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THE WASHOUT OF METHYL IODIDE BY HYDRAZINE SPRAYS
FINAL REPORT

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THE WASHOUT OF METHYL IODIDE BY HYDRAZINE SPRAYS
-- FINAL REPORT --

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ABSTRACT

This investigation was undertaken to determine the effectiveness and merit of hydrazine for use as a spray additive for washing methyl iodide from containment atmospheres following a reactor accident. Two principal areas were studied -- the physiochemical aspects of the hydrazine-water-methyl iodide system and the washout of methyl iodide with hydrazine solution sprays. The partition coefficient of methyl iodide in water was measured and found to be related to temperature by the following relation: $\log H = -4.82 + \frac{1597}{T}$ for a temperature range of 5°C to 90°C. In the expression H is the partition coefficient (liquid concentration/gas concentration) and T is the absolute temperature in °K. Methods and apparatus were developed for measuring the reaction rate of methyl iodide and aqueous solutions of hydrazine. Rate constants were measured for temperatures from 24.6°C to 64.7°C and for various hydrazine concentrations. The reaction rate was determined to be second order. The activation energy was calculated to be 20.2 Kcal/mol. Reaction rates with 1,1-dimethylhydrazine monomethyl hydrazine, and some sulfur based compounds were determined for comparative purposes. The reaction rate with hydrazine was found to be essentially independent of OH^- concentration. Various correlating indices were investigated. The nucleophilic character of the reactant and the relative reaction rates in solvents other than water can be used to help predict relative reaction rates.

Theory of stagnant droplet and flowing film removal of an airborne gas such as methyl iodide was developed with computer solutions of the droplet removal equations. Input data are partition coefficient, reaction rate, droplet diameter, and exposure time. Experiments in two spray chambers gave washout half-times of methyl iodide which varied with spray rate, concentration of hydrazine, and temperature. The observed washout rate in the vessels used and reactive spray droplet removal theory permitted extrapolation to full-size containment vessels. Five percent hydrazine should show a half-time of removal of about 60 minutes for nominal 550 μ droplets and spray flow rate of 0.0068 cm^3/cm^2 sec with wall flow rate of 0.1 cm^3/cm sec for a cylindrical vessel 80 ft. in height and 32 ft. in diameter.

Radiation stability of hydrazine determined in recent experiments show that 5% hydrazine would be decomposed to the extent of about 50% for an absorbed dose of 10^8 Rad. One of the products is hydrogen. The conclusion is reached that the radiation sensitivity of hydrazine outweighs the desirable qualities as a spray additive.

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INTRODUCTION

The work described in this report represents an effort to arrive at a quantitative understanding of the absorption of airborne methyl iodide by reactive sprays within nuclear reactor containment systems. Although aqueous hydrazine solutions were used chiefly, the results can be applied to other reactive solutions if the reaction rate with methyl iodide is known. An earlier report[1] described the results of this research through September, 1967. The present report will be devoted primarily to work completed since the progress report was issued. Work reported earlier will be repeated only where necessary for continuity or reference.

The use of sprays in a reactor containment vessel represents an engineered safeguard for controlling fission products released following postulated loss-of-coolant meltdown accidents. The spray system will be employed to suppress pressure build-up and to remove fission product aerosols and gases released from overheated fule. Iodine-131 is the isotope expected to constitute the greatest radiological hazard if released to man's environment. Radioiodine released from nuclear fuels has been found to exist in several chemical forms including elemental and organic forms. Of the organic forms, methyl iodide appears to be the most abundant. Methyl iodide is much more inert than elemental iodine, and hence is removed much more slowly by water sprays than elemental iodine.

The purpose of this study was to determine the rate of removal of methyl iodide by sprays of water solutions of reactive additives. Hydrazine solutions were the subject of most of this effort, but the results would be expected to apply to solutions of other reactive additives such as sodium thiosulfate. The goal of the effort was to provide information sufficient to permit prediction of methyl iodide absorption rate in large scale reactor containment vessels.

A detailed investigation of a reactive additive for removing methyl iodide must embrace many facets of the rather complex process of removal with reactive sprays. Much of the work to date leading to an understanding of the spray removal process has been focused on iodine removal. The relatively high solubility of elemental iodine in water and its high chemical reactivity enhance the liquid phase mass transfer to a point where transfer of iodine to the surface of the drop limits the removal rate. Models have been developed for this case which account for experimental results reasonably well.

For methyl iodide, which is much less soluble and more inert chemically than elemental iodine, the rate controlling process for reactions considered to date is the reaction rate within the liquid. Although investigators have studied these cases, few experimental data are available to substantiate the models developed. When reaction rates control the absorption process, it is necessary to know the rates and mechanisms of the reactions throughout the range of temperatures and pressures of interest. The partition coefficient between the gas phase and the liquid must also be known since the partition coefficient will establish the driving force for the transfer process.

Chemical properties other than the primary reaction must also be investigated. For example the effect of boron additives, reactions with the solvent (hydrolysis), and consumption of the reactive additive by oxygen or other constituents in the atmosphere are potentially important. Radiation stability, stability during storage, thermal stability, and toxicity are factors which must be considered in making judgments of the merit of a spray additive.

The demonstration of spray removal efficiency should account for droplet size, liquid flow rate, wall film absorption, and temperature effects, along with the chemical properties of the additive solution considered.

This effort was carried out in two parallel studies. One was a study of physical solubility and reaction kinetics within the liquid, and the other was a small engineering-scale demonstration of absorption within spray chambers. These two aspects of the study will be described separately.

PHYSIOCHEMICAL STUDIES OF METHYL IODIDE AND HYDRAZINE

In addition to the mechanical aspects of interfacial exposure, the rate of absorption of methyl iodide by aqueous solutions of hydrazine is influenced by the physical solubility of methyl iodide in the solution, by the diffusivity of methyl iodide in the liquid, and by the kinetics of chemical reactions which occur. The purpose of this part of the study was to provide numerical values of solubility and reaction rates for the solutions of interest here. Correlations are available for predicting liquid phase diffusivities and the physiochemical effort was limited to measurement of the partition coefficient and reaction rates.

Exploratory studies demonstrated[1][2] that for airborne methyl iodide in contact with aqueous hydrazine solutions the removal from the gas phase was given by

$$\frac{dC}{dt} = -\frac{kCNA}{V} \qquad (1)$$

where C = gas phase concentration of methyl iodide
k = a constant
N = mole fraction of hydrazine hydrate in liquid
A = area of gas-liquid interface
V = volume of the gas phase.

This rate law leads to the conclusion that the removal is by absorption into the liquid, and that the gas phase reaction between hydrazine vapor and methyl iodide is slow. Direct measurement of the concentration decay in the absence of a liquid phase but where hydrazine vapor was present also showed that the homogenous gas phase reaction was very slow and could be ignored.[1] Thus, effort was concentrated on measurement of the homogenous solution reaction rate, and on the solubility of methyl iodide in water.

THE PARTITION OF METHYL IODIDE BETWEEN VAPOR AND WATER

The partition coefficient is defined as the ratio of the concentration of a solute gas in the liquid phase to the concentration in the gas phase at equilibrium. It is a controlling parameter because it determines the interfacial compositions, which in turn determines the magnitude of concentration driving force in the liquid phase. As used here, the concentrations are for unreacted species. The partition coefficient thus is the equilibrium constant for the reaction:

$$CH_3I_{(g)} = CH_3I_{(\ell)} \qquad (2)$$

Available Data

Experimental measurements of methyl iodide partition coefficient available up to September, 1967 have been described earlier.[1][3] Based on literature values, and on data obtained earlier in this work, the partition coefficient was found to be nearly independent of methyl iodide concentration, in accordance with Henry's law. For a temperature range of 5°C to 70°C, the partition coefficient could be represented by the following equation,

$$\log (H) = -4.82 + \frac{1597}{T} \qquad (3)$$

where log (H) is the logarithm to the base 10 of the partition coefficient and T is the absolute temperature in °K.

Proper interpretation of absorption measurements performed in this study requires knowledge of the partition coefficient at temperatures up to 125°C. Hence extension of data to higher temperatures is needed. Measurements at higher temperatures are complicated by the need for a pressurized system, and by the reaction of dissolved methyl iodide with water. For example, the hydrolysis rate of methyl iodide in pure water is estimated from reported data[4] to be 0.5%/min at 85°C and 19%/min at 120°C. Based on analysis of these complicating factors, it was determined that extension of the partition coefficient to 85°C would be feasible with existing apparatus. A new method would be required for measurements beyond this temperature.

Experimental Methods Used

a. Single Phase Analysis

This method was used earlier to obtain measurements up to 70°C, and is more fully described in references [1] and [3]. In this technique, the gas phase concentration of methyl iodide is compared for two vessels, only one of which contains water. Identical aliquots of methyl iodide are introduced into both vessels. From a material balance, neglecting chemical reaction, the partition coefficient may be related to the gas phase concentrations in the two vessels:

$$H = \left[\frac{C^\circ}{C} - 1\right] \frac{V_g}{V_L} - \frac{C^\circ}{C} \qquad (4)$$

In equation (4) C° is the methyl iodide concentration in the vapor when no liquid is present, C is the concentration in the vapor when liquid is present, and V_g and V_L are the volumes of the gas and liquid phases respectively. The concentration was measured as a function of time by withdrawing small samples which were analyzed chromatographically.

b. Analysis of Both Phases

An alternative method was used to provide comparative values of partition coefficients at 85°C. In this method, samples of known volume were withdrawn from both the gas and liquid phases and analyzed for unreacted methyl iodide. Analysis was by means of a system assembled for measurement of the solution reaction rate. The samples withdrawn from an equilibrium contacting vessel were injected into water contained in a sparge vessel. The methyl iodide present in an unreacted form was stripped from this vessel by a stream of pure nitrogen. Samples of the exiting gas were analyzed chromatographically which permitted calculation of the integrated amount of methyl iodide swept from the sparge vessel. The dilutions of the sample by the nitrogen flow required the use of methyl iodide concentrations 100 to 1000 times greater than employed in method a. The sparge vessel is shown schematically in Figure 1.

The partition coefficient may be calculated directly as the ratio between the amounts swept from the sparge cell, for liquid and gas samples of the same volume.

Results of Partition Coefficient Measurement

The results of the measurement at 85°C using the method in which samples were withdrawn from the gas phase only are listed in Table I.

The methyl iodide concentration shown is the equilibrium value measured in the gas phase, in terms of peak height for a 30 $\mu\ell$ aliquot and an attenuation of 4X. For these conditions, a peak height of 100 corresponds to a quantity of methyl iodide of approximately 10^{-10} grams.

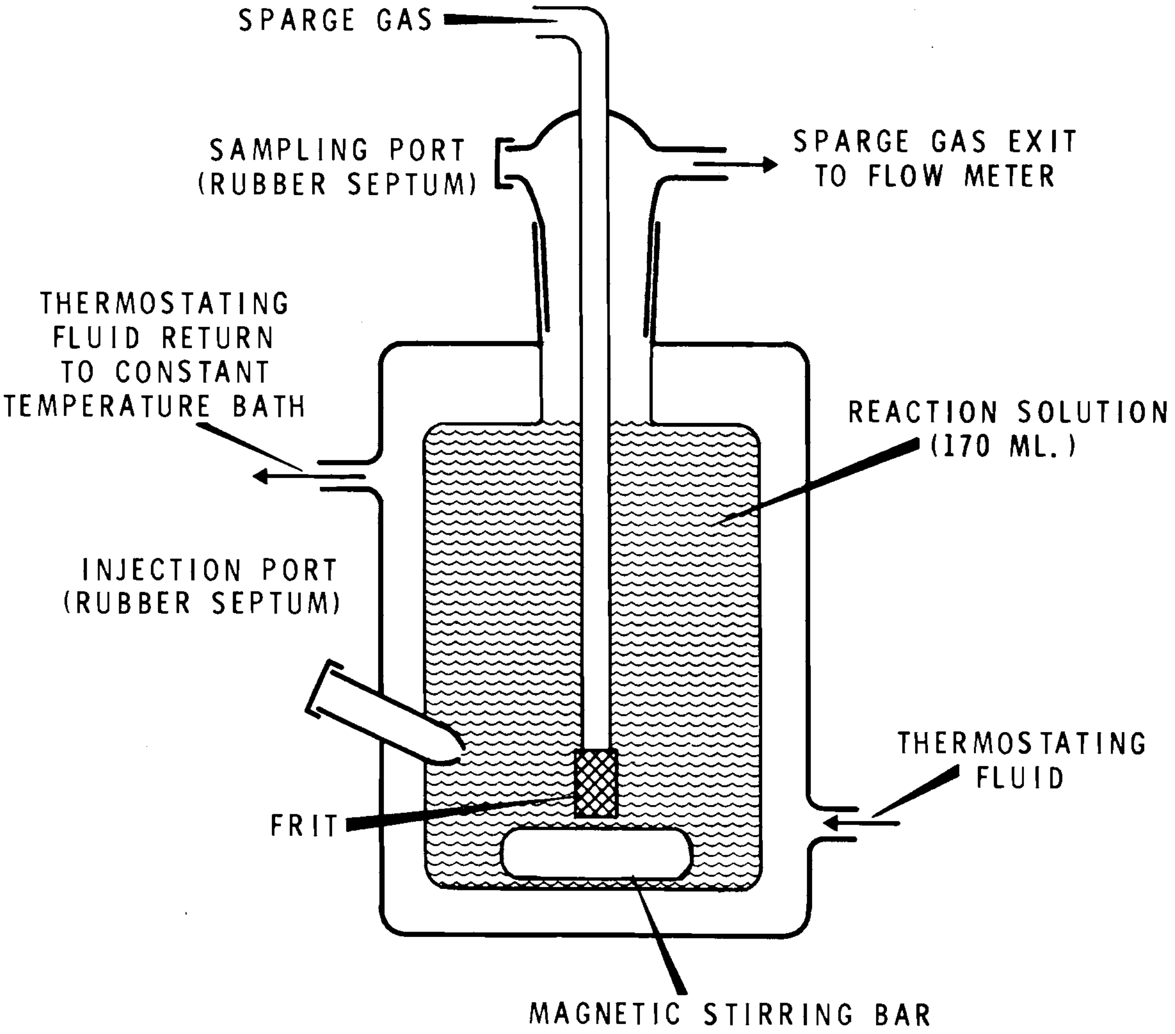

Figure 1. Reaction Cell

TABLE I

PARTITION COEFFICIENT OBTAINED FROM GAS PHASE ANALYSIS

(Gas Volume = 30.3 ml, Liquid Volume - 25.0 ml, Temperature = 85°C)

Determination	Methyl Iodide Concentration (peak height)	Partition Coefficient	Deviation From Average
1	52.0	0.85	+0.12
2	67.4	0.40	-0.32
3	48.7	0.99	+0.26
4	55.0	0.75	+0.03
5	68.7	0.37	-0.36
6	51.5	0.87	+0.14
7	52.0	0.85	+0.12
		Avg. = 0.72 ± 0.24	

The results of measurements obtained in the method in which both gas and liquid samples were analyzed are presented in Table II.

TABLE II

PARTITION COEFFICIENT MEASUREMENTS FROM ANALYSIS OF BOTH PHASES

(Temperature = 89.7°C)

Determination	Partition Coefficient	Total Methyl Iodide In Equilibrium Vessel (relative units)	Time of Measurement From Start Of Experiment (Hours)
1A	0.40	10.5	0.0
1B	0.40	8.4	1.0
1C	0.36	4.8	3.3
1D	0.37	3.4	4.2
2A	0.44	3.2	0
2B	0.32	2.6	1
2C	0.34	1.3	3
3A	0.56	not measured	0
3B	0.40	not measured	1
4A	0.34	not measured	0

The total amount of methyl iodide in the equilibrium vessel decreased with time due to hydrolysis. The observed hydrolysis rate of 0.5%/min is smaller than the predicted rate of 1.2%/min for the liquid phase. This lower rate observed would be expected since an interphase transport is involved, and the flask was agitated only prior to sampling.

Discussion of Partition Coefficient Measurements

The results obtained by the two methods are not identical, but at the same time do overlap if deviations are considered. The average partition coefficient measured at 85°C is 0.72 which is significantly higher than the value of 0.44 predicted from straight line extrapolation of lower temperature data [equation (3)]. Hydrolysis within the liquid phase would increase the amount of methyl iodide taken up by the liquid which would result in a measured coefficient higher than for no reaction. Another cause of error is the presence of a large amount of water in the vapor phase which interferes with the chromatographic analysis.

The average partition coefficient obtained from sampling and analysis of both phases is 0.38 which is in good agreement with the value predicted using equation (3). This method must be considered as the more reliable of the two used here because the hydrolysis rate and water interference are greately reduced. Since the data obtained agree with straight line extrapolation of lower temperature measurements, it is concluded that over the range 5°C to 90°C, the partition coefficient is represented by equation (3).

From a practical standpoint, washout is of greatest concern at temperatures above 100°C. Hence, extension of solubility measurements up to 130°C is needed for interpretation of washout results. The known reaction of methyl iodide with pure water at these temperatures requires development of a new experimental apparatus, permitting more rapid equilibration and measurement than is possible with the static-type equipment used here.

REACTION RATES OF METHYL IODIDE IN AQUEOUS SOLUTION

Due to its low solubility in water methyl iodide absorption will be controlled by resistance within the liquid phase unless it reacts very rapidly in the liquid. The gas phase concentration of methyl iodide expected in a reactor containment vessel is very low, of the order of 1 milligram per cubic meter. Due to its low solubility, the liquid phase concentrations would be even lower. The concentration of additive molecules in the liquid is orders of magnitude higher than the methyl iodide concentration, and for this reason the reaction will be kinetically pseudo-first order. For reactions which are second order, the pseudo-first order rate constant would be proportional to the additive concentration.

