4	0.0850242	28.4	0.1053819
18.5	0.0659161	23.5	0.0854226	28.5	0.1057986
18.6	0.0662983	23.6	0.0858213	28.6	0.1062157
18.7	0.0666808	23.7	0.0862203	28.7	0.1066361
18.8	0.0670637	23.8	0.0866197	28.8	0.1070510
18.9	0.0674468	23.9	0.0870194	28.9	0.1074692
19.0	0.0678302	24.0	0.0874195	29.0	0.1078879
19.1	0.0682140	24.1	0.0878199	29.1	0.1083069
19.2	0.0685981	24.2	0.0882207	29.2	0.1087263
19.3	0.0689825	24.3	0.0886218	29.3	0.1091461
19.4	0.0693672	24.4	0.0890233	29.4	0.1095663
19.5	0.0697523	24.5	0.0894252	29.5	0.1099870
19.6	0.0701376	24.6	0.0898273	29.6	0.1104080
19.7	0.0705233	24.7	0.0902299	29.7	0.1108294
19.8	0.0709093	24.8	0.0906328	29.8	0.1112512
19.9	0.0712956	24.9	0.0910361	29.9	0.1116734
20.0	0.0716822	25.0	0.0914397	30.0	0.1120960

<u>%</u>	<u>A</u>	<u>%</u>	<u>A</u>	<u>%</u>	<u>A</u>
30.1	0.1125190	35.1	0.1342053	40.1	0.1570362
30.2	0.1129424	35.2	0.1346503	40.2	0.1575055
30.3	0.1133662	35.3	0.1350956	40.3	0.1579754
30.4	0.1137905	35.4	0.1355415	40.4	0.1584458
30.5	0.1142151	35.5	0.1359877	40.5	0.1589167
30.6	0.1146401	35.6	0.1364345	40.6	0.1593882
30.7	0.1150656	35.7	0.1368817	40.7	0.1598602
30.8	0.1154915	35.8	0.1373294	40.8	0.1603327
30.9	0.1159177	35.9	0.1377775	40.9	0.1608058
31.0	0.1163444	36.0	0.1382261	41.0	0.1612793
31.1	0.1167715	36.1	0.1386752	41.1	0.1617535
31.2	0.1171990	36.2	0.1391247	41.2	0.1622281
31.3	0.1176269	36.3	0.1395748	41.3	0.1627033
31.4	0.1180553	36.4	0.1400252	41.4	0.1631791
31.5	0.1184840	36.5	0.1404762	41.5	0.1636553
31.6	0.1189132	36.6	0.1409276	41.6	0.1641322
31.7	0.1193428	36.7	0.1413795	41.7	0.1646095
31.8	0.1197728	36.8	0.1418319	41.8	0.1650874
31.9	0.1202032	36.9	0.1422848	41.9	0.1655659
32.0	0.1206341	37.0	0.1427381	42.0	0.1660449
32.1	0.1210653	37.1	0.1431919	42.1	0.1665245
32.2	0.1214970	37.2	0.1436462	42.2	0.1670046
32.3	0.1219292	37.3	0.1441010	42.3	0.1674852
32.4	0.1223617	37.4	0.1445563	42.4	0.1679665
32.5	0.1227947	37.5	0.1450120	42.5	0.1684483
32.6	0.1232281	37.6	0.1454683	42.6	0.1689306
32.7	0.1236619	37.7	0.1459250	42.7	0.1694135
32.8	0.1240962	37.8	0.1463822	42.8	0.1698969
32.9	0.1245309	37.9	0.1468399	42.9	0.1703810
33.0	0.1249660	38.0	0.1472981	43.0	0.1708656
33.1	0.1254015	38.1	0.1477568	43.1	0.1713507
33.2	0.1258375	38.2	0.1482160	43.2	0.1718365
33.3	0.1262740	38.3	0.1486757	43.3	0.1723227