Available Data

Kinetic data on the reaction of methyl iodide with chemical species in water solution were reviewed in our progress report.[1] Data were not available on the methyl iodide-hydrazine reaction, and preliminary scouting techniques were explored. The high volatility of methyl iodide over water presents a number of difficulties in making kinetic measurements. A reactor in which no vapor phase exists has been described[5] but this equipment was found to be unsatisfactory for use in this study. Initial measurements reported in reference [1] used a reactor having no vapor space, and relied on an ion exchange bed for separation of reacted and unreacted forms of methyl iodide. Difficulties in this method caused inaccuracies in measurements, and the data reported in reference [1] for methyl iodide and hydrazine must be considered as relative only. The experimental method described below overcomes these problems, and the data obtained are considered reliable, and supersede the reaction rates reported earlier.[1]

Experimental Method

An experimental method well suited for reaction rate measurements for volatile reactants was recently used to study the reaction between oxygen and molten sulfur.[6] In this method, further described in reference [7], the stripping of a volatile reactant by an inert gas sparge stream is measured as a function of time. The rate and extent of removal of a volatile reactant is dependent on the stripping efficiency of the sparge stream, and on the depletion of the reactant within the liquid by chemical reaction. The observed depletion rate may be related mathematically to the kinetics of the sparge stream stripping and the homogenous liquid phase reaction rates. The stripping method is depicted schematically in Figure 2.

A material balance on the volatile reactant within the measuring cell permits the reaction rate to be related to the amount of reactant ultimately stripped from solution. If no reaction occurred within the liquid phase, then

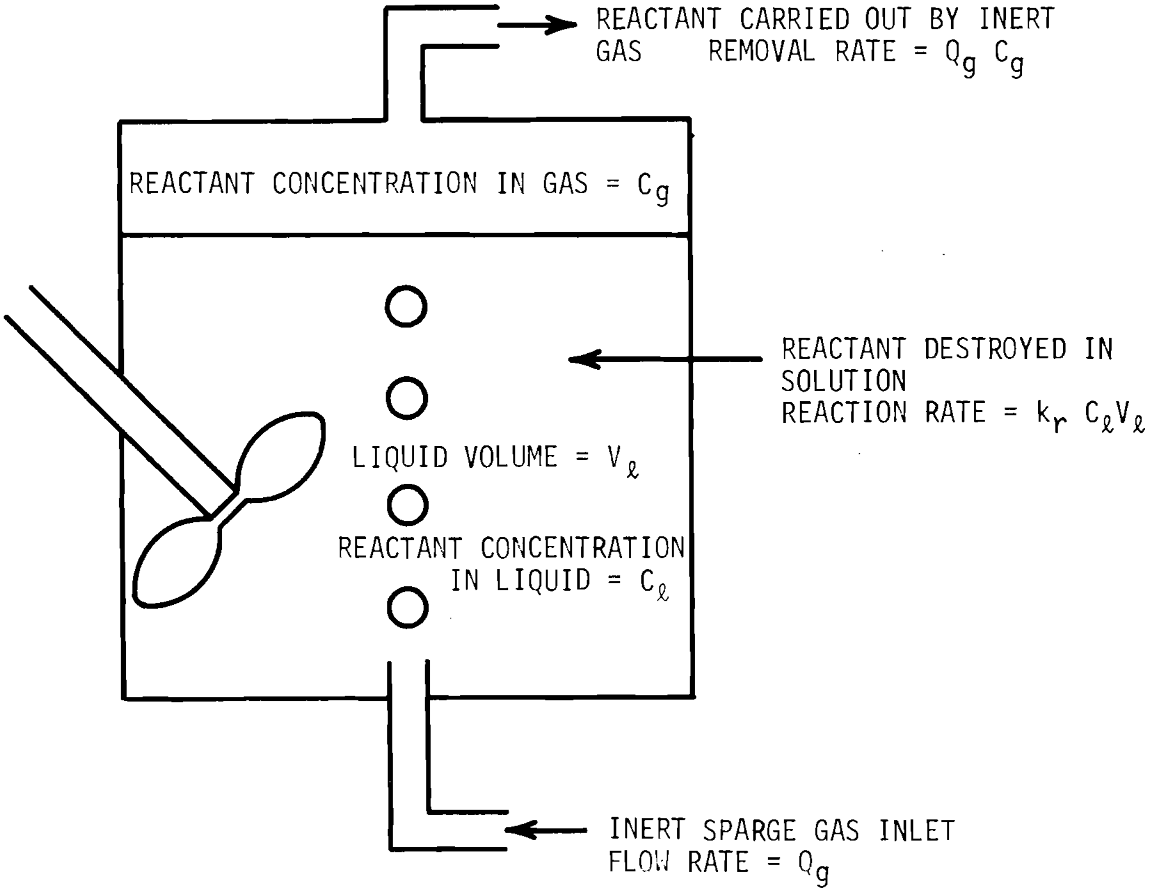

Figure 2. Schematic Diagram of Reaction Measuring Cell

all of the reactant initially present would finally be removed. In the mathematical analysis, it is assumed that both stripping and reaction are first order processes. For a pseudo-first order reaction the results of the mathematical analysis is

$$\frac{1}{k_{obsd}} = \frac{1}{k_r}\left[1 - \frac{A_s}{A_o}\right], \tag{5}$$

where k_{obsd} = observed first order decay rate of concentration in exiting gas,
k_r = first order solution reaction rate,
A_s = total amount of reactant stripped from solution = $\int_0^\infty Q_g\, C_g\, dt$,
A_o = amount of reactant present initially.

The amount of reactant initially present, A_o, is not easily determined on a quantitative basis, and may be eliminated as an unknown by performing a series of experiments in which only Q_g, the gas flow, is varied.

The concentration of methyl iodide in the exiting gas stream was measured by means of a Varian Model 1527-B Gas Chromatograph equipped with an electron capture detector. Additional details of the chromatographic system are described elsewhere.[1][7] Samples of the gas stream were withdrawn at one minute intervals for at least one half-life, and then at 3 to 5 minute intervals until the gas concentration had decreased to approximately one-tenth of the initial concentration.

Methyl iodide and 95% hydrazine were obtained from Eastman Organic Chemicals* and used without further purification. Stock solutions of hydrazine were prepared by dilution of the 95% hydrazine. Solutions were analyzed for hydrazine by the direct iodate method (using solvent) described by Audrieth.[8] Methyl iodide stock solutions (ca. 10^{-4} g moles/liter) were prepared by dilution of an aqueous solution of methyl iodide saturated at room temperature. There was appreciable change in the concentration of methyl iodide in the stock solution over a 24-hour period so that a fresh stock solution was prepared for each series of experiments. Nitrogen (99.7%) was used both as a carrier gas for the gas chromatograph and as the sparge gas in the experiments. No detectable peaks (other than an oxygen peak due to a residual volume of air in the sampling syringe) were found in chromatograms of the nitrogen used. Several cylinders of nitrogen were discarded because of evidence of impurities.

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* Eastman Organic Chemicals Co., Distillation Products Industries, Division of Eastman Kodak Co., Rochester, New York

The reaction vessel used to study the reactions of methyl iodide with hydrazine and other reactants is shown in Figure 1. Temperature of the solution in the reaction vessel was controlled by circulation of water from a constant temperature bath through the outer jacket of the vessel. Methyl iodide was introduced into the reaction vessel by injecting 50 to 100 $\mu\ell$ aliquots of aqueous stock solution of methyl iodide (ca. 10^{-4} moles/liter) through a rubber septum. The flow rate of the sparge gas was controlled by a microregulating valve and measured with a soap bubble meter before and after each experiment. Flow rates were chosen such that the amount of methyl iodide stripped from solution varied as widely as possible. For the lower flow rates, relatively little methyl iodide escaped from the reaction vessel, whereas for the large flow rates, a large fraction of the methyl iodide introduced into the vessel was stripped from solution. Flow rate ranges chosen in this way permit most accurate interpretation of the experimental data.

A typical concentration-time history for the gas leaving the reaction vessel is shown in Figure 3. The concentration is shown in terms of peak height in millimeters for a 30 $\mu\ell$ aliquot at an attenuation of 4X. The reactive solution for this experiment was 170 ml of 0.758 molarity hydrazine with 0.05 molarity sodium hydroxide. The temperature was 34.7 ± 0.01°C, and the nitrogen sparge flow rate was 14.6 ± 0.3 ml/min. The concentration may be represented as the differences of two exponential curves as indicated in equation (6).

$$\text{Peak Height} = (140)[\exp(-0.187t) - \exp(-1.109t)], \qquad (6)$$

where t = time in minutes.

The second exponential arises because of mixing which occurs in the gas volume between the reaction solution and the sampling port. If this mixing volume were zero, only the first exponential term would be required. The value of the exponent of the first term is equal to the k_{obsd} as shown in equation (5).

The area under the concentration curve shown in Figure 3 is directly proportional to the amount of methyl iodide stripped from the reaction cell. Integration of the equation which describes the concentration curves shown in Figure 3 leads to an expression for the amount of methyl iodide sparged from solution, A_S, in terms of the initial concentration and the decay constants

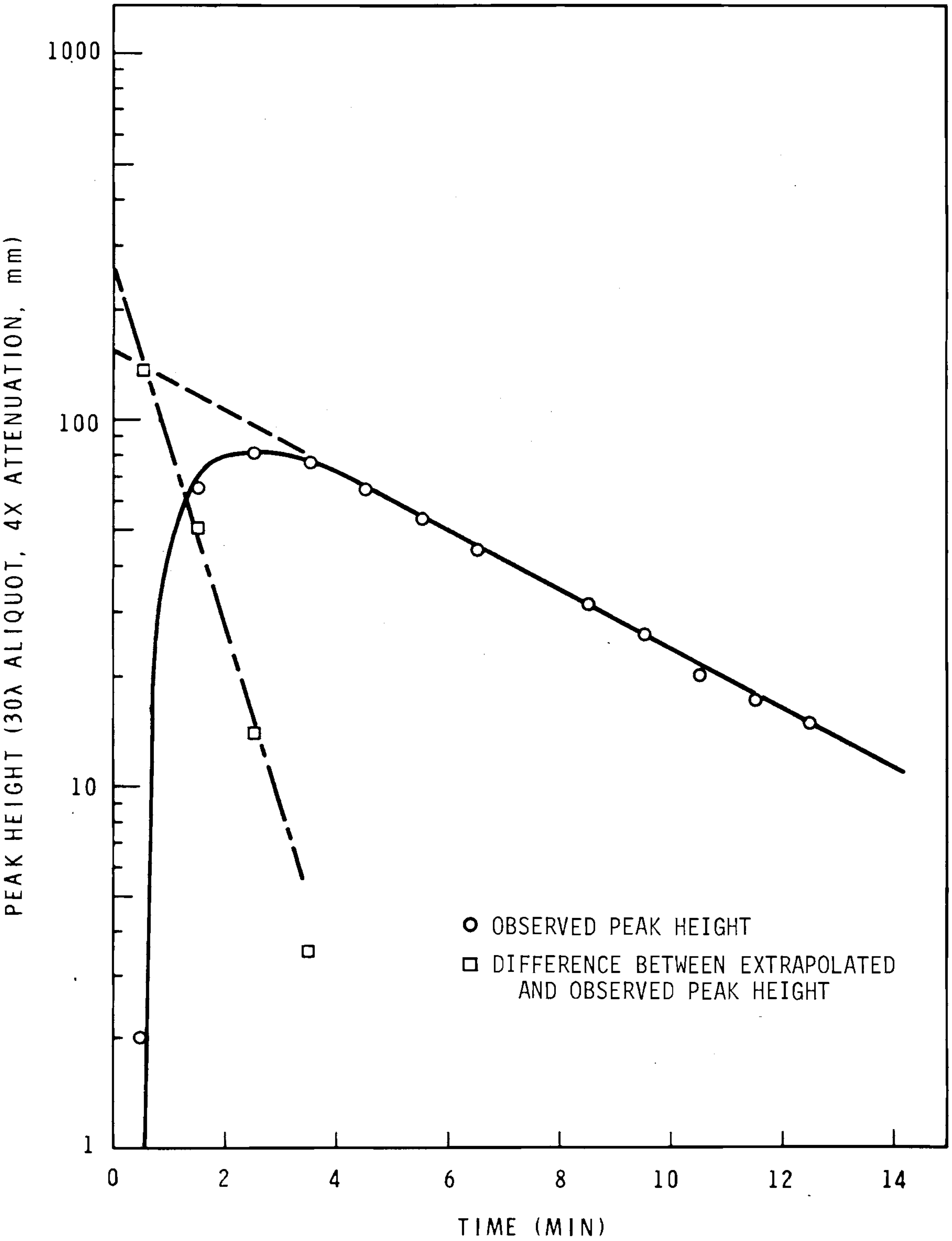

Figure 3. Methyl Iodide Concentration in a Gas Leaving Reaction Vessel

of equation (6). The resulting expression is

$$A_s = C_g^\circ Q_g \left[\frac{1}{k_{obsd}} - \frac{1}{k_2} \right], \tag{7}$$

in which C_g° is the initial concentration of gas bubbles leaving the surface of the liquid, Q_g is the gas sparge rate, k_{obsd} is the observed concentration decay rate, and k_2 is a constant related to the mixing of the sparge gas in the vapor space above the reaction solution. C_g° is best estimated by extrapolating the concentration curve to zero time as indicated in Figure 3. k_2 may be obtained from the concentration-time history shown in Figure 3 by subtracting from the measured curve, the curve extrapolated to zero time.

From equation (5) it will be noted that, as A_s/A_o approaches zero, k_{obsd} approaches k_r. Thus, the solution reaction rate may be obtained by carrying out a set of sparge runs, each of which would yield data plots similar to Figure 3. By plotting k_{obsd} for each of these runs as a function of A_s/A_o, one may determine k_r as the limit of k_{obsd} when the amount sparged is extrapolated to zero. In this work, four separate experiments were completed, at varying flow rates of sparge gas. Typical results are shown in Figure 4 where the amount stripped is shown versus the reciprocal of the observed rate constant. A straight line relationship is found which permits easy extrapolation to zero. For the example, shown in Figure 4, the reaction rate of methyl iodide is found to be 1/6.3 or 0.159 min^{-1}.

Results

a. Reaction of Methyl Iodide with Hydrazine

The results obtained for hydrazine represent the bulk of the work carried out, although data were obtained for comparison purposes for several other reactants. The rate of reaction was determined as a function of hydrazine concentration, sodium hydroxide concentration, salt concentration (NaCl, $Na_2B_4O_7$, Na_2CO_3) and temperature. The data obtained are summarized in Table III.

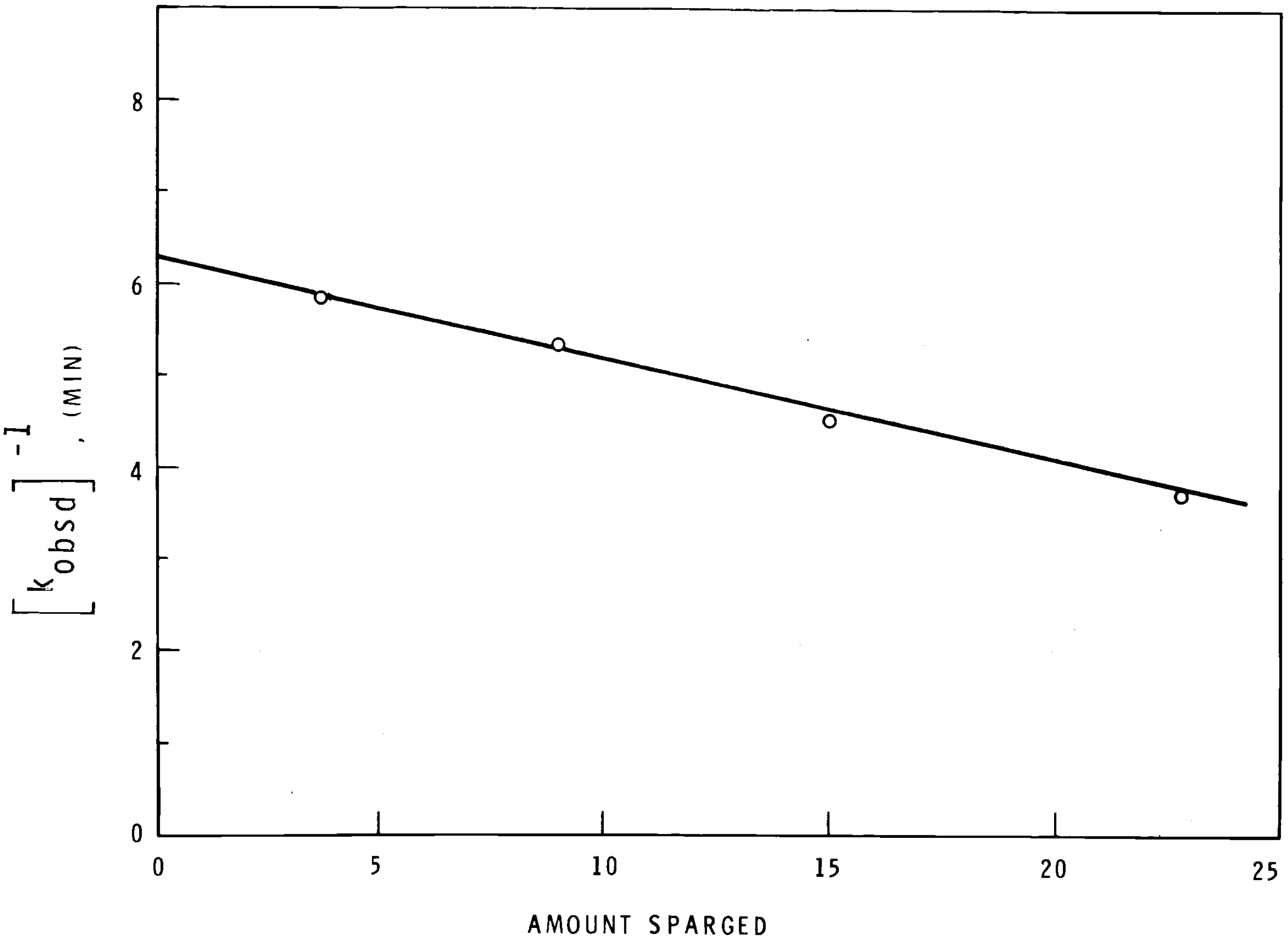

Figure 4. Reciprocal of Observed Rate Constant as a Function of Relative Amount of Methyl Iodide Sparged from Cell