33.4	0.1267108	38.4	0.1491358	43.4	0.1728096
33.5	0.1271481	38.5	0.1495965	43.5	0.1732971
33.6	0.1275859	38.6	0.1500577	43.6	0.1737851
33.7	0.1280240	38.7	0.1505193	43.7	0.1742737
33.8	0.1284627	38.8	0.1509815	43.8	0.1747628
33.9	0.1289017	38.9	0.1514442	43.9	0.1752526
34.0	0.1293412	39.0	0.1519074	44.0	0.1757429
34.1	0.1297812	39.1	0.1523711	44.1	0.1762339
34.2	0.1302216	39.2	0.1528353	44.2	0.1767254
34.3	0.1306624	39.3	0.1533000	44.3	0.1772175
34.4	0.1311037	39.4	0.1537652	44.4	0.1777101
34.5	0.1315454	39.5	0.1542309	44.5	0.1782034
34.6	0.1319876	39.6	0.1546972	44.6	0.1786973
34.7	0.1324303	39.7	0.1551639	44.7	0.1791918
34.8	0.1328734	39.8	0.1556312	44.8	0.1796868
34.9	0.1333169	39.9	0.1560990	44.9	0.1801825
35.0	0.1337609	40.0	0.1565673	45.0	0.1806787

<u>%</u>	<u>A</u>	<u>%</u>	<u>A</u>	<u>%</u>	<u>A</u>
45.1	0.1811756	50.1	0.2068290	55.1	0.2342586
45.2	0.1816731	50.2	0.2073592	55.2	0.2348275
45.3	0.1821711	50.3	0.2078901	55.3	0.2353973
45.4	0.1826698	50.4	0.2084217	55.4	0.2359679
45.5	0.1831691	50.5	0.2089540	55.5	0.2365393
45.6	0.1836690	50.6	0.2094871	55.6	0.2371116
45.7	0.1841695	50.7	0.2100208	55.7	0.2376848
45.8	0.1846706	50.8	0.2105553	55.8	0.2382588
45.9	0.1851724	50.9	0.2110905	55.9	0.2388337
46.0	0.1856747	51.0	0.2116265	56.0	0.2394095
46.1	0.1861777	51.1	0.2121632	56.1	0.2399861
46.2	0.1866813	51.2	0.2127006	56.2	0.2405637
46.3	0.1871855	51.3	0.2132387	56.3	0.2411421
46.4	0.1876904	51.4	0.2137776	56.4	0.2417213
46.5	0.1881959	51.5	0.2143172	56.5	0.2423015
46.6	0.1887020	51.6	0.2148576	56.6	0.2428826
46.7	0.1892087	51.7	0.2153987	56.7	0.2434645
46.8	0.1897161	51.8	0.2159405	56.8	0.2440474
46.9	0.1902241	51.9	0.2164831	56.9	0.2446311
47.0	0.1907328	52.0	0.2170265	57.0	0.2452158
47.1	0.1912421	52.1	0.2175706	57.1	0.2458013
47.2	0.1917520	52.2	0.2181154	57.2	0.2463878
47.3	0.1922626	52.3	0.2186611	57.3	0.2469752
47.4	0.1927738	52.4	0.2192075	57.4	0.2475635
47.5	0.1932857	52.5	0.2197546	57.5	0.2481527
47.6	0.1937982	52.6	0.2203025	57.6	0.2487428
47.7	0.1943114	52.7	0.2208512	57.7	0.2493339
47.8	0.1948252	52.8	0.2214007	57.8	0.2499259
47.9	0.1953397	52.9	0.2219510	57.9	0.2505189
48.0	0.1958548	53.0	0.2225020	58.0	0.2511128
48.1	0.1963707	53.1	0.2230538	58.1	0.2517076
48.2	0.1968871	53.2	0.2236064	58.2	0.2523034
48.3	0.1974043	53.3	0.2241598	58.3	0.2529001