TABLE III

RATE CONSTANT FOR THE REACTION OF METHYL IODIDE AND HYDRAZINE IN A 0.053 MOLES/LITER SODIUM HYDROXIDE SOLUTION

(Methyl iodide initial equals ca. 3×10^{-8} moles/liter)

Temperature (°C)	Hydrazine Concentration (mole liter^{-1})	(w/o)	Reaction Rate Constant (sec$^{-1} \times 10^{3}$)
24.6	0.749	2.40	0.81
	1.16	3.71	1.27
	1.53	4.90	1.80
34.7	0.174	0.56	0.64
	0.374	1.20	1.23
	0.758	2.43	2.65
	1.51	4.83	5.3
49.3	0.076	0.24	1.3
	0.184	0.59	2.73
	0.361	1.16	5.38
	0.771	2.47	10.97
64.7	0.0354	0.11	2.25
	0.0707	0.23	4.5

In Figure 5, the first order rate constant is plotted as a function of hydrazine concentration. The reaction rate constant is seen to be directly proportional to the hydrazine concentration for the reaction at 24.7 and 34.7°C. This agrees with the hypothesis of a simple substitution reaction as suggested in our earlier work.[1][2] At 49.3°C the extrapolation of the rate constant to zero composition of hydrazine gives a finite value of the rate constant which represents the reaction rate of methyl iodide with the solvent, the aqueous alkaline solution. From the reported rate constants and activation energies for the reaction of methyl iodide with water and hydroxide ion,[4][12] the rate constant for the reaction of methyl iodide with the solvent is calculated to be 6×10^{-5} sec^{-1}. The extrapolated value from the data in Table III is 1.6×10^{-4} sec^{-1}. Considering that both of these values are the result of extrapolations and not direct determinations, the comparison is to be considered fair.

The direct proportionality of the rate constant for the reaction of methyl iodide with the hydrazine concentration in Table III and the exponential decrease of the methyl iodide concentration as shown in Figure 3 indicate the

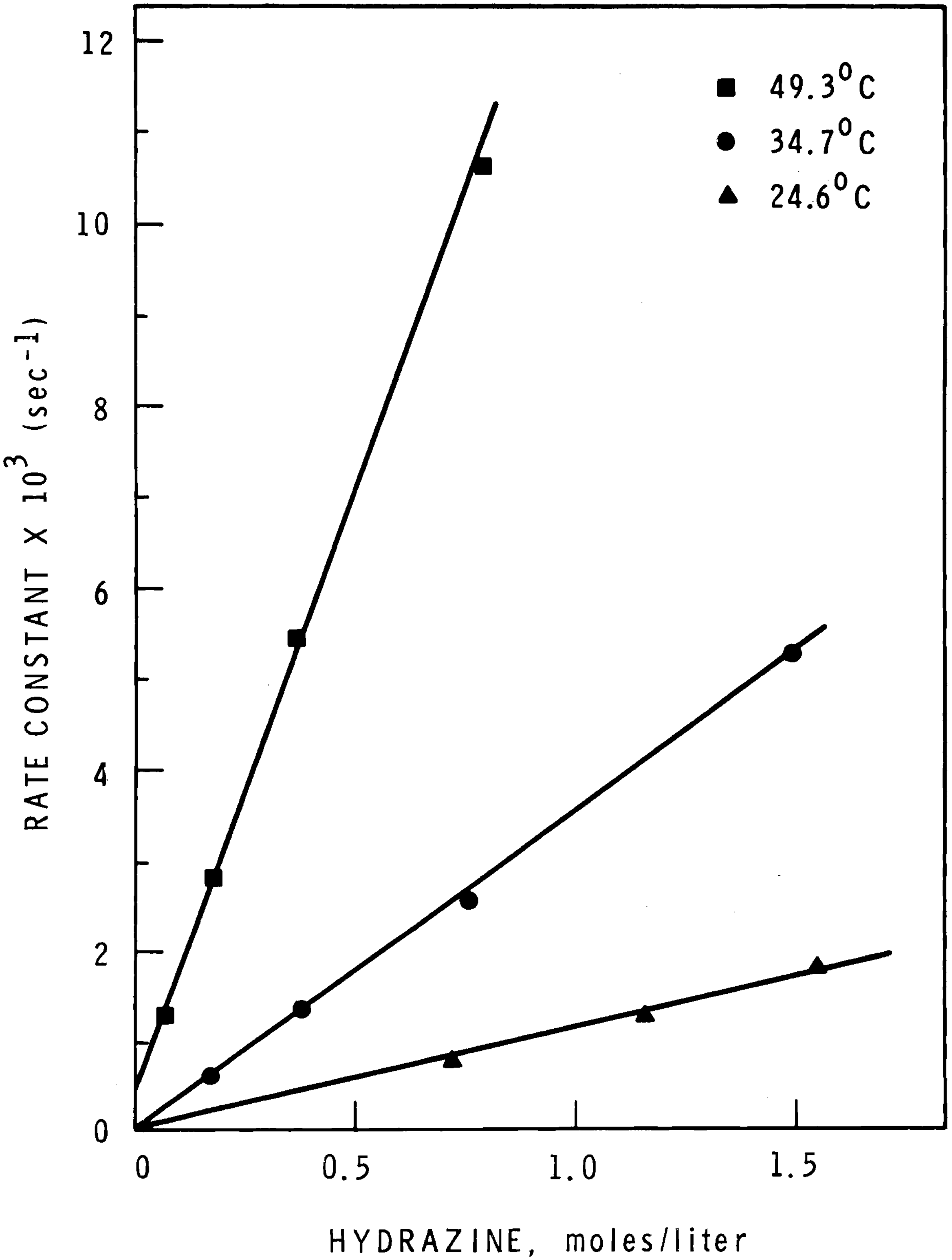

Figure 5. Rate Constant as a Function of Hydrazine Concentration in 0.053N Sodium Hydroxide

reaction is second order. The rate expression for the disappearance of methyl iodide considering both the reaction with hydrazine and with the solvent is

$$-\frac{d[CH_3I]}{dt} = k_h[N_2H_4][CH_3I] + k_{OH}[OH^-][CH_3I] + k_w[CH_3I] \qquad (8)$$

where k_h is the second order rate constant for the reaction of methyl iodide and hydrazine, k_{OH} is the second order rate constant for the reaction of methyl iodide and hydroxide ion, k_w is the first order rate constant for the reaction of methyl iodide and water (where the concentration of water is assumed to be constant at 55.5 moles liter^{-1}) and where the bracketed expressions are the concentrations in moles liter^{-1}.

The second order rate constant for the methyl iodide-hydrazine reaction calculated from the data in Table III is shown in Table IV, and Figure 6. The units shown for the reaction rate are M^{-1} S^{-1} where M = concentration in molarity, and S = time in seconds. The activation energy for the reaction between methyl iodide and hydrazine is 20.2 ± 0.4 kcal/mole.

TABLE IV

SECOND ORDER RATE CONSTANT FOR THE REACTION OF METHYL IODIDE AND HYDRAZINE

Temperature (°C)	Second Order Rate Constant (liters moles^{-1}sec^{-1})	Pseudo First Order Rate Constant For 3.2 w/o Hydrazine Solution -- (sec^{-1})
24.7	1.1×10^{-3}	1.1×10^{-3}
34.7	3.5×10^{-3}	3.5×10^{-3}
49.3	1.5×10^{-2}	1.5×10^{-2}
64.7	6.4×10^{-2}	6.4×10^{-2}

The relative magnitude of the reaction rate constants is such that for a 1 mole liter^{-1} hydrazine (3.2 w/o) and 0.05 mole liter^{-1} (0.2 w/o) sodium hydroxide solution the hydrolysis by water and hydroxide ion account for only 0.02 and 0.4 percent of the total reaction with methyl iodide at 50°C. Since the activation energies of the three reaction paths are within 10% of each other, the relative contribution of each reaction path will not change greatly

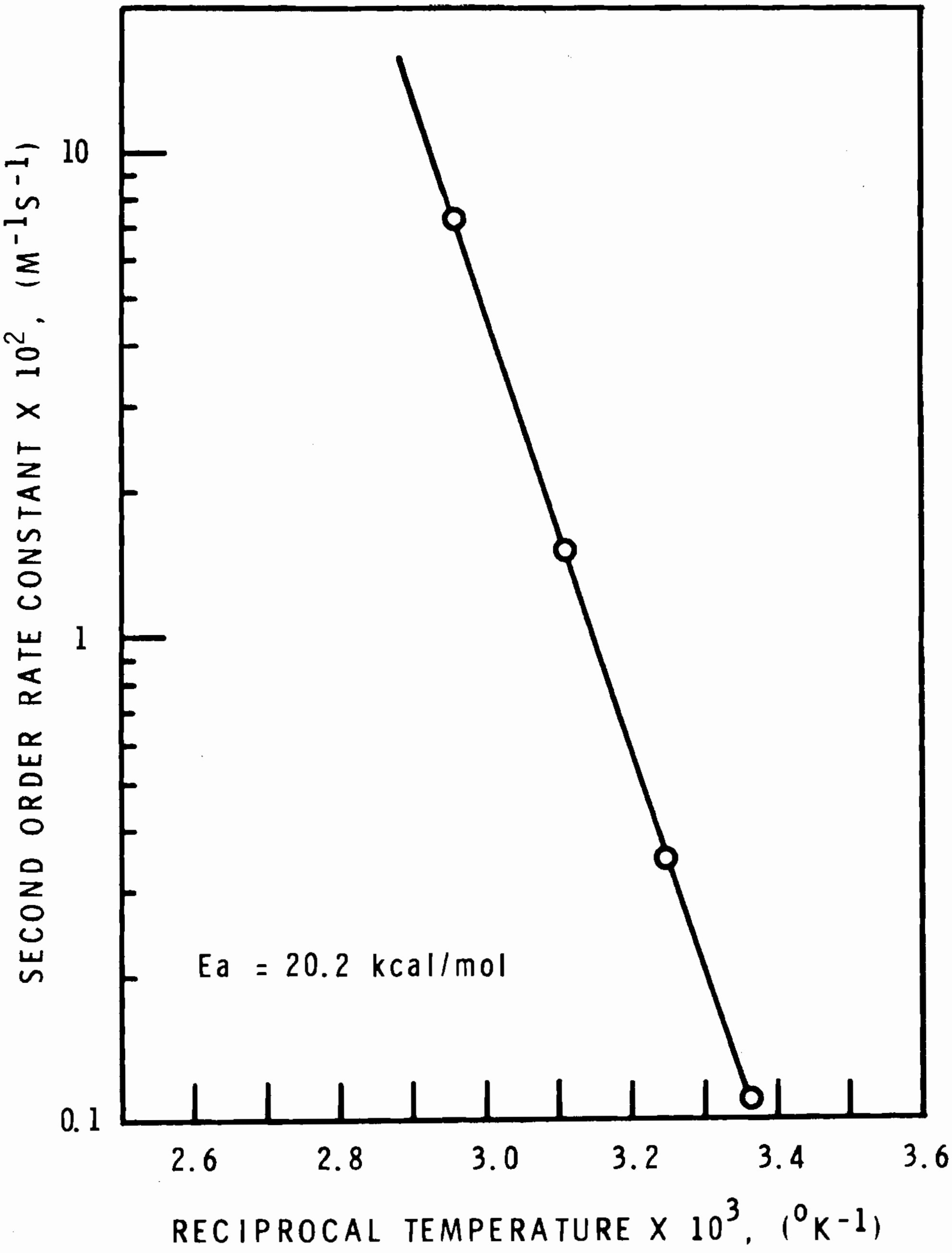

Figure 6. Rate Constant for Methyl Iodide-Hydrazine Reaction in 0.053N NaOH

going from 50°C to 100°C. More dilute hydrazine solutions will have a greater contribution by the hydrolysis reactions to the over-all reaction

b. Reaction of Methyl Iodide with 1,1-Dimethylhydrazine

The reaction of methyl iodide with substituted hydrazines was of interest because of the potential of increased reaction rate of alkylated hydrazines over the rate of reaction of hydrazine. Since no quantitative measure of the reaction rate constant has been reported, the reaction of methyl iodide with 1,1-dimethylhydrazine was examined by the sparge removal technique described earlier in this report.

The results of this study are summarized in Table V.

TABLE V

THE REACTION RATE OF METHYL IODIDE WITH 1,1-DIMETHYLHYDRAZINE

(Carried out in a 0.052 moles/liter sodium hydroxide solution with an initial concentration of methyl iodide of 3×10^{-8} moles/liter.)

1,1-Dimethylhydrazine Concentration (moles/liters)	Second Order Reaction Rate Constant (liters $moles^{-1}sec^{-1}$)	Temperature (°C)
0.13	8.1×10^{-3}	24.7
0.26	7.2×10^{-3}	24.7
0.53	7.8×10^{-3}	24.7
0.09†	7.4×10^{-3}	22.4
0.13	2.1×10^{-2}	34.7
0.26	2.0×10^{-2}*	34.7
0.13**	2.2×10^{-2}	34.8

† Determined by chromatographic separation method ($CH_3I = 1.4 \times 10^{-4}$M).
* Data inconsistent -- measurement unreliable.
** Sodium hydroxide equals 0.005 moles/liter.

The average of the three values of the rate constant for the reaction with 1,1-dimethylhydrazine at 24.7°C is 7.7×10^{-3} liter $mole^{-1}sec^{-1}$ which is a factor of 7 greater than the rate constant for the reaction with hydrazine. The activation energy was estimated to be 18.4 ± 1.2 kcal/mole.

The solutions of 1,1-dimethylhydrazine* showed visible evidence of change in a few hours when exposed to air. Attempts to measure the extent of the change by the determination of the titer of these solutions with respect to potassium iodate (see analysis of hydrazine solutions by the Direct Iodate Method) using solvent[9] were not entirely successful. The oxidation of 1,1-dimethylhydrazine by potassium iodate is not a "simple" four electron change as is the oxidation of hydrazine by potassium iodate.[10]

The nature of the change in the solutions of 1,1-dimethylhydrazine is not known but is presumed to be a photooxidation since dealkylation has not been reported to occur. Since this system appeared to be more unstable chemically than the hydrazine system, experimental work on the 1,1-dimethylhydrazine system was discontinued even though the reaction rate constant was larger than that of hydrazine.

c. Reaction of Methyl Iodide with Monomethylhydrazine

From the citation by Clark[9] monomethylhydrazine solutions were expected to be much more reactive towards methyl iodide than hydrazine. When hydrazine and methyl iodide are reacted, using appreciable quantities of both reactants, the product of the reaction is 1,1-dimethylhydrazine and not monomethylhydrazine. This observation implies that the second step in the alkylation of hydrazine must be much more rapid than the first step. The present work, however, shows that the reaction rate of monomethylhydrazine with methyl iodide is less than the reaction rate of hydrazine with methyl iodide.

Monomethylhydrazine solutions† were studied by the sparge removal technique in order to determine the rate of reaction of monomethylhydrazine with

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* The 1,1-dimethylhydrazine used in this study was obtained from Distillation Products Industries and used without further purification. The concentration of 1,1-dimethylhydrazine was calculated from the dilutions which were made in the same manner as with hydrazine.

† Monomethylhydrazine sulfate was obtained from Distillation Products Industries and a weighed amount was dissolved in distilled water. The sulfate ion was removed from the solution by precipitation as barium sulfate by the addition of 30% excess barium chloride solution (1 mole/liter). After centrifuging and separating the barium sulfate the solution was analyzed for monomethylhydrazine by the Direct Iodate Method. The analysis and the calculation of the amount of monomethylhydrazine present were in excellent agreement. Monomethylhydrazine like hydrazine titrates in a straightforward manner with potassium iodate in strong hydrochloric acid solution.[10]

methyl iodide. A 170 ml volume of a 0.076 moles/liter monomethylhydrazine and 0.052 moles/liter sodium hydroxide solution at 35.4°C had a pseudo-first order reaction rate constant of less than 1.1×10^{-5} sec^{-1}. This is equivalent to a second order reaction rate constant of ca. 1.5×10^{-4} liter $mole^{-1}sec^{-1}$ or lower.