48.4	0.1979221	53.4	0.2247139	58.4	0.2534978
48.5	0.1984405	53.5	0.2252689	58.5	0.2540964
48.6	0.1989597	53.6	0.2258247	58.6	0.2546960
48.7	0.1994795	53.7	0.2263812	58.7	0.2552966
48.8	0.2000000	53.8	0.2269386	58.8	0.2558981
48.9	0.2005212	53.9	0.2274968	58.9	0.2565006
49.0	0.2010430	54.0	0.2280557	59.0	0.2571041
49.1	0.2014656	54.1	0.2286155	59.1	0.2577086
49.2	0.2020888	54.2	0.2291761	59.2	0.2583140
49.3	0.2026127	54.3	0.2297375	59.3	0.2589205
49.4	0.2031373	54.4	0.2302998	59.4	0.2595279
49.5	0.2036626	54.5	0.2308628	59.5	0.2601364
49.6	0.2041886	54.6	0.2314267	59.6	0.2607458
49.7	0.2047152	54.7	0.2319914	59.7	0.2613563
49.8	0.2052426	54.8	0.2325570	59.8	0.2619677
49.9	0.2057707	54.9	0.2331234	59.9	0.2625802
50.0	0.2062995	55.0	0.2336906	60.0	0.2631937

%	<u>A</u>	%	<u>A</u>	%	<u>A</u>
60.1	0.2638082	65.1	0.2959419	70.1	0.3313117
60.2	0.2644238	65.2	0.2966150	70.2	0.3320580
60.3	0.2650403	65.3	0.2972894	70.3	0.3328060
60.4	0.2656580	65.4	0.2979651	70.4	0.3335556
60.5	0.2662766	65.5	0.2986421	70.5	0.3343070
60.6	0.2668963	65.6	0.2993204	70.6	0.3350600
60.7	0.2675171	65.7	0.3000000	70.7	0.3358418
60.8	0.2681389	65.8	0.3006809	70.8	0.3365713
60.9	0.2687617	65.9	0.3013632	70.9	0.3373295
61.0	0.2693856	66.0	0.3020468	71.0	0.3380894
61.1	0.2700106	66.1	0.3027317	71.1	0.3388511
61.2	0.2706367	66.2	0.3034810	71.2	0.3396146
61.3	0.2712638	66.3	0.3041057	71.3	0.3403798
61.4	0.2718921	66.4	0.3047947	71.4	0.3411468
61.5	0.2725214	66.5	0.3054850	71.5	0.3419156
61.6	0.2731518	66.6	0.3061768	71.6	0.3426862
61.7	0.2737833	66.7	0.3068699	71.7	0.3434586
61.8	0.2744158	66.8	0.3075644	71.8	0.3442328
61.9	0.2750495	66.9	0.3082604	71.9	0.3450088
62.0	0.2756844	67.0	0.3089577	72.0	0.3457867
62.1	0.2763203	67.1	0.3096564	72.1	0.3465665
62.2	0.2769573	67.2	0.3103566	72.2	0.3473481
62.3	0.2775955	67.3	0.3110581	72.3	0.3481316
62.4	0.2782348	67.4	0.3117611	72.4	0.3489170
62.5	0.2788752	67.5	0.3124656	72.5	0.3497043
62.6	0.2795168	67.6	0.3131715	72.6	0.3504935
62.7	0.2801595	67.7	0.3138788	72.7	0.3512846
62.8	0.2808034	67.8	0.3145876	72.8	0.3520776
62.9	0.2814484	67.9	0.3152979	72.9	0.3528726
63.0	0.2820946	68.0	0.3160096	73.0	0.3536696
63.1	0.2827419	68.1	0.3167229	73.1	0.3544685
63.2	0.2833904	68.2	0.3174376	73.2	0.3552694
63.3	0.2840401	68.3	0.3181538	73.3	0.3560723
63.4	0.2846910	68.4	0.3188715	73.4	0.3568772