Because of the discouragingly low value of the second order reaction rate constant for monomethylhydrazine with methyl iodide, these studies were not continued. The data which were obtained demonstrate that the reactions of alkylated hydrazines with alkyl halides are not thoroughly understood and merit further experimental effort.

d. Reaction of Methyl Iodide with Sodium Sulfite

The use of sodium sulfite as a reactant for methyl iodide was tried because of the nucleophilic character* of the sulfite ion. Sodium sulfite is also a reductant so that, like hydrazine and sodium thiosulfate, sodium sulfite will reduce iodine, presumably at a rapid rate. The rate of reaction of methyl iodide in sodium sulfite solutions was determined by the sparge removal technique which was described earlier in this report. Sodium sulfite obtained from Baker and Adamson Chemical Company was used in these experiments. The results of the reaction rate determination for sodium solutions at 24.70°C are shown in Table VI.

TABLE VI

REACTION RATES OF METHYL IODIDE IN SODIUM SULFITE SOLUTIONS

(At 24.70°C and 0.052 moles/liter sodium hydroxide
and 4×10^{-8} moles/liter methyl iodide.)

Sodium Sulfite Concentration (moles $liter^{-1}$)	pH	Pseudo-First Order Reaction Rate Constant (sec^{-1})	Bimolecular Reaction Rate Constant (liter $mole^{-1}sec^{-1}$)
0.020	12.10	0.84×10^{-3}	4.2×10^{-2}
0.040	12.05	1.65×10^{-3}	4.1×10^{-2}
0.080	12.05	3.3×10^{-3}	4.1×10^{-2}

---

* A discussion of nucleophilic character and its use in the prediction of reaction rates will be considered in a later section of this report on the correlation of reaction rate constants.

e. Reaction of Methyl Iodide with Sodium Sulfide

The rate of reaction of methyl iodide with sulfide ion was examined by the chromatographic separation technique[1] between 21.5°C and 23.5°C. Despite the uncertainty of this method, it was felt that the data represents an order of magnitude value for the rate of reaction. Both sodium sulfide and ammonium sulfide were examined and the second order reaction rate constant was calculated assuming the reaction to be second order. These data are given in Table VII. As seen in Table VII, the rate of reaction of methyl iodide with sulfide ion is 2 to 3 times that of the reaction with thiosulfate or sulfite ion and 40 to 90 times that of the reaction with hydrazine for equal molar solutions of the reactants.

TABLE VII

REACTION RATES OF METHYL IODIDE WITH SULFIDE ION

Reactant	Reactant* Concentration (moles/liter)	Additives (moles/liter)	Temp. (°C)	Second Order Reaction Rate Constant (liter $mole^{-1} sec^{-1}$)
Sodium Sulfide	0.1	None	23.3	$>4 \times 10^{-2}$
"	0.01	[NaOH] = 0.5	22.7	9.4×10^{-2}
"	0.01	[NaOH] = 0.05	23.2	8.3×10^{-2}
"	0.01	[NaOH] = 0.05	22.7	9.6×10^{-2}
"	0.01	[HCl] = 0.001	21.4	5×10^{-2}
Ammonium Sulfide	0.018	None	RT	6×10^{-2}
"	0.18	None	RT	7×10^{-2}
"	0.018	[NaOH] - 0.05	RT	8×10^{-2}
"	0.018	$[Na_2B_4O_7] = 0.1$	21.5	7×10^{-2}

* Methyl Iodide concentration $\sim 10^{-4}$ moles/liter.

Discussion of Results

a. Effect of pH and Ionic Strength on Reaction Rates

The rate of reaction of methyl iodide with hydrazine is essentially independent of the hydroxide ion concentration over a rather wide range of concentration of the hydroxide ion or hydrogen ion. The rate of reaction measured in a 0.026 mole liter^{-1} hydrochloric acid solution is only 7% lower than the rate of reaction in alkaline solution as shown by the magnitude of the second order reaction rate constant given in Table VIII.

TABLE VIII

THE EFFECT OF HYDROXIDE ION CONCENTRATION AT 34.77°K

Hydrazine Concentration (moles/Liter)	Hydroxide Ion Concentration (g ion/liter)	Sodium Chloride Concentration (moles/liter)	Second Order Reaction Rate Constant (liter moles^{-1}sec^{-1})
0.758	0.053	0	3.50×10^{-3}
0.76	0.026	0	3.36×10^{-3}
0.742	0.026	0.05	3.57×10^{-3}
0.054	7×10^{-5}	0.053	3.28×10^{-3}

This is unlike the case of the reaction of hydrazine and iodine where the rate of reaction was found to be proportional to the hydroxide ion concentration.[11]

The velocity of the reaction of sulfite ion with methyl iodide was found to be dependent on both the ionic strength and pH of the solution. The results of experiments where both ionic strength and pH were varied are shown in Table IX.

The pH dependence of the reaction velocity is a result of the sulfite-bisulfite equilibrium. As the pH of the solution is lowered, the fraction of sulfite ion concentration of the total sulfite and bisulfite concentration is lowered. The ratio of the second order rate constant of the reaction of methyl iodide with sulfite ion to that with bisulfite is ∿ 50, as seen in Table IX. At pH ∿ 12 the $[SO_3^{2-}]/([SO_3^{2-}] + [HSO_3^-])$ ratio is ≥ 0.99, while at a pH of 4.5, the $[HSO_3^-]/([SO_3^{2-}] + [HSO_3^-])$ ration is ≥ 0.99. Exact calculation of the ratio is prevented by our inability to assess the contribution of the secondary salt effect, i.e., the effect of ionic strength on the activities of the bisulfite and sulfite ions in the equilibrium expression.

$$K = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} \cdot \frac{\gamma_{H^+}\,\gamma_{SO_3^{2-}}}{\gamma_{HSO_3^-}} \qquad (9)$$

TABLE IX

EFFECT OF pH AND IONIC STRENGTH ON REACTION VELOCITY OF METHYL IODIDE AND SODIUM SULFITE AT 24.73 ± 0.03°C

pH	Ionic Strength	Total Sulfite + Bisulfite Concentration (M)	Pseudo-First Order Reaction Rate Constant × 10^3 (sec^{-})	$\left(\frac{\text{Column 4}}{\text{Column 3}}\right) \times 10^2$ (M^{-} sec-)
11.90	0.315	0.0742	2.88	3.9
11.75	0.414*	0.0872	3.18	3.7
11.80	0.508*	0.0944	3.27	3.47
11.70	0.814*	0.0965	2.86	3.0
8.50	0.298†	0.053	2.05	3.9
8.00	0.194†	0.073	2.58	3.53
7.50	0.241†	0.066	2.14	3.2
7.12	0.230†	0.061	1.50	2.43
4.45	4.68	4.68	3.0	0.064
4.50	0.10	0.10	<0.4	<0.4

* Sodium chloride added to adjust ionic strength.

† Sodium hydroxide (initially 0.026 moles liter^{-1}) neutralized with hydrochloric acid to give final pH.

where the bracketed terms are the concentrations and the γ's are the activity coefficients of hydrogen ion, sulfite ion, and bisulfite ion.

b. Correlation of Reaction Rate Constants of Methyl Iodide

Kinetic data are available in the literature for the reaction of methyl iodide with numerous anions and one cation in an aqueous system. The reaction rates vary by a factor of 4×10^5. In all the cases which have been examined, the rate expression is a simple second order rate law involving the reactant and methyl iodide concentrations reacting species on the methyl iodide molecule. In general, the reaction can be pictured as the attack of the reactant on the carbon atom with the displacement of the iodide ion.

A summary of the rate constants for the reactions which have been reported in the literature is given in Table X.

Numerous attempts have been made to correlate the reaction rate constant with both kinetic and non-kinetic parameters. Ideally one could calculate the expected reaction rate constant from such non-kinetic parameters as basicity or electrode potential. One reasonably successful correlation of the reaction rate is in terms of nucleophilic character or nucleophilicity of the reactant.[20] The nucleophilic character, E_n, is calculated from the electrode potential oxidative dimerization of the nucleophile.

$$2X^- = X_2 + 2e^- \qquad (10)$$

where E_0 is the electrode potential of equation.[10] The nucleophilic character is then calculated using

$$E_n = E_0 + 2.60 \qquad (11)$$

For cases such as Cl^-, Br^-, etc., the nucleophilic character is calculated directly from the electrode potentials. For a substance such as hydrazine, the oxidative dimerization is a hypothetical reaction, i.e., $2N_2H_4 = N_4H_8^{++} + 2e^-$. In this case we are forced to evaluate E_n from kinetic data. Summaries of the nucleophilic character have been presented.[20][21]

In Figure 7, a correlation of the data and the nucleophilic parameter is shown. This correlation is to be considered fairly successful in that it does give a relationship over a 10^5 range of reaction rate constants. However, the prediction of reaction rates for materials such as hydrazine depends on one

TABLE X

SUMMARY OF REACTION RATES

Reference	Reactant	Bimolecular Reaction Rate Constant at 25.0°C (liter $mole^{-1}sec^{-1}$)	Activation Energy (Kcal/mole)	Temperature Range Studied (°C)	Bimolecular Reaction Rate Constant Extrapolated Value At 120°C (liter $mole^{-1}sec^{-1}$)
8	H_2O	$1.4 \times 10^{-9\dagger}$	>24.8*	30° - 93°	0.00006
13	F^-	7.08×10^{-8}	25.2 ± 0.5	--	0.002
14	Cl^-	3.30×10^{-6}	21.97 ± 0.34	--	0.025
8	Br^-	4.16×10^{-5}	19.31 ± 0.50	--	0.11
8	OH^-	6.36×10^{-5}	22.22 ± 0.23	30° - 70°	0.55
15	SCN^-	3.58×10^{-4}	19.95 ± 0.40	25° - 35°	1.2
16	I^-	4.71×10^{-4}	17.58 ± 0.20	--	1.6
17	CN^-	5.76×10^{-4}	20.47 ± 0.12	20° - 55°	2.5
This Work	N_2H_4	1.1×10^{-3}	20.2 ± 0.40	25° - 65°	10
18	Ag^+ (NO_3^- or ClO_4^-)	2.61×10^{-3}	19.4 ± 0.80	15° - 45°	7 ± 3
This Work	1,1-dimethylhydrazine	7.7×10^{-3}	18.4 ± 1.2	25° - 35°	13 ± 5
8	$S_2O_3^=$	2.84×10^{-2}	18.88	10° - 25°	64
10	$S_2O_3^=$	3.31×10^{-22}	18.88	15° - 25°	75
This Work	$SO_3^=$	3.3×10^{-2}	Not determined	25°	--

† Calculated from first order rate constant assumes molar concentration of water to be 55 moles/liter.

* Activation Energy is a function of temperature. A minimum of 24.8 Kcal/mole at ca. 45°C.

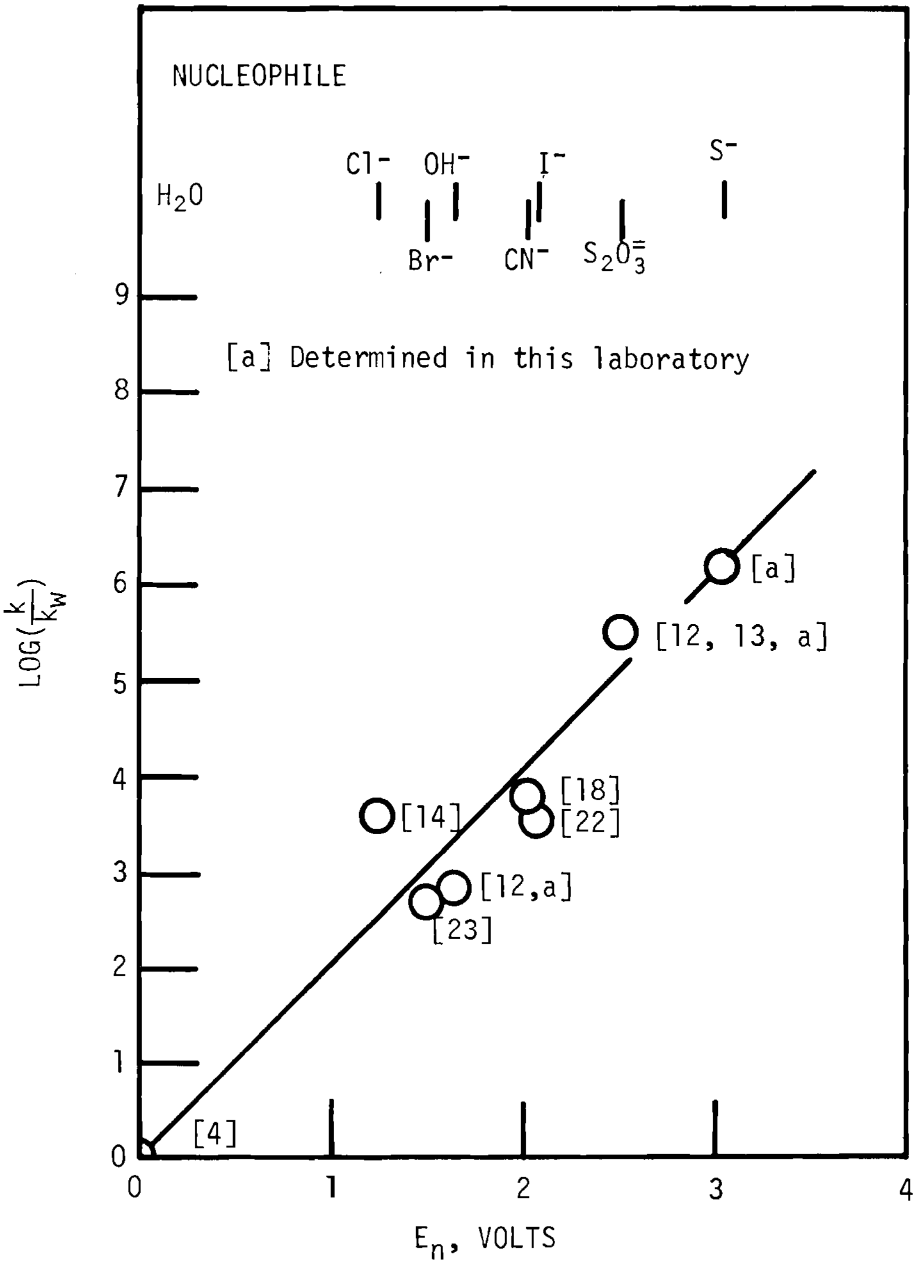

Figure 7. Correlation of Reaction Rate Constants

determining E_n from either basicity or from kinetic measurements. If the use of kinetic data to evaluate E_n is required, perhaps a simpler direct correlation of the kinetic data is possible.

One correlation which can be applied to predict reaction rates in aqueous solution is obtained if the reaction rates are known for a different solvent system. The reaction rate of methyl iodide with many reactants in methanol solutions has been more thoroughly examined than for aqueous solutions. The methanol data may be used in aqueous solutions by means of a correlation such as

$$\log(k_{H_2O}) = \log(k_{CH_3OH}) + A, \qquad (12)$$

where k_{H_2O} is the reaction rate in water and k_{CH_3OH} is the reaction rate in methanol, both expressed in the same units and where A is an empirical constant. Using the values of the reaction rates in methanol solution cited in reference [20] one obtained the correlation shown in Figure 8.

Correlations of this sort are useful in that certain rates are predicted to be larger than others, in fact, larger than that of sulfide, sulfite, or thiosulfate ions. For example, several nucleophiles have been examined in methanol solution which react rapidly with methyl iodide. In Table XI, are presented the second order reaction rate constants, first in methanol then in aqueous solutions, and the pseudo first order reaction rate constant for a 1 wt.% solution. These latter two values were determined from use of the correlation shown in Figure 8, together with the rate constants for sodium thiosulfate and hydrazine.

$$\log k_{CH_3OH} = \log k_{H_2O} + 0.20 \qquad (13)$$

$$\frac{k_{CH_3OH}}{k_{H_2O}} = 1.58. \qquad (14)$$

Although these rates are more rapid than the nucleophiles currently considered, their potential as spray additives would be dependent as well on the rate and extent of the oxidation and hydrolysis reactions of these nucleophiles.

TABLE XI

PREDICTED REACTION RATES OF METHYL IODIDE WITH NUCLEOPHILES IN AQUEOUS SOLUTION

Nucleophile	Second Order Reaction Rate Constant at 25°C		Pseudo-First Order Reaction Rate Constant At 25°C In Water (1 w/o Solution) (sec^{-1})
	Measured In Methanol (liter $mole^{-1}sec^{-1}$)	Predicted In Water (liter $mole^{-1}sec^{-1}$)	
Sodium Selenophenoxide [Na^+, $C_6H_5Se^-$]	7.0	4.4	0.25
Triethylphosphine [$(C_2H_5)_3P$]	0.066	0.042	0.004
Triphenylphosphine [$(C_6H_5)_3$ P]	0.013	0.008	0.0003
Sodium Thiophenoxide [Na^+, $C_6H_5O^-$]	1.07	0.68	0.06
Sodium Selenocynate [Na^+, $SeCN^-$]	0.009	0.006	0.0005
Sodium Thiosulfate	--	0.033*	0.002
Hydrazine	--	0.001*	0.0003

* Measured values.

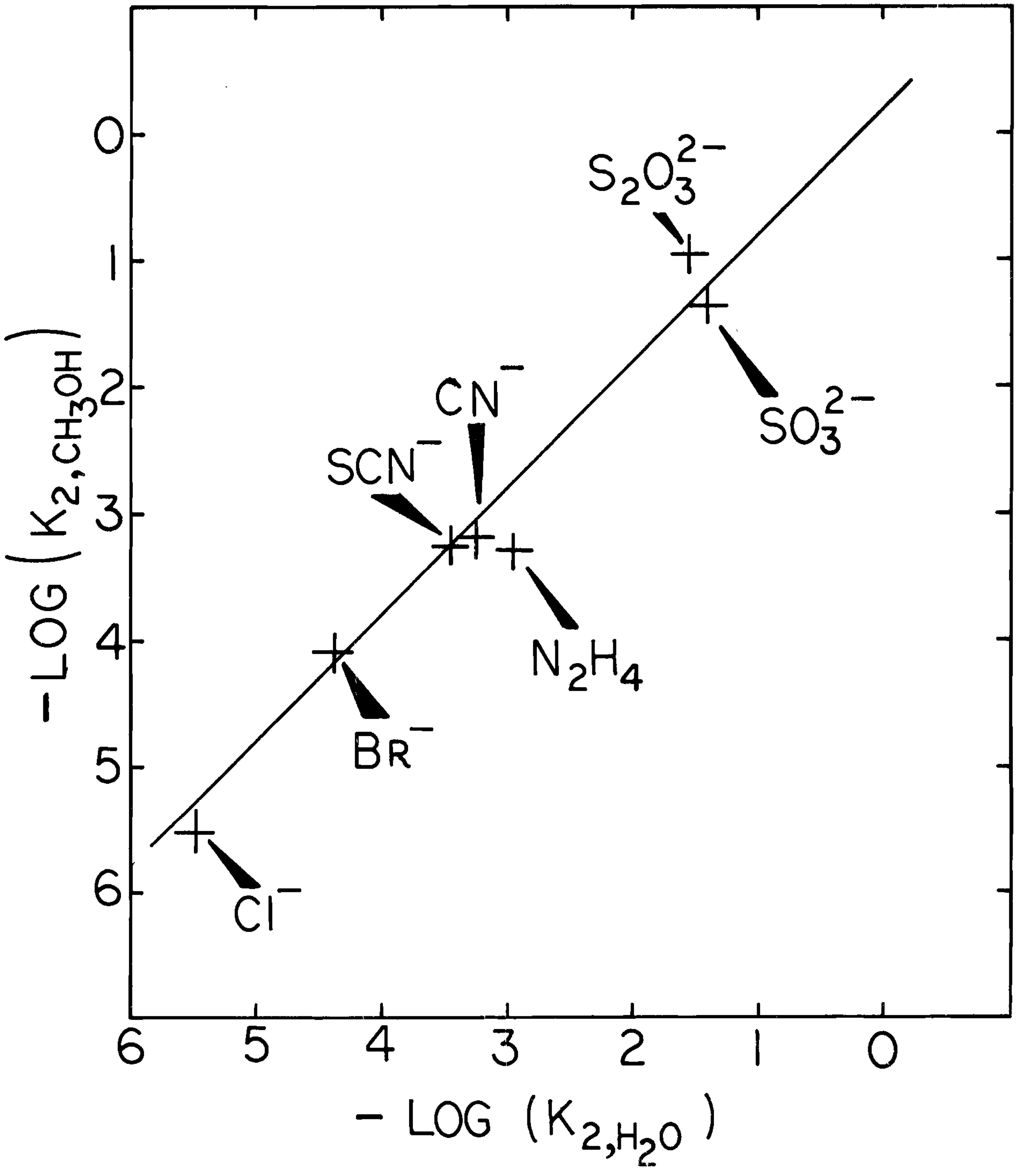

Figure 8. Correlation of Methyl Iodide Reaction Rates in Water and Methanol

c. Summary of Reaction Rates of Methyl Iodide with Various Reagents

The application of these reaction rate constants to the prediction of the pseudo-first order reaction rate constants which are expected for the spray removal solutions is easily made. The bimolecular reaction rate constant is converted to a pseudo-first order reaction rate constant, i.e., fraction of methyl iodide which reacts per second, for a given reactant composition. The results of such a calculation is shown in Table XII where a 1 wt.% solution was chosen for comparison.

TABLE XII

COMPARISON OF REACTION RATES FOR 1 wt.% SOLUTIONS

Reactant	Pseudo-First Order Rate Constant At 25°C (sec^{-1})	Half-Life of Methyl Iodide In 1 wt.% Solution Of Additive At 25°C (sec)
Sodium Sulfite	2.6×10^{-3}	267
Sodium Thiosulfate	1.8×10^{-3}	385
1,1-dimethylhydrazine	1.3×10^{-3}	533
Hydrazine	3.4×10^{-4}	2038
Sodium Hydroxide	1.6×10^{-5}	43×10^{3}

The relative magnitude of the reaction rate will change although the order of the rates will not change radically going from 25°C to 80°C. The relative rate should change by about a factor of 200, based on an activation energy of 20 kcal/mole.

Thus, it is seen that from a 1×10^{-3} sec. rate constant at 25°C, the rate constant at 80°C should be 2×10^{-1}, i.e., 20% reaction per second.

WASHOUT OF METHYL IODIDE BY SPRAYS

Application of a reactive spray for the washout of methyl iodide in containment systems requires data which allow a prediction of the washout rate as a function of spray rate, drop size, solution concentration, and temperature. Ideally, a model accounting for the important variables would be developed and substantiated by demonstration experiments.

Methyl iodide absorption by liquid films on wall surfaces is important even for large vessels. In our experiments and theory, we have considered vessels in which the walls and bottom pool provide the only interfacial exposure. In real containment systems, equipment within the containment vessel would provide additional film exposure which would enhance the washout rate compared to vessels considered in this study.

The demonstration experiments performed here were of relatively small scale compared to full size containment vessels. The spray chambers used were cylindrical vessels 10 ft. and 8 ft. in height. Application of experimental results to full size containment systems must be based on use of models developed for the washout process which account for vessel size.

ABSORPTION OF A GAS BY A REACTIVE LIQUID

In absorption, solute gas diffuses from the bulk of the gas to the surface of the liquid. The rate of this transport is governed by the magnitude of the concentration gradient and of the diffusional processes (laminar and turbulent) which transport the diffusing substance down the concentration gradient. At the gas-liquid interface the gas dissolves in the liquid. For the dilute solutions and low mass transfer rates which will be encountered here, the interfacial composition would be expected to obey Henry's law.

$$C_s = H C_{gi} \tag{15}$$

where C_s = concentration of absorbed component in liquid at interface,
H = Henry's law constant (partition coefficient)
C_{gi} = concentration of solute gas on the gas side of the interface.

The gas dissolved in the liquid will be transported away from the interface by diffusional processes. If a chemical reaction occurs within the liquid, the absorbed substance will be destroyed in the liquid at a rate depending on its concentration and the reaction rate. As a limit, if the chemical reaction rate were sufficiently rapid, diffusional resistance in the liquid phase would be small, and the absorption rate would be governed by diffusional processes in the gas phase.

THEORETICAL MODEL FOR SPRAY WASHOUT

Absorption Processes in a Spray Chamber

Absorption in a spray chamber occurs at all gas-liquid interfaces. The overall absorption rate would be the integral of the absorption rates per unit interfacial area for all interfaces. A schematic representation of the flow paths in a spray chamber is shown in Figure 9. Liquid enters the chamber through a spray nozzle where it is broken into drops moving initially at high velocity. A fraction of the incoming spray drops impinge against the chamber wall and other surfaces. At the bottom of the chamber, liquid is collected for disposal or recycle.

The airborne concentration of a solute gas can be related to the flow parameters by making a material balance on the solute gas in the chamber. For the spray chamber depicted in Figure 9, the resulting material balance equation is

$$L\,C_{1i} + G = C_g\,(L_W + L_D\,B) + \frac{d}{dt}\,(V\,C_g), \tag{16}$$

in which L = total liquid flow rate,

C_{1i} = concentration of solute gas in liquid entering chamber,

G = generation rate of solute gas within chamber,

C_g = gas phase concentration of solute,

L_W = liquid flow rate along wall surface,

L_D = drop flow rate,

A = solute absorbed per unit volume of wall liquid per unit gas phase concentration,

B = solute absorbed per unit volume of drop liquid per unit gas phase concentration,

t = time from spray initiation.

It should be noted that the use of mass transfer coefficients defined in terms of absorption per unit volume of wall film and drop liquid is somewhat artificial. Their use is prompted by a desire to show the relative influence of wall film and drops on the overall absorption. Actually, the absorption

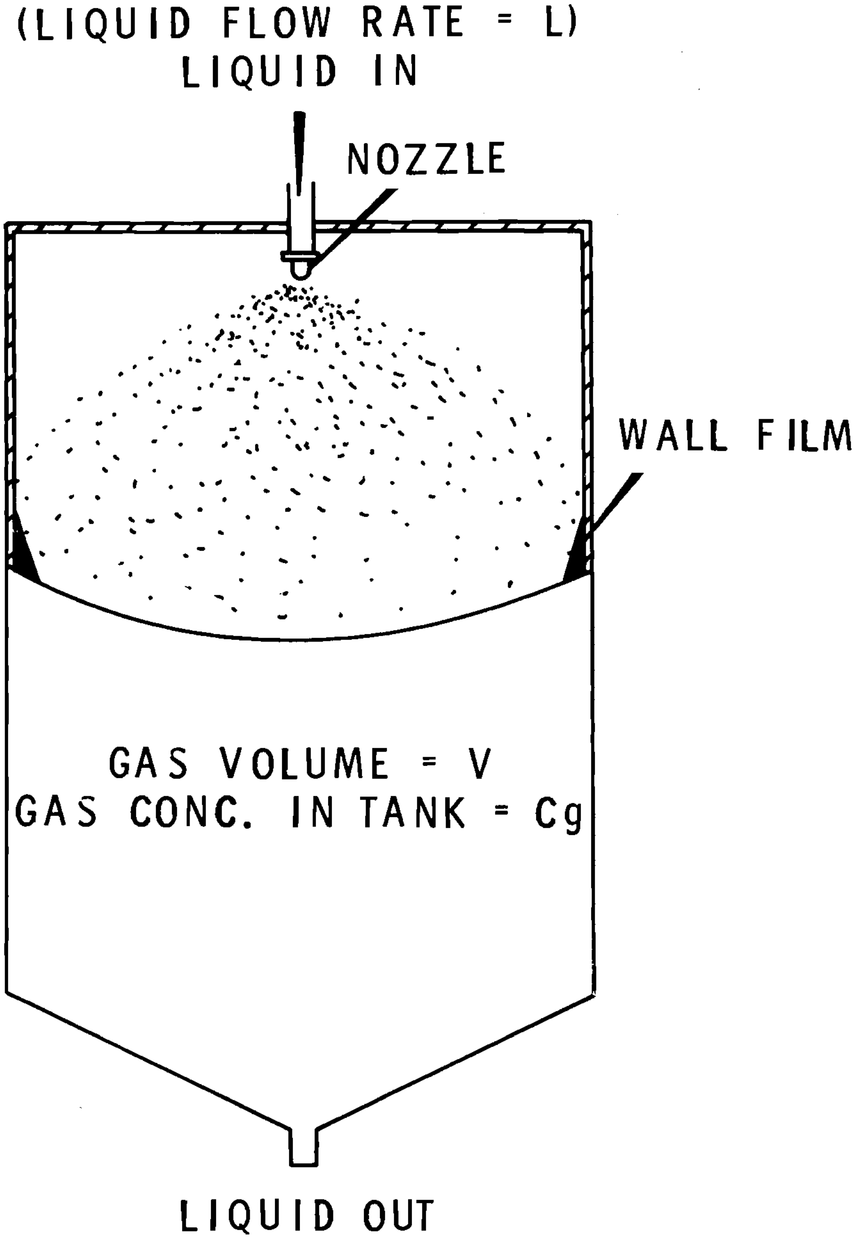

Figure 9. Liquid Flow in a Spray Tower

is not divided in this way. Each parcel of liquid entering the chamber is exposed to the gas in the form of drops and films. This must be recognized in interpreting the experiments and in applying the theory.

Equation (16) relates the gas phase concentration to time and the washout parameters for the specific system considered. The form of the time solution to equation (16) depends on the values of C_{1i}, the inlet concentration, and G, the rate of generation of the solute species.

For spray systems of greatest practical interest, the inlet concentration, C_{1i}, would be virtually zero. Unreacted solute would be present only for very slow reaction rates for which no appreciable enhancement of absorption per pass would be achieved.

The generation rate of the solute gas, G, in a reactor system would likely vary with time. Also, the absorption coefficients, A and B, are temperature sensitive, and hence would vary during the spraying period. For long time periods in which significant changes in G, A, and B would occur, the time variation of these quantities woud have to be accounted for in solving equation (16).

For the special case in which it is assumed that only C_g changes with time, the solution to equation (16) is

$$C_g = \frac{G}{L_W A + L_D B} + \left(\frac{}{L_W A + L_D B} + C_{go} \right) \exp - \frac{(L_W A + L_D B)\, t}{V}, \qquad (17)$$

where C_{go} is the gas phase concentration at the beginning of the spray period. As a further simplification, if the generation rate is neglected (puff release) the washout becomes exponential with the washout half-time equal to

$$t_{1/2}\ (\text{washout}) = \frac{0.693\ V}{L_W A + L_D B}. \qquad (18)$$

The absorption coefficients A and B are controlling parameters and it has been a goal of this work to evaluate the numerical dependency of A and B on the basic physical and chemical parameters of the spray system.

Absorption by Falling Drops

The absorption coefficient B represents the total absorption by drops per unit volume per unit gas phase concentration. In this section we consider the theoretical aspects of absorption with simultaneous chemical reaction into falling drops.

Liquid drops formed by spray nozzles result from the collapse of films or jets. The drops oscillate for a time until viscous damping absorbs the energy of oscillation associated with the collapse of a filament or a sheet into drops. Thus, initially at least, absorption will take place into the surface of a drop agitated by oscillation and aerodynamic drag.

A solely theoretical treatment of absorption by liquid as it is being formed into spray is not possible because of flow complexities. For large spray chambers or for small drops, the distance traveled by a drop in coming to terminal velocity is small compared to the total fall distance. Thus, for a major fraction of the exposure time, the drop will fall with respect to the air with a velocity close to the terminal settling velocity.

The drop exposure time may be most simply estimated as equal to the fall height divided by the settling velocity. This would be expected to be a reasonable approximation for many practical systems.

At the surface of a drop, the diffusion flux must be the same in the gas and the liquid phases:

$$D_\ell \frac{\partial C}{\partial N} = k_g (C_g - C_{gi}) \qquad (19)$$

where D_ℓ = liquid phase diffusivity

$\frac{\partial C}{\partial N}$ = concentration gradient in liquid at drop surface

k_g = gas phase mass transfer coefficient

C_g = concentration of solute in bulk of gas

C_{gi} = concentration of solute in gas at drop surface.

The interfacial concentrations are related according to equation (1). Using equation (1) in equation (19), the boundary conditions may be written as

$$\frac{\partial C}{\partial N} = h (C^* - C_s), \qquad (20)$$

where $C^* = H\, C_g$

$h = \frac{k_g}{HD}$

If local variations in k_g are neglected, the boundary condition, equation (20), applies for the whole surface of the drop. The drop differential equation for absorption with chemical reaction, accounting for surface resistance of the form shown in equation (20) has been solved by Dankwerts.[24] His expression for the total amount absorbed, Q, by a stagnant drop in time, t, is

$$Q = 8\pi h^2 C^* D_\ell a^2 \sum_{n=1}^{\infty} \frac{kt(k + D_\ell \alpha_n{}^2) - D_\ell \alpha_n{}^2(\exp[-t(k + D_\ell \alpha_n{}^2)] - 1)}{(k + D_\ell \alpha_n{}^2)^2[a\alpha_n{}^2 + h(ah - 1)]} \tag{21}$$

where k = first order reaction rate constant
α_n = nth root of $a\alpha \cot(a\alpha) + ah - 1 = 0$
a = radius of drop.

The absorption coefficient, B, of equation (16) may be expressed as

$$B = \frac{Q}{C_g \frac{4}{3} \pi a^3}, \tag{22}$$

with Q being evaluated from equation (21). Equation (21) describes absorption by stagnant drops, accounting for mass transfer resistance in both the gas and liquid phases. For many situations, one of the phase resistances is negligible, allowing more simple expressions for Q than represented by equation (21).

For highly soluble gases or where chemical reactions are extremely rapid, liquid phase transfer resistance would be negligible. The total amount of solute absorbed by a drop in time, t_e, would be

$$Q_{\text{gas film}} = 4\pi a^2 k_g t_e C_g, \tag{23}$$

and the absorption parameter for drops, B, would be

$$B_{\text{gas film}} = \frac{3 k_g t_e}{a}. \tag{24}$$

Calculations of washout based on equation (24) have been discussed by others.[25][26]

Absorption of slightly soluble substances such as methyl iodide is controlled by liquid phase resistance unless the reaction rates are extremely rapid. For no gas phase resistance, equation (21) may be simplified by taking the limit as h becomes very large. The resulting equation is

$$Q = 8\pi aDC^* \sum_{n=1}^{\infty} \frac{ka^2t + \dfrac{Dn^2\pi^2}{k + \dfrac{Dn^2\pi^2}{a^2}} \left(1 - \exp\left[- t\left(k + \dfrac{Dn^2\pi^2}{a^2}\right)\right]\right)}{ka \quad + Dn^2\pi^2} . \tag{25}$$

We have evaluated equation (25) for a range of reaction velocities, drop sizes, fall heights (exposure times), and temperatures. Selected values of the calculated data are shown in Figures 10 and 11. In Figure 10 the amount absorbed per drop per unit surface concentration, Q/C*, is shown as a function of drop diameter for reaction velocities of 0.01 to 100 $\sec^{-1}$. Also shown on this figure are values of Q/C* for no diffusional transfer resistance in either phase. This is a limiting situation in which the whole drop is assumed to contain the equilibrium solute concentration for the entire exposure time. The absorption up to time t_e would be

$$Q_{max} = \frac{4}{3} \pi a^3(k\ t_e + 1)C^*. \tag{26}$$

Equation (25) reduces to equation (26) for small a and large t. From Figure 11 it is apparent for drops less than about 500 μ and for reaction velocities less than about 1 $\sec^{-1}$, that diffusional mass transfer resistance does not play a major role. Thus, oscillation and circulation within these drops would not appreciably affect the rate of absorption because the drops would be well mixed by diffusion alone.