63.5	0.2853431	68.5	0.3195908	73.5	0.3576842
63.6	0.2859963	68.6	0.3203156	73.6	0.3584931
63.7	0.2866508	68.7	0.3210339	73.7	0.3593041
63.8	0.2873064	68.8	0.3217577	73.8	0.3601172
63.9	0.2879633	68.9	0.3224831	73.9	0.3609323
64.0	0.2886213	69.0	0.3232101	74.0	0.3617496
64.1	0.2892806	69.1	0.3239386	74.1	0.3625689
64.2	0.2899412	69.2	0.3246687	74.2	0.3633903
64.3	0.2906029	69.3	0.3254003	74.3	0.3642139
64.4	0.2912659	69.4	0.3261336	74.4	0.3650396
64.5	0.2919301	69.5	0.3268685	74.5	0.3658674
64.6	0.2925956	69.6	0.3276049	74.6	0.3666974
64.7	0.2932623	69.7	0.3283430	74.7	0.3675296
64.8	0.2939303	69.8	0.3290827	74.8	0.3683640
64.9	0.2945996	69.9	0.3298241	74.9	0.3692006
65.0	0.2952701	70.0	0.3305670	75.0	0.3700395

<u>%</u>	<u>A</u>	<u>%</u>	<u>A</u>	<u>%</u>	<u>A</u>
75.1	0.3708805	80.1	0.4161728	85.1	0.4698541
75.2	0.3717239	80.2	0.4171523	85.2	0.4710428
75.3	0.3725695	80.3	0.4181352	85.3	0.4722368
75.4	0.3734173	80.4	0.4191214	85.4	0.4734363
75.5	0.3742675	80.5	0.4201110	85.5	0.4746412
75.6	0.3751200	80.6	0.4211040	85.6	0.4758517
75.7	0.3759749	80.7	0.4221003	85.7	0.4770678
75.8	0.3768320	80.8	0.4231002	85.8	0.4782897
75.9	0.3776916	80.9	0.4241035	85.9	0.4795172
76.0	0.3785535	81.0	0.4251103	86.0	0.4807506
76.1	0.3794178	81.1	0.4261206	86.1	0.4819899
76.2	0.3802846	81.2	0.4271346	86.2	0.4832351
76.3	0.3811537	81.3	0.4281521	86.3	0.4844863
76.4	0.3820253	81.4	0.4291733	86.4	0.4857437
76.5	0.3828994	81.5	0.4301981	86.5	0.4870072
76.6	0.3837760	81.6	0.4312266	86.6	0.4882770
76.7	0.3846551	81.7	0.4322589	86.7	0.4895531
76.8	0.3855366	81.8	0.4332949	86.8	0.4908357
76.9	0.3864208	81.9	0.4343347	86.9	0.4921247
77.0	0.3873074	82.0	0.4353784	87.0	0.4932203
77.1	0.3881967	82.1	0.4364259	87.1	0.4947226
77.2	0.3890885	82.2	0.4374774	87.2	0.4960316
77.3	0.3899830	82.3	0.4385328	87.3	0.4973474
77.4	0.3908801	82.4	0.4395921	87.4	0.4986702
77.5	0.3917798	82.5	0.4406555	87.5	0.5000000
77.6	0.3926822	82.6	0.4417230	87.6	0.5013369
77.7	0.3935873	82.7	0.4427945	87.7	0.5026810
77.8	0.3944951	82.8	0.4438702	87.8	0.5040324
77.9	0.3954056	82.9	0.4449501	87.9	0.5053913
78.0	0.3963189	83.0	0.4460342	88.0	0.5067576
78.1	0.3972350	83.1	0.4471225	88.1	0.5081315
78.2	0.3981538	83.2	0.4482152	88.2	0.5095132
78.3	0.3990755	83.3	0.4493122	88.3	0.5109027
78.4	0.4000000	83.4	0.4504135	88.4	0.5123001