For larger drops of liquid of high reactivity the degree of mixing would be important in determining the overall absorption. A number of studies of drop absorption have been carried out to assess the effect of drop circulation and oscillation on absorption. Examples of these studies are the works of Garner and Lane[27], Kronig and Brink[28], Calvert and Constan[29], and Garner and Haycock.[30] Soldano[31] at ORNL has reported methyl iodide absorption by suspended drops 4.2 mm in diameter. Unfortunately the data available do not permit satisfactory estimation of drop mixing for reactive drops smaller than 2000 μ in diameter, which are of prime interest here. A conservative estimate of the absorption may be obtained by considering the drop to be stagnant.

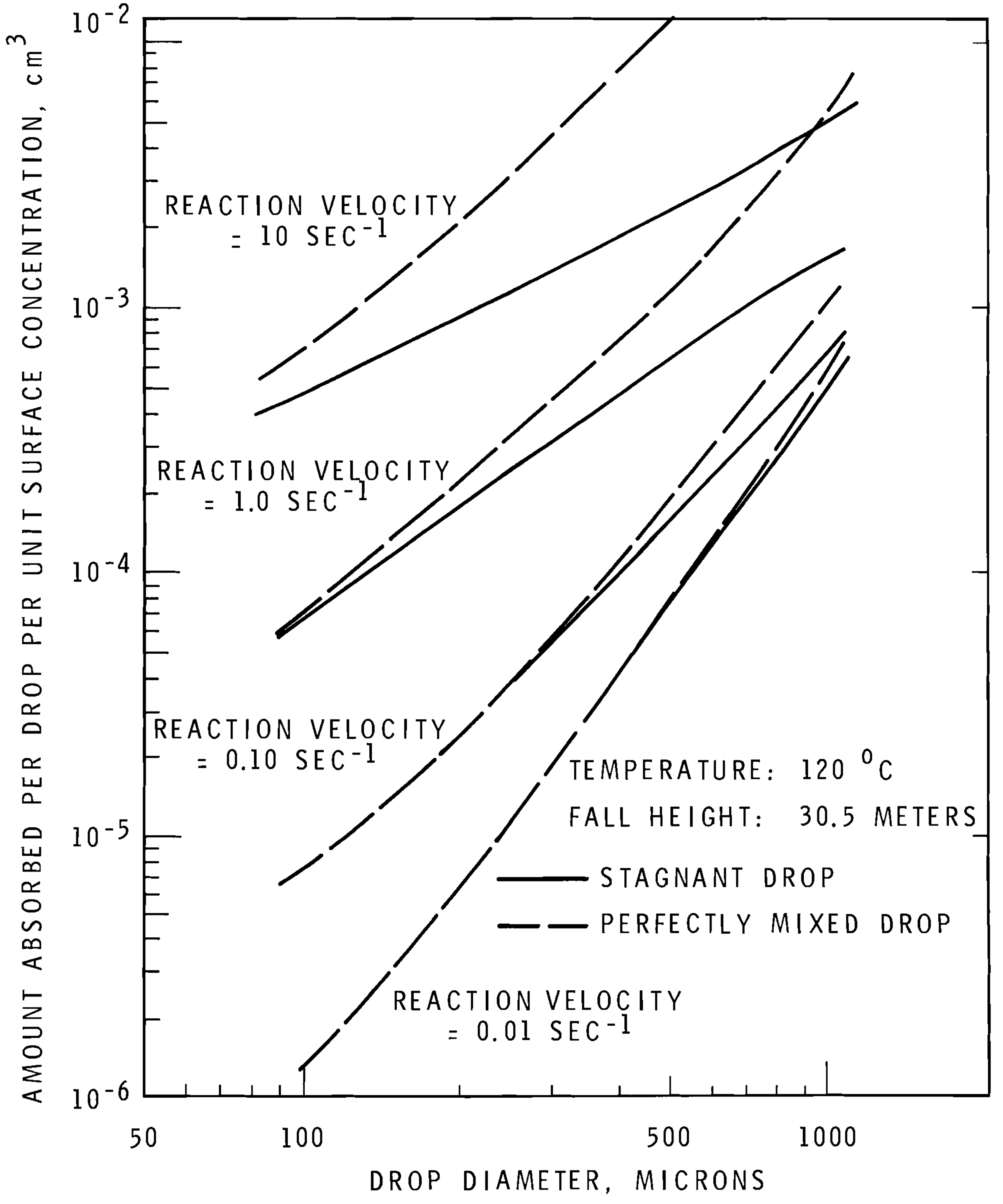

Figure 10. Drop Absorption with First Order Chemical Reaction

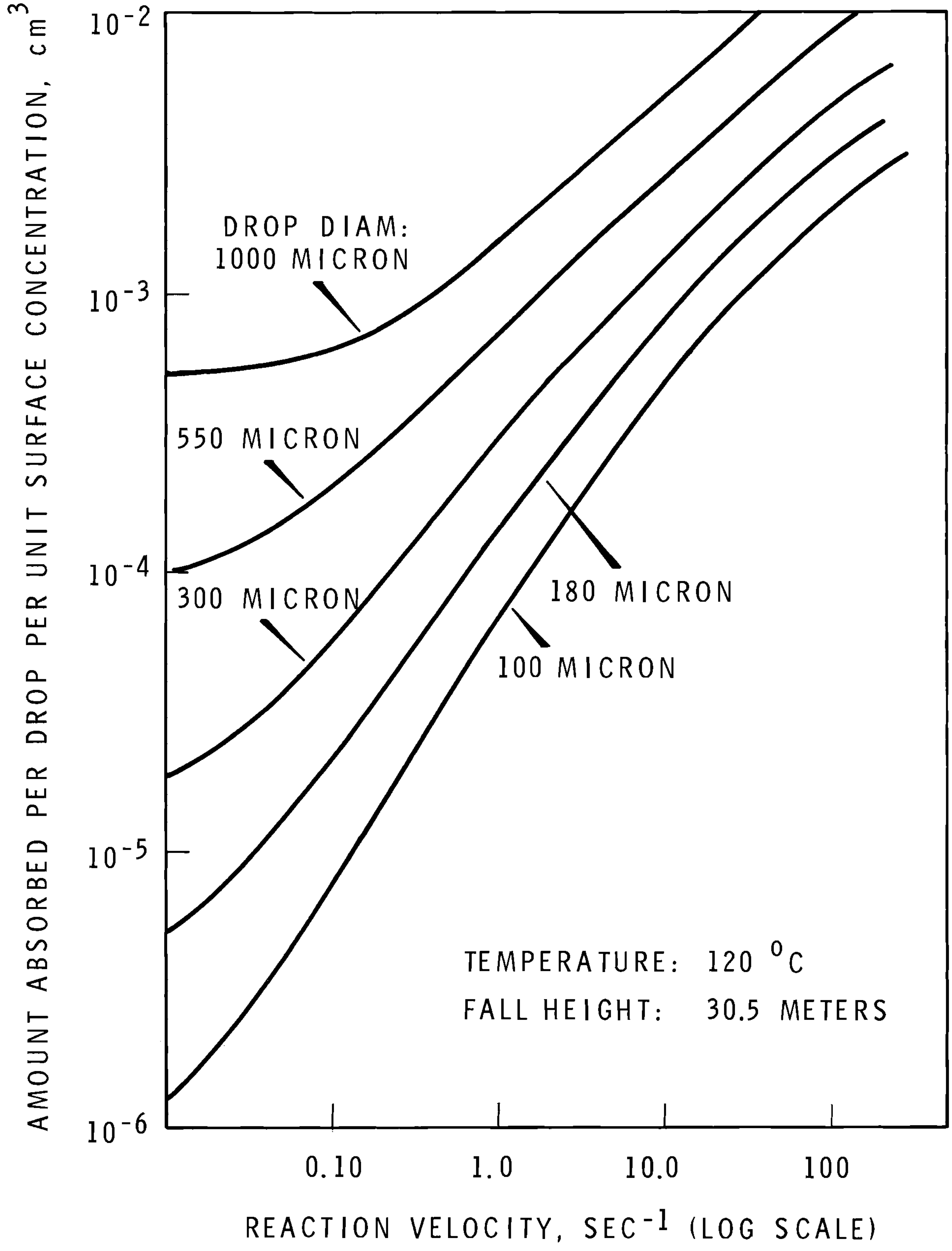

Figure 11. Effect of Reaction Velocity on Absorption by Stagnant Drops

In Figure 11, the effect of reaction velocity on absorption is shown for drops exposed for times equivalent to fall distance of 100 feet. For 1000 μ diameter drops the absorption is not appreciably enhanced for reaction rates lower than about 0.1 sec^{-1}. For smaller drops, slower reaction rates give enhancement over physical absorption because of greater contact times. For drops larger than 1000 μ, the stagnant drop model shows that the reaction rate for appreciable enhancement of absorption is greater than 0.1 sec^{-1}.

From this brief discussion of drop absorption we have concluded that conservative calculation of drop absorption can be achieved using a stagnant drop model. It should be noted that absorption with chemical reaction into drops under conditions where liquid resistance plays a major role has not been explored sufficiently from an experimental viewpoint. Additional experimental studies are needed.

Absorption by Liquid Film on Wall

For many spray chambers an appreciable amount of liquid sprayed from the nozzle impinges against the wall. The surface area exposed by the wall of a chamber is significant compared to falling drops. For a cylindrical chamber three meters in height, with a height to diameter ratio of two, the wall surface area is calculated to be 3.2 times larger than the surface area for 1000 μ diameter drops, at a spray density of 0.0067 $cm^3/sec\ cm^2$ (0.1 gpm/ft^2). For a 100 ft. tall chamber, other factors remaining the same, the wall area is only 32% of that calculated for the drops.

The following brief treatment of wall film absorption is an attempt to arrive at predictive equations expected to give conservative results. Indeed, a complete treatment of absorption with chemical reaction is not yet available.

The flow characteristics and absorption by liquid flowing down a wall has been extensively studied during the last 25 years. Many of the studies carried out prior to 1964 have been summarized by Fulford.[32] Based on the theoretical and experimental studies, the general characteristics of wetted wall flow may be stated as follows. At low flow velocities, laminar flow persists, the velocity profile is parabolic, and the free surface velocity is 3/2 the average velocity. At Reynolds numbers in the range of 5 - 25, waves begin to appear on the surface, though the flow is still substantially laminar. At Reynolds numbers of 250 - 500 the flow becomes turbulent.

For the laminar flow regime, absorption with a first order chemical reaction is described by

$$V_{max} \left[1 - \left(\frac{x}{\delta}\right)^2\right] \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial x^2} - kC \tag{27}$$

where V_{max} = velocity at surface of film
x = distance from surface of film
δ = thickness of film
z = distance measured along film
D = liquid phase diffusivity
C = concentration of dissolved solute
k = first order rate constant.

Equation (26) has not been solved for the general case, but several solutions applicable to special situations have been presented.

For short laminar films, the solute does not have time to penetrate far into the film, and hence the absorption takes place as though the film were infinite in thickness. The differential equation for such films may be obtained from equation (27) by setting $x = 0$. This is the penetration theory approximation, and the mathematical solution is given by Dankwerts.[33] Most experimental data obtained with short wetted wall columns, for laminar flow, agree reasonably well with the penetration theory solution.

Calculations based on laminar flow theory indicate that the penetration theory would not be applicable because the solute would diffuse all the way through the film. A lower limit to the absorption in thin films can be calculated by considering the steady state solution to equation (27). Solution of equation (27) for $\partial C/\partial z = 0$ gives

$$\frac{dQ}{dt} = C^*\sqrt{kD}\ \tanh \sqrt{k/D}\ \delta, \tag{28}$$

where $\frac{dQ}{dt}$ = absorption rate per unit area
δ = thickness of the film.

The film thickness, δ, used in equation (28) may be estimated from laminar flow theory and experimental measurements of the wall flow rate.

Non-idealities in an actual film, such as turbulence and wave effects would increase the washout over that predicted by equation (28). Based on equation (28), the washout parameter of equation (16) would be

$$A = \frac{H\sqrt{kD}\ \tanh\ (\sqrt{k/D}\ \delta)}{L_W/A_W}, \qquad (29)$$

where A_W = wetted wall area.

Discussion of Theoretical Model

Absorption of a gas by a liquid, especially under conditions of simultaneous chemical reaction, is not a well understood phenomenon, and it is worthwhile to note several areas where discrepancy between theoretical and experimental results may arise.

First, the fluid dynamics within a spray chamber are not subject to precise calculation. For the wall film, smooth laminar flow with complete wall coverage would not be attained in any real spray chamber. However, even for the ideal laminar flow case, precise calculation may not be possible. For example, absorption may itself cause turbulence at the interface by changing the surface tension and density. This effect, often referred to as the "Marongoni Effect", has been shown to effectively enhance mass transfer compared to that predicted by the penetration theory. As an example, Brian, et. al, have recently published data which indicate that absorption of CO_2 in monoethanolamine enhances the mass transfer in a short wetted wall column by more than a factor of 5.[34]

This enhancement is the result of a relatively high mass transfer rate. For the washout of methyl iodide and iodine, the concentrations are exceedingly dilute, resulting in very low mass transfer rates on an absolute scale. For this reason, it is unlikely that significant enhancement would occur as a result of the Marongoni Effect. Water vapor condensing on drop and wall surfaces would probably not induce interfacial turbulence of large significance.

In addition to difficulties arising from interfacial turbulence, one must recognize that the wall film flow is not ideal and laminar. Preferential wetting of the surface may cause dropwise drain-off, or formation of rivulets, which are considerably more difficult to handle theoretically. Also, as spray drops impact against the surface, mixing would be induced in the film.

Absorption into pools found at the bottom of a spray chamber represents another area where enhanced absorption could occur. For this surface, effective mixing would result from drops striking the surface.

Falling drops would be expected to oscillate shortly after formation, and be deformed by aerodynamic drag. Coalescence of drops would increase the average drop size with increasing distance from the nozzle. These effects are difficult to assess quantitatively, but would be expected to enhance absorption compared to that calculated for drops falling at terminal velocity of the size measured at the maximum distance from the nozzle.

The effect of steam condensation on drop absorption is another factor which needs to be considered. The bulk flow caused by the condensation would be expected to enhance the gas phase transfer coefficient. The condensation would be largely completed in a few tenths of a second, hence the net increase in the gas film coefficient would not be of great consequence, even for elemental iodine. The liquid water condensed on the drop would presumably coat the outside of the drop, effectively separating the reactive molecules from the solute.

An estimate of the thickness of the water layer may be made by considering the magnitude of the latent heat of condensation and the sensible heat gain of the drop. Drops would likely undergo a temperature increase of less than 100°C, corresponding to a heat gain of about 100 cal/gram. This is equivalent to the latent heat of condensation of 0.18 grams/gram of water, indicating a drop weight increase of 18%. This increase in drop size corresponds to an increase of 6% in drop radius, amounting to a layer 30 microns thick for a 1000 micron diameter drop. Molecular diffusivities in water at an average temperature of 70°C are of the order of 4×10^{-5} cm^2/sec. Based on a simple one dimensional diffusion calculation[35], the surface concentration would reach 50% of the bulk concentration in a time of about 0.1 second. Thus, diffusional processes would very rapidly eradicate any large concentration gradients of reactive additive, and it is concluded that condensation would not greatly influence the absorption after the first few tenths of a second. Since drop residence times are of the order of seconds, the condensation would not greatly influence the overall absorption.

From this superficial look at absorption with chemical reaction, we conclude that the model developed in this report, since it is based on non-turbulent flow, will predict absorption rates conservatively.

EXPERIMENTAL METHOD

The purpose of the spray washout experiments was to demonstrate on a small engineering scale, the effectiveness of methyl iodide washout by sprays of aqueous hydrazine solution. Most of the experiments were carried out in a cylindrical chamber 4 feet in diameter by 10 feet in height, made from 304-L stainless steel. This vessel was limited to atmospheric pressure, and hence all of the tests performed in this vessel were at temperatures equal to or less than 100°C. Spray washout at temperatures to 123°C was carried out in a pressure vessel 3 feet in diameter by 8 feet in height. This vessel was painted to prevent corrosion.

The experiments performed may be divided into three sets. In the first set of experiments the spray liquid was recirculated continuously, and the quantity of methyl iodide remaining airborne was determined as a function of time. These experiments were performed in the 4 foot diameter stainless vessel, at temperatures initially close to 100°C. No heat was added during the spray period, hence the temperature decreased with time. The second set of runs consisted of three spray tests carried out at temperatures near 120°C. In two of these runs, once-through spray periods were employed in which wall film liquid and liquid collected in the bottom of the chamber were separately analyzed to permit assessment of wall absorption. The third set of experiments was designed to more precisely measure wall and drop absorption and a drop collector for evaluating drop absorption was used. These latter experiments were carried out in the 4-foot diameter stainless steel vessel, at temperatures near 90°C. All of the experimental runs were conducted using methyl iodide labelled with ^{131}I. Initial airborne methyl iodide concentrations were between 0.1 and 10 milligrams per cubic meter. The results of these experiments will now be briefly discussed.

RESULTS OF EXPERIMENTS

Recirculating Spray Runs in a Stainless Steel Spray Chamber

The goal of these runs was to demonstrate the spray washout of methyl iodide for a system simulating a post-accident containment vessel. Initial temperatures of the spray chamber were near 100°C, and the spray solution was at near room temperature (20°C) initially. The temperature within the chamber decreased with time, simulating behavior anticipated following a postulated reactor accident.

Drop size distributions for all of the nozzle combinations used were measured near the bottom of the chamber. The drops were collected at an oil-kerosene interface after falling through a thin layer of kerosene. The drop sizing was carried out at room temperature, under the nozzle pressure employed in the run. This nozzle pressure was 100 psi in all of the runs.

Liquid flow along the wall was measured by means of a collector ring installed near the bottom of the tank. Wall liquid and liquid-collected in the bottom of the tank were mixed in the pipe leading to the liquid reservoir.

A detailed description of the experimental apparatus is given in an earlier report.[1] Methyl iodide traced with ^{131}I was injected into the tank and allowed to mix before the spray was initiated. Airborne concentrations in these runs were calculated from a material balance, based on liquid samples collected at time intervals throughout the run, and the small residual of methyl iodide remaining airborne at the end of the run.

Ammonium hydroxide (0.75 moles/liter) was used in all of the solutions to provide excess base to react with carbon dioxide initially in the air.

The results of five of the recirculating spray runs are tabulated in Table XIII. In run 12, boric acid neutralized with ammonium hydroxide was added to demonstrate that the washout rate would not be adversely affected by the presence of borate ion.

The results of the recirculating spray runs listed in Table I show that the washout rate is proportional to the hydrazine concentration and the liquid flow rate. As expected, the washout rate is much slower than the rate predicted for a gas-phase limited process.

Higher Temperature Spray Washout

These runs, three in number, were carried out in a pressure vessel 3 feet in diameter by 8 feet in height. The atmosphere was saturated with respect to one atmosphere of air at 20°C.

In two of these runs, a once through spray period was employed to allow assessment of absorption by the wall film. A wall trough was provided to permit collection of liquid flowing down the wall, and this was analyzed for comparison with liquid falling as drops which accumulated in the bottom of the tank.

TABLE XIII

RESULTS OF RECIRCULATING SPRAY WASHOUT OF METHYL IODIDE BY AQUEOUS HYDRAZINE SPRAYS

Run No.	Drop Size MMD microns	Liquid Flow Rate cm^3/sec	Fraction Of Liquid Flowing On Wall	Initial Gas Temp. (°C)	Initial Hydrazine Concen. (wt.%)	Duration Of Run (min)	Initial Washout Half-Time (min)
8	280	56.8	52%	95	4.3	62	82
9	280	56.8	52%	95	4.3	327	82
10	260	33.4	36%	93	4.3	354	125
11	280	56.8	52%	95	16	350	22
12	280	58.0	52%	95	17	291	21

The gas phase activity was measured as a function of time using a sampling train consisting of a membrane filter, silver screens, silver membrane filter, activated charcoal filter paper, and activated charcoal beds arranged in series. The methyl iodide was largely collected within the charcoal beds.

The results of the three runs at higher temperature are briefly tabulated in Table XIV.

Steam was added at a rate high enough to balance the heat loss throughout the runs. Thus, the temperature of the system was more nearly constant than in the recirculating runs at atmospheric pressure. In one of these runs the spray solution was heated to the tank temperature, and in the other two runs, the spray liquid was introduced at room temperature.

The drop size was measured for the same nozzles operating at room temperature and one atmosphere of pressure. For 100 psi pressure drop across the nozzles, the drop size measured 8 feet below the nozzle was 340 microns mass median diameter. For a single nozzle of the same type, the drop size was measured to be 140 microns, indicating that for the 9 nozzle spray header, drop coalescence was significant.

From the results listed in Table XIV, it may be noted that washout half-times of about 8 minutes were realized.

The wall liquid was found to be more effective, on a volume basis, than the falling drops. This is shown in the last column where the ratio of wall liquid activity to bottom liquid activity is shown. The bottom liquid activity includes absorption into the pool, and hence drop activity would be less than indicated by this measurement.

Drop and Wall Film Absorption Experiments in the Stainless Steel Chamber

The goal of these experiments was to provide direct experimental measurements of the washout parameters A and B for wall films and falling drops respectively. In each experiment, the wall film flow was collected separately from the drops falling into the bottom of the chamber. Two drop catchers were placed near the bottom of the chamber to collect liquid falling in the form of drops with immediate removal from the chamber atmosphere. These drop catchers were designed to prevent absorption by the drop liquid subsequent to impact against the collecting surface. Methyl iodide-free air was continually purged through the flask to prevent airborne methyl iodide from reaching the liquid

TABLE XIV

RESULTS OF HIGH TEMPERATURE SPRAY WASHOUT OF METHYL IODIDE BY HYDRAZINE SOLUTIONS

Run No.	Initial Temp. (°C)	Spray Liquid Flow Rate (ml/sec)	Reactive Spray Solution Composition	Fraction Of Spray Flowing Down Wall	Overall Washout Half-Time (min)	Fractional Absorption Due to Wall Liquid
HT-1	120	36.6	10 wt.% N_2H_4 0.06 NH_4OH 3000 ppm H_3BO_3	0.28	8	
HT-2	120	60.7	6.5 wt.% N_2H_4 0.06 N NH_4OH 3000 ppm H_3BO_3	0.28	9	0.58
HT-3	123	37.8	10 wt.% N_2H_4 0.05 N NaOH 3000 ppm H_3BO_3	0.28	7	0.39

surface. Ten ml of 10% sodium thiosulfate solution was added to the flask to react rapidly with methyl iodide carried within drops into the catcher in an unreacted form. Drops impacting against the inlet chimney were not collected, but instead drained away at the outside of the flask. Only those drops falling nearly vertically entered the flask. Gas phase concentrations of methyl iodide were measured using beds of activated charcoal operated in series.

The results of these runs are shown in Table XV. The drop absorption coefficient, B, shown in Table XV is the average of the values obtained for the two catchers used in each experiment.

As noted before, the drop size shown was measured from drops collected near the bottom of the 10 foot tall chamber. Thus, the mass median diameter measured at this position would probably represent drops larger than the average in the chamber, since coalescence would cause an increase in size with increasing distance from the nozzles.

The temperature within the chamber decreased several degrees centigrade over the 7 minute spray period. The spray solution was heated to the tank temperature before each test to reduce temperature variations.

Unfortunately, these runs are few in number, and hence do not permit evaluation over ranges of temperature, flow rates, and drop sizes. They do demonstrate that wall film absorption, on a unit volume basis, may be considerably larger than absorption by the falling drops.

COMPARISON OF EXPERIMENTAL MEASUREMENTS WITH THEORY

The experimental measurements have been compared with absorption theory briefly discussed in this paper. The basic physical data necessary to carry out the numerical predictions based on theory, were taken from literature values, from general correlations, and from measurements performed as part of this study.

The partition coefficient for methyl iodide in water, for the low concentration ranges of interest here, has been measured as part of this study. Unfortunately the measurements do not extend to temperatures above 90°C, hence extrapolation to the temperatures used in the spray experiments was required. Extrapolation was on the basis of the equation (3)

$$\log (H) = -4.82 + \frac{1597}{T} \qquad (3)$$

TABLE XV

RESULTS OF WALL FILM AND DROP ABSORPTION EXPERIMENTS IN ONCE-THROUGH SPRAY RUNS

Run No.	Average Temp. (°C)	Solution Composition	Wall Flow RAte cm^3/sec cm	Drop Flow Rate (cm^3/sec)	A Wall Film Absorption Coefficient	B Drop Absorption Coefficient	Mass Median Drop Diameter
13	89	2.15 wt.% N_2H_4	0.138	47.8	6.27	1.06	320μ
14	88	1.0 wt.% $Na_2S_2O_3$	0.125	42.4	4.78	1.45	320μ
15	86	4.38 wt.% N_2H_4	0.143	52.4	8.55	1.95	320μ
17	87	1 wt.% $Na_2S_2O_3$	0.151	55.2	4.4	1.23	320μ

in which log (H) = logrithm to base 10 of partition coefficient,
T = absolute temperature, °K.

Extrapolation of these measurements to higher temperature according to equation (3) is justified only because data at higher temperature are not yet available.

The liquid phase reaction rates between methyl iodide and hydrazine and sodium thiosulfate have been measured. For hydrazine, the second order rate constant at 25°C is 1.1×10^{-3} $\sec^{-1}M^{-1}$ with an activation energy of 20.2 KCal/mole. For sodium thiosulfate, the second order rate constant at 25°C was taken as 2.84×10^{-2} $\sec^{-1}M^{-1}$, and the activation energy was taken as 18.88 KCal/mole. The pseudo first order reaction rate at the temperature of interest was calculated by multiplying the second order rate constant by the reactant concentration, moles/liter. The temperature correction was based on the standard Arrhenius equation,

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 \quad T_2} \right) \tag{31}$$

where k_2 = rate at temperature T_2
k_1 = rate at temperature T_1
E_a = activation energy
R = gas constant.

The liquid phase diffusivity of methyl iodide in water was calculated from a correlation presented by Wilke and Chang.[36]

The fluid dynamics of the flowing wall film were calculated from laminar flow theory, neglecting shear at the gas-liquid interface. For these assumptions, the liquid velocity at the gas-liquid interface is

$$U_s = \left[\frac{9\Gamma^2 g}{8 \nu} \right]^{1/3}, \tag{32}$$

where U_s = downward velocity at interface
Γ = flow per length of surface
g = acceleration due to gravity
ν = kinematic viscosity of liquid.

The thickness of the liquid layer predicted by the laminar flow theory is

$$\delta = \frac{3\Gamma}{2U_s} \tag{33}$$

where δ = thickness of the liquid film.

For the recycle experiments and the high temperature experiments, the results of which are shown in Tables XIII and XIV, only the overall washout half-time was compared to theory. In the theoretical calculation, the contribution of wall film and drop absorption must be each evaluated, and this is shown in Table XVI where the experimental results are compared with the theory.

Absorption at the top and bottom of the spray chambers was accounted for theoretically by assuming that the overall absorption per unit area for the top and bottom was the same as at the wall. This represents a correction of about 20% for the chambers used in this study.

From the comparison shown in Table XVI, it is evident that the washout is considerably more rapid than predicted by the stagnant film theory. The stagnant film theory gives results quite close to those predicted by the penetration theory for a laminar film. If one assumes that the wall film is well mixed, the predicted washout rate is increased by about a factor of 2 over that shown in Table XVI for the stagnant film. The observed rate is still a factor of 2 greater than for the well mixed film.

The results obtained in the once through spray in which drop catchers were employed are compared in Table XVII to the predictions based on stagnant film and drop theory. It should be noted that the predicted wall film absorption coefficients have not been corrected to account for absorption at the top and bottom of the chamber. For the once through runs, the measured washout rates are 1.5 - 3 times faster than predicted from the stagnant film theory. This ratio of measured to theoretical is somewhat lower than found in the recycle experiments. Absorption into the pool at the bottom of the chamber was not included in these experiments, whereas in the recycle experiments, the bottom pool was a factor. Based on this, absorption into the bottom pool would be considered more effective per unit area than wall film absorption. This was also implied from measurements in which bottom liquid absorption was compared to wall liquid absorption. Contact time and agitation in the bottom pool would likely be greater than for the wall film, which would enhance the absorption.

In comparing the measured washout rates with theory, the dominant feature is that the measured rates are 2 - 5 times faster than the predicted. Part of this discrepancy is no doubt due to the assumptions used in the theory, which were chosen to give conservative predictions of washout rate. For the falling film, it was assumed that ideal laminar flow persisted. Waves, rivulets, mixing at surface irregularities, and turbulence would enhance wall film

TABLE XVI

COMPARISON OF MEASURED WASHOUT WITH THEORY

Run No.	A Wall Film Absorption Coefficient	B Falling Drop Absorption Coefficient	Calculated $\frac{\text{Drop Abs.}}{\text{Wall Film Abs.}}$	Predicted Washout Half-Time (min)	Measured Washout Half-Time (min)	$\frac{\text{Theoretical Half-Time}}{\text{Measured Half-Time}}$
8	4.97	0.76	0.15	295	82	3.6
9	4.68	0.72	0.15	313	82	3.8
10	9.26	0.92	0.18	379	125	3.0
11	13.60	1.37	0.09	113	22	5.1
12	12.93	1.38	0.10	115	21	5.5
HT-1	42.8	1.21	0.07	37.7	8	4.7
HT-2	20.5	0.90	0.11	45.9	9	5.1
HT-3	46.5	1.33	0.07	33.7	7	4.8

TABLE XVII

COMPARISON OF ONCE-THROUGH RUNS WITH THEORY

Run No.	Reactant Concentration	Predicted Wall Abs. Coeff. A	Predicted Drop Abs. Coeff. B	A Expmtl. / A Theo.	B Expmtl. / B Theo.	Predicted Drop Abs. / Wall Film Abs.	Measured Drop Abs. / Wall Film Abs.
13	2.5 wt.% N_2H_4	2.57	0.58	2.44	1.84	0.20	0.15
14	1.0 wt.% $Na_2S_2O_3$	3.39	0.61	1.41	2.38	0.16	0.27
15	4.38 wt.% N_2H_4	3.37	0.73	2.54	2.67	0.21	0.22
17	1.0 wt.% $Na_2S_2O_3$	2.39	0.67	1.52	1.83	0.22	0.27

absorption over that predicted by the theory. For the falling drops, the drop size was measured at the bottom of the spray chambers, hence the measured size is a maximum. The volume average over the whole chamber would be smaller, and this would account for part of the observed enhancement of absorption compared to that predicted theoretically.

Improved accuracy of the input data may have resulted in better agreement with theory. It was necessary to extrapolate from measurements at lower temperatures, or to predict values from correlations. Measurements of solubility and reaction rate for methyl iodide at higher temperatures are badly needed so that better interpretation of experiments and predictions may be attained.

PREDICTED METHYL IODIDE WASHOUT IN LARGE CHAMBERS

Reactor containment vessels are much larger than those used in the experiments reported here. Hence application of the small scale tests to large scale systems of practical interest must be based on knowledge of the scale factors which apply. We have attempted to show the effect of spray chamber size on methyl iodide washout rate by calculating the washout rate expected for cylindrical chambers from laminar flow theory described earlier.

In Figure 12 the washout rate of methyl iodide in spray chambers is shown as a function of chamber size. The spray density was assumed to be 0.0068 cm^3/cm^2sec, drop diameter was taken as 550 microns, and the wall flow rate was chosen as 0.1 cm^3/cm sec. The first order rate constant was chosen as 6.55 sec^{-1}, the value predicted for 5 wt.% hydrazine solution at 120°C.

The increase in washout half-time with increasing chamber size is a reflection of the importance of wall absorption, which is predicted to account for over 50% of the total even for a cylinder 100 ft. in height. The curve shown is not highly sensitive to changes in the assumed conditions. For larger drops, the wall would be relatively more important, and the curve shown in Figure 12 would be steeper. For smaller drops or higher reaction rates, the curve would tend to level out, vessel size being of less importance.

Based on this calculation we would expect a washout half-time of about 60 minutes for a vessel 80 feet in height for 5 wt.% hydrazine, for the nominal spray conditions specified in Figure 12.