78.5	0.4009274	83.5	0.4515193	88.5	0.5137056
78.6	0.4018576	83.6	0.4526296	88.6	0.5151192
78.7	0.4027907	83.7	0.4537444	88.7	0.5165412
78.8	0.4037268	83.8	0.4548638	88.8	0.5179715
78.9	0.4046658	83.9	0.4559878	88.9	0.5194104
79.0	0.4056078	84.0	0.4571165	89.0	0.5208580
79.1	0.4065528	84.1	0.4582498	89.1	0.5223144
79.2	0.4075008	84.2	0.4593880	89.2	0.5237797
79.3	0.4084518	84.3	0.4605309	89.3	0.5252541
79.4	0.4094059	84.4	0.4616787	89.4	0.5267377
79.5	0.4103631	84.5	0.4628315	89.5	0.5282306
79.6	0.4113235	84.6	0.4639892	89.6	0.5297331
79.7	0.4122869	84.7	0.4651519	89.7	0.5312452
79.8	0.4132536	84.8	0.4663197	89.8	0.5327671
79.9	0.4142234	84.9	0.4674926	89.9	0.5342990
80.0	0.4151965	85.0	0.4686707	90.0	0.5358411

<u>%</u>	<u>A</u>	<u>%</u>	<u>A</u>
90.1	0.5373935	95.1	0.6340694
90.2	0.5389564	95.2	0.6365759
90.3	0.5405299	95.3	0.6391174
90.4	0.5421143	95.4	0.6416952
90.5	0.5437097	95.5	0.6443107
90.6	0.5453164	95.6	0.6469652
90.7	0.5469345	95.7	0.6496602
90.8	0.5485643	95.8	0.6523973
90.9	0.5502059	95.9	0.6551783
91.0	0.5518595	96.0	0.6580048
91.1	0.5535255	96.1	0.6608789
91.2	0.5552040	96.2	0.6638025
91.3	0.5568952	96.3	0.6667778
91.4	0.5585995	96.4	0.6698073
91.5	0.5603170	96.5	0.6728934
91.6	0.5620481	96.6	0.6760388
91.7	0.5637929	96.7	0.6792466
91.8	0.5655519	96.8	0.6825198
91.9	0.5673251	96.9	0.6858619
92.0	0.5691131	97.0	0.6892767
92.1	0.5709160	97.1	0.6927683
92.2	0.5727341	97.2	0.6963411
92.3	0.5745679	97.3	0.7000000
92.4	0.5764176	97.4	0.7037504
92.5	0.5782837	97.5	0.7075987
92.6	0.5801664	97.6	0.7115501
92.7	0.5820661	97.7	0.7156133
92.8	0.5839832	97.8	0.7197961
92.9	0.5859182	97.9	0.7241076
93.0	0.5878715	98.0	0.7285582
93.1	0.5898434	98.1	0.7331598
93.2	0.5918345	98.2	0.7379359
93.3	0.5938452	98.3	0.7428718
93.4	0.5958760	98.4	0.7480158
93.5	0.5979274	98.5	0.7533788
93.6	0.6000000	98.6	0.7589858
93.7	0.6020943	98.7	0.7648665
93.8	0.6042108	98.8	0.7710572
93.9	0.6063503	98.9	0.7776020
94.0	0.6085132	99.0	0.7845565
94.1	0.6107004	99.1	0.7919916
94.2	0.6129123	99.2	0.8000000
94.3	0.6151499	99.3	0.8087069
94.4	0.6174138	99.4	0.8182879
94.5	0.6197048	99.5	0.8290024
94.6	0.6220237	99.6	0.8412599
94.7	0.6243714	99.7	0.8557750
94.8	0.6267489	99.8	0.8740079
94.9	0.6291520	99.9	0.9000000
95.0	0.6315969		

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