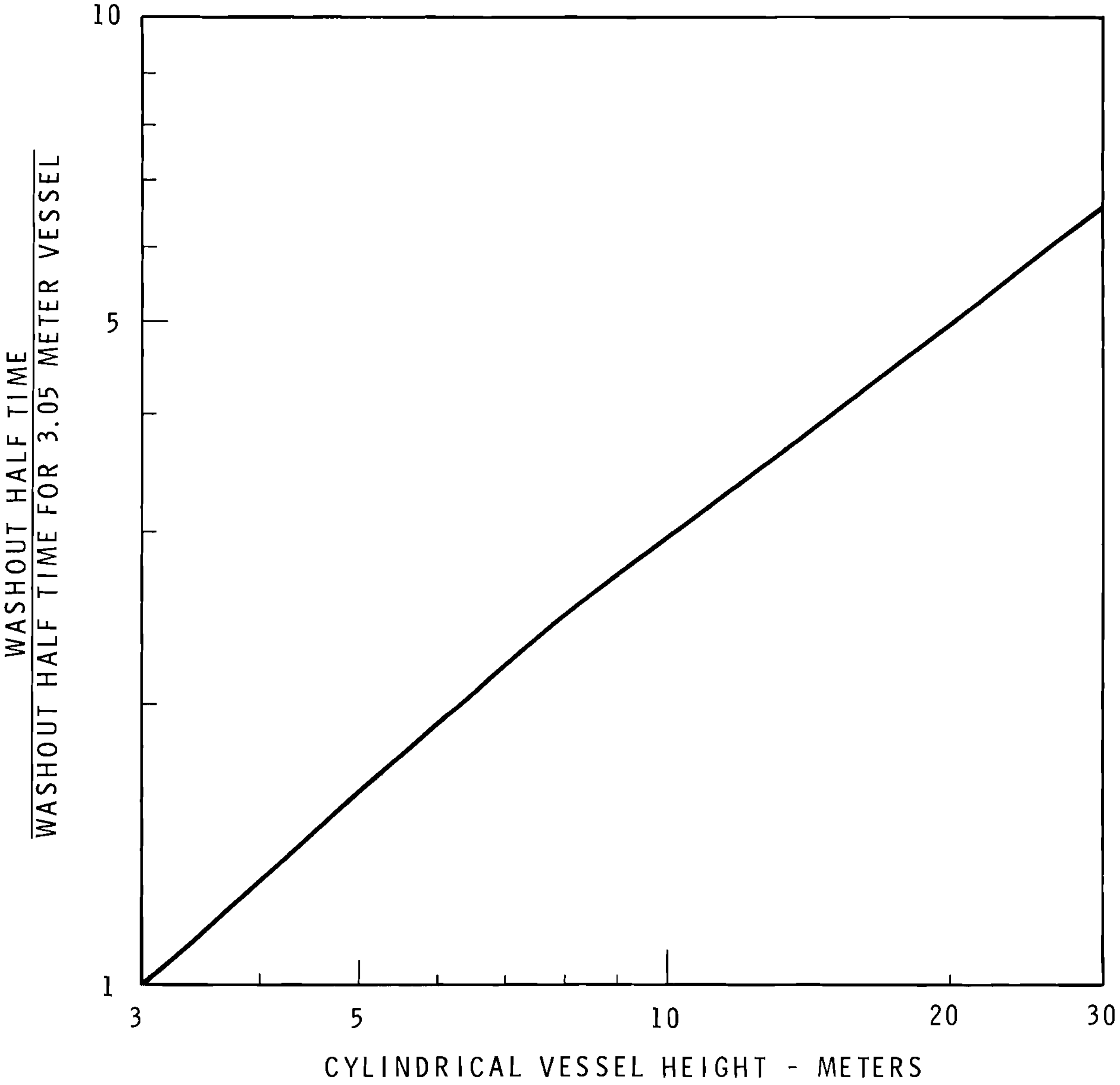

Figure 12. Predicted Effect of Vessel Size on Washout Rate for Methyl Iodide

SUMMARY OF WASHOUT OF METHYL IODIDE BY SPRAYS

The absorption of methyl iodide by sprays of aqueous solutions of hydrazine and sodium thiosulfate is controlled by liquid phase mass transfer resistance. Hence its removal rates are much slower than that of elemental iodine which would be controlled by gas film resistance. For reactive solutions such as 5 wt.% hydrazine and 1 wt.% sodium thiosulfate, absorption by liquid flowing along the wall is important even for large vessels. Measured rates of absorption are 2 - 5 times more rapid than calculated from a model based on a laminar wall film and stagnant drops falling at terminal velocity. Based on the absorption model developed, the washout half-time would be expected to increase with chamber size, for reaction rates studied here. From measured absorption rates in cylindrical vessels 8 and 10 ft. tall, the washout half-time in a cylindrical vessel 80 ft. in height and 32 ft. in diameter would be expected to be about 1 hour for 5 wt.% hydrazine solution, at a temperature of 120°C.

EVALUATION OF HYDRAZINE AS A SPRAY ADDITIVE

The incentive for adding a reactive chemical compound to a containment spray system is to enhance the removal of airborne fission product iodine. Elemental iodine is removed reasonably well with water containing a small amount of sodium hydroxide. Hence, the additive would primarily influence the absorption of organic iodides, of which the most abundant species appears to be methyl iodide. The use of a spray additive to enhance methyl iodide absorption must not impose serious penalties of cost or risk.

QUALITIES FOR A SPRAY ADDITIVE

In our progress report[1] the properties important for a spray additive were discussed. Qualities by which a spray additive should be judged include: (1) enhancement of methyl iodide absorption rate, (2) stability against thermal and radiation inducted degradation, (3) compatibility with components within the containment system, (4) safety hazards associated with use, (5) storability, and (6) costs.

It is difficult to make firm judgments of the value of an additive on an absolute basis because the criteria are more qualitative than quantitative. The qualities listed above are most easily applied as standards in comparing two proposed additives.

CHEMICAL AND PHYSICAL PROPERTIES OF HYDRAZINE

In a previous report[1] some of the chemical properties of hydrazine were described in light of the qualities needed in a spray additive. Additional information developed since publication of the previous report will be briefly discussed here.

Enhancement of Methyl Iodide Absorption Rate

The results of this study have shown that the washout rate is directly related to the solution reaction rate. Reaction rates measured here permit a comparison of enhancement for hydrazine and other chemical additives. Data presented in Table X indicate that hydrazine ranks approximately equal to sodium thiosulfate at 120°C when compared on equal wt.% bases. If 5 wt.% hydrazine is compared with 1 wt.% thiosulfate, hydrazine appears to be favored by roughly a factor of 3.

As noted in this report, the washout half time for methyl iodide is likely to be about 1 hour for a containment vessel 80 ft. high and 32 ft. in diameter, using 5 wt.% hydrazine. This represents a great enhancement over removal with water alone, but is still slow compared to removal for elemental iodine.

Radiolysis of Hydrazine

Radiolysis of a spray solution is important because of: (1) decomposition of the reactive additive and, (2) production of hazardous substances such as hydrogen gas. The radiation chemistry of hydrazine solutions is a very complex subject. In this brief discussion we will consider only the decomposition of hydrazine and the generation of hydrogen gas by radiolysis of water solution.

The decomposition of hydrazine by ionizing radiation is measured in terms of the number of molecules of hydrazine which decompose per 100 electron volts of energy absorbed by the solution. This measure is called the $G(-N_2H_4)$ value. A direct effect of the hydrazine decomposition is a reduction of the hydrazine concentration which would slow the rate of absorption of airborne methyl iodide.

The decomposition products are the gases nitrogen, ammonia, and hydrogen. The hydrogen produced is potentially of great significance because hydrogen is highly explosive.

Most studies[37][38][39] of radiolysis of hydrazine solution were carried out in an oxygen free system, and hence wouldn't necessarily represent the behavior in a containment system where 1 atmosphere of air would be present. In one study[37] some aspects of the effect of oxygen on the chemistry of radiolysis were examined. For the oxygen-free systems several conclusions of importance may be drawn. These are: (1) $G(-N_2H_4)$ increases with increasing hydrazine concentration up to 0.015 moles per liter. The $G(-N_2H_4)$ value remained constant at 5.2 for concentrations between 0.015 and 0.05 moles per liter which was the highest concentrations studied. (2) $G(- N_2H_4)$ decreases with increasing pH. (3) $G(-N_2H_4)$ is equal in magnitude to $G(NH_3)$ and $G(H_2)$ is equal in magnitude to $G(N_2)$.

In the presence of oxygen, the decomposition is complicated by additional reaction products, one of which is hydrogen peroxide. In the presence of oxygen $G(-N_2H_4)$ is a function of pH, showing a maximum value of 20 at a pH of 12. The mechanisms of the decomposition are complex, but are believed to involve free radicals.

Recent measurements of radiolytic decomposition of hydrazine and hydrogen generation in aqueous solutions at room temperature in the presence of oxygen have been reported.[40] A $G(-N_2H_4)$ of 8 to 10 was measured for a 5 wt.% solution of hydrazine. While this is a relatively high G value, the hydrazine solution would maintain about 50% of its initial absorption rate for methyl iodide at a radiation exposure to 10^8 R. The percent decomposition of hydrazine is shown in Table XVIII.

TABLE XVIII

RADIOLYTIC DECOMPOSITION OF 5 Wt.% HYDRAZINE SOLUTION

Radiation Dose Absorbed (Rads)	% of Initial Hydrazine Remaining	Iodine Capacity Of Solution (equiv./liter)
0	100	6.24
1×10^7	94	5.87
2×10^7	87	5.43
5×10^7	70	4.37
8×10^7	52	3.25

The radiolytic production of hydrogen was reported to be equivalent to $G(H_2) = 3.3$.[41] If this hydrogen production rate is assumed for the conditions postulated following a reactor accident, it is concluded that explosive mixtures of hydrogen could be formed.

Compatibility with Copper Alloy Flow System Components

Hydrazine is an amine type compound. As a class these compounds cause stress corrosion of copper containing alloys. If copper containing alloys are to be used as heat exchangers, the use of hydrazine must be given considerably more study to verify that corrosion will not unduly accelerate failure of the emergency steam suppression system.

Conclusions Concerning Hydrazine as a Spray Additive

Based on the results of this study, hydrazine possesses properties which make it attractive as a spray additive. There are factors which appear as deterrents when hydrazine is compared to other potential additives such as sodium thiosulfate. The most serious is hydrogen produced radiolytically, which could represent a significant explosion hazard within the containment system. Radiolysis of water alone and metal-water reactions may produce volumes of hydrogen of concern under the accident conditions postulated, hence, additives which contribute additional potential for hydrogen generation should be considered for sprays only if they afford a marked advantage in methyl iodide removal efficiency.[42] A second is the potential for causing stress corrosion in copper alloy heat exchangers. This could be circumvented by the use of stainless steel heat exchangers, but this would involve a capital outlay which would likely not be required for an additive such as sodium thiosulfate.

Thus, it is recommended that additional work on hydrazine be deferred pending further investigation of other potential additives.

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LITERATURE CITED

[1] L.C. Schwendiman, J. Mishima, A.K. Postma, L.L. Burger, and R.A. Hasty. "The Washout of Methyl Iodide by Hydrazine Sprays, Progress Report," BNWL-530, Battelle-Northwest, Richland, Washington, December 1, 1967.

[2] R.A. Hasty. "Reaction of Hydrazine and Iodomethane -- Removal of Iodomethane from a Gas Phase in Contact with Alkaline Hydrazine Solution," J. Chem. and Eng. Data, 13, pp 134-138 (1968).

[3] R.A. Hasty. "The Partition Coefficient of Methyl Iodide Between Vapor and Water," Canadian J. of Chemistry, 46, pp 1643 (1968).

[4] E.A. Moelwyn-Hughes. "The Kinetics of Hydrolysis," Proc. Royal Soc. (London) A, 220, pp 386-396 (1953).

[5] E.A. Moelwyn-Hughes. "The Kinetics of the Reaction Between Methyl Bromide and Thiosulfate Ion in Water," Transactions of the Faraday Society (London), 37, pp 279-281, (1941).

[6] T.K. Wiewiorowski and B.L. Slaten. "Molten Sulfur Chemistry. IV. The Oxidation of Liquid Sulfur," J. of Physical Chemistry, 71, pp 3014-3019, (1967).

[7] R.A. Hasty. "The Rate of Reaction of Methyl Iodide and Hydrazine in Aqueous Solution," BNWL-SA-1740, Battelle-Northwest, Richland, Washington, July, 1968.

[8] L.F. Audrieth and Betty Ackerson. The Chemistry of Hydrazine, p. 157, John Wiley and Sons, Inc., New York, New York (1951).

[9] C.C. Clark. Hydrazine, Matheson Chemical Company, Baltimore, Md. (1953).

[10] W.R. McBride, R.A. Henry, and S. Skolnik. "Potentiometric Titration of Organic Derivatives of Hydrazine with Potassium Iodate," Analytical Chemistry, 25, pp 1042-1046 (1953).

[11] K.K. SenGupta and S.K. SenGupta. "Kinetics of the Reaction Between Hydrazine and Iodine Solutions," Zeitschrift für Physikalische Chemie (Neue Folge), 45, pp 378-382, (1965).

[12] E.A. Moelwyn-Hughes. "The Kinetics of Certain Reactions Between Methyl Halides and Anions in Water," Proceedings of the Royal Society (London), A, 196, pp 540-553 (1949).

[13] A. Slator. "The Chemical Dynamics of the Reactions Between Thiosulfate and Organic Compounds. Part I. Alkyl Haloids," J. of Chemical Society, 85, pp 1286-1304 (1904).

[14] R.H. Bathgate and E.A. Moelwyn-Hughes. "The Kinetics of Reactions for Four Methyl Halides in Aqueous Solution," J. of Chem. Soc., pp 2642-2648 (1959).

[15] E.A. Moelwyn-Hughes. "The Kinetics of Two Ionic Exchange Reactions of The Methyl Halides in Water," J. Chem. Soc., pp 7779-7784 (1934).

[16] G.C. Lalor and E.A. Moelwyn-Hughes. "The Kinetics of the Reaction Between Methyl Iodide and the Thiocyanate Ion in Aqueous Solution," J. of Chem. Soc., pp 2201-2205 (1965).

[17] E.R. Swart and L.J. LeRoux. "The Effect of Solvent on a Simple Ion-Dipole Reaction. Part II. The Rate of the Methyl Iodide-Iodide Ion Exchange in Five Different Solvents," J. of Chem. Soc., pp 406-410 (1957).

[18] B.W. Marshall and E.A. Moelwyn-Hughes. "The Kinetics of the Reaction Between the Methyl Halides and Potassium Cyanide in Aqueous Solution," J. of Chem. Soc., pp 7119-7126 (1965).

[19] D.W. Colcleugh and E.A. Moelwyn-Hughes. "The Kinetics of the Reaction of Methyl Iodide with Silver Nitrate and Silver Perchlorate in Aqueous Solution," J. of Chem. Soc., pp 2542-2545 (1964).

[20] J.O. Edwards. "Correlation of Relative Rates and Equilibria with a Double Basicity Scale," J. of American Chem. Soc., 76, pp 1540-1547 (1954).

[21] R.G. Pearson, H. Sobel and J. Songstad. "Nucleophilic Reactivity Constants Toward Methyl Iodide and Trans- $Pt(py)_2CL_2$," J. Am. Chem. Soc., 90 pp 319-326 (1968).

[22] R.A. Ogg. "The Hydrolysis of Methyl Iodide," J. of the Am. Chem. Soc., 60, p. 2000 (1938).

[23] E.A. Moelwyn-Hughes. "The Kinetics of Two Ionic Exchange Reactions of the Methyl Halides in Water," J. Chem. Soc., p. 779 (1938).

[24] P.V. Dankwerts. "Absorption by Simultaneous Diffusion and Chemical Reaction into Particles of Various Shapes, and into Falling Drops," Trans. Faraday Soc., 47, pp 1014-1023 (1951).

[25] V. Griffith. "Use of Sprays as a Safeguard in Reactor Containment Structures," Nuclear Safety, 6, NO. 2, pp 186-194, Winter 1964-65.

[26] L.F. Parsly. Removal of Elemental Iodine from Steam-Air Atmospheres by Reactive Sprays, ORNL-TM-1911 (October, 1967).

[27] F.H. Garner and J.J. Lane. "Mass Transfer to Drops of Liquid Suspended in a Gas Stream. Part II. Experimental Work and Results," Trans. Instn. Chem. Engrs., 37, pp 162-172 (1959).

[28] R. Kronig and J.C. Brink. "On the Theory of Extraction from Falling Droplets," Appl. Sci. Res., A2, pp 142-154 (1949).

[29] G.L. Constan and Seymour Calvert. "Mass Transfer in Drops Under Conditions that Promote Oscillation and Internal Circulation," A.I.Ch.E. Journal, 9, No. 1, pp 109-115 (1963).

[30] F.H. Garner and P.J. Haycock. "Circulation in Liquid Drops," Proc. Royal Soc., (London), 252A, pp 457-475 (1959).

[31] B.A. Soldano and W.T. Ward. Uptake of I_2 and CH_3I by Suspended Drops of Water Solution, ORNL Nuclear Safety Research and Development Program Bi-Monthly Report for January-February 1968, USAEC Report ORNL-TM-2164, March 26, 1968.

[32] G.D. Fulford. Advances in Chemical Engineering, Vol. 5, Academic Press, New York, pp 151-236 (1964).

[33] P.V. Dankwerts. "Absorption by Simultaneous Diffusion and Chemical Reaction," Faraday Soc. Trans., 46, p. 300 (1961).

[34] P.L.T. Brian, J.E. Vivian, and D.C. Matiatos. "Interfacial Turbulence During the Absorption of Carbon Dioxide into Monoethanolamine," A.I.Ch.E. Journal, 13, pp 28-36 (1967).

[35] H.S. Carslaw and J.C. Jaeger. "Conduction of Heat in Solids," Oxford Univ. Press, p. 101 (1959).

[36] C.R. Wilke and Pin Chang. "Correlation of Diffusion Coefficients in Dilute Solutions," A.I.Ch.E. Journal, 1, pp 264-270 (1955).

[37] H. Lucien and M.L. Pinns. "The X-Ray Irradiation of Hydrazine and 1,1-Dimethylhydrazine," NASA Technical Note, NASA, TN, D-2452, Lewis Research Center, Cleveland, Ohio, August, 1964.

[38] M. Lefort and M. Haissinsky. "Decomposition Radiochemique de L'Hydrazine en Solution Aqueuse," J. de Chemie Physique, 53, pp 527-535 (1956).

[39] H.A. Dewhurst and M. Burton. "Radiolysis of Aqueous Solutions of Hydrazine," J. of the Am. Chem. Soc., 77, pp 5781-5785 (1955).

[40] H.E. Zittel. "Radiolysis Studies," Reported in ORNL Nuclear Safety Research and Development Program Bimonthly Report for January-February 1968, USAEC Report ORNL-TM-2164, pp 60-63, Oak Ridge National Laboratory, March, 26, 1968.

[41] H.E. Zittel. "Radiation Stability of Sprays," Reported in ORNL Nuclear Safety Research and Development Bimonthly Report for July-August, USAEC Report ORNL-TM-2283, pp 70-73, Oak Ridge National Laboratory, July 30, 1968.

[42] Howard McLain. Potential Metal-Water Reactions in Light-Water-Cooled Power Reactors, ORNL-NSIC-23, August, 1968.

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