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SUBJECT: Mass Transfer and Kinetics of Methyl Iodide to Aqueous Drops Containing Mercury

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ABSTRACT

Experiments were performed in a wind tunnel in the presence of artificial light to simulate hydrocarbon interactions with an airborne aqueous drop containing mercury salts. Each drop containing either mercuric sulfate or chloride (concentrations of 10^{-3} to 10^{-9} M) was suspended for 1 to 10 sec in a tunnel containing methyl iodide (CH_3I) (gas concentrations varied 2.3 to 7 x 10^{-7} M). The mass transfer of the CH_3I to the drop and subsequent reaction in the drop were studied. The presence of ethyl mercury iodide was identified in the liquid drop. A mass transfer-kinetic model was developed to quantize the process, and the reaction of CH_3I was found to be pseudo-second order.

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1. SUMMARY

Since considerable attention has recently been focused on the ecological hazards of mercury and its compounds in the environment, the overall objective of this study was to investigate one possible pathway for mercury pollution of the biosphere. The mass transfer of methyl iodide to an aqueous drop containing mercury and the kinetics of the resulting reactions in the presence of artificial light were studied as a model for the reaction of airborne mercury with hydrocarbons in the presence of sunlight. The drops were suspended in a vertical wind tunnel (methyl iodide concentration ~ 2.3 to 7×10^{-7} M) in the presence of ultraviolet light for 1 to 10 sec. The gas and liquid drop concentrations were monitored using several different analytical methods: gas chromatography, neutron activation, mass spectrometry, and flameless atomic absorption.

A model based on simultaneous mass transfer and kinetics was developed to define the process. The mass transfer coefficient (K_D) for the methyl iodide was determined as a function of drop lifetime. The coefficient initially increased very rapidly reaching a maximum value at around 3 sec before a rapid decline to the molecular diffusivity. The reaction of methyl iodide with the mercury salt in the drop was found to be pseudo second order. The reaction rate constant was also calculated. The mass transfer and kinetics of the CH_3I to the drop can be adequately represented by:

$$\frac{d[CH_3I]_d}{dt} = -0.093 \times 10^9 [CH_3I]_d^2 + \frac{K_D A_D}{V_D}(2.81[CH_3I]_g - [CH_3I]_d) \quad (1)$$

The qualitative effects of mercury concentration and pH in the drop were studied. The presence of ethyl mercury iodide in the liquid phase was identified. Methane was found in the gas phase and the presence of either methyl, dimethyl, or ethyl mercury iodide compounds was hypothesized.

2. INTRODUCTION

Recent evidence defining several modes of mercury-biosphere transformations has caused justifiable anxiety concerning the biological hazard of mercury pollution. Although mercury pollutants are often of the inorganic or phenyl mercury forms, methyl and dimethyl mercury invariably appear to be the end products of mercury-environment transactions (4, 6). It has been postulated that mercury may be methylated by living organisms (4), certain lake bottom sediments, or decomposing fish (4, 6) (which presumably contain microorganisms capable of this alkylation under anaerobic conditions). Since methyl and dimethyl mercury are readily soluble in water and are easily assimilated by living organisms, they are potentially exchangeable with all phases of the biosphere. Since coal with up to 300 ppm of mercury is burned by some power plants (6), airborne mercury hydrocarbon interactions

become quite important in evaluating chemical pathways for mercury transport into the biosphere.

The purpose of this project was to simulate interactions between airborne mercury and hydrocarbons in the atmosphere as an alternate mechanism for methylation of mercury. Water droplets containing mercuric salts were suspended and exposed to ultraviolet light in a wind tunnel of air contaminated with methyl iodide. This produced a dynamic simulation of photolytic conditions in the atmosphere, i.e., air, water, and sunlight. Mercuric sulfate was used because mercuric sulfide is a known substantial pollutant which is easily oxidized to the sulfate form; mercuric chloride was used because previous mercury research has been conducted with this compound (4). Methyl iodide absorption into water droplets has been investigated by Soldano and Ward (5), thus providing a cross check for the mass transfer data.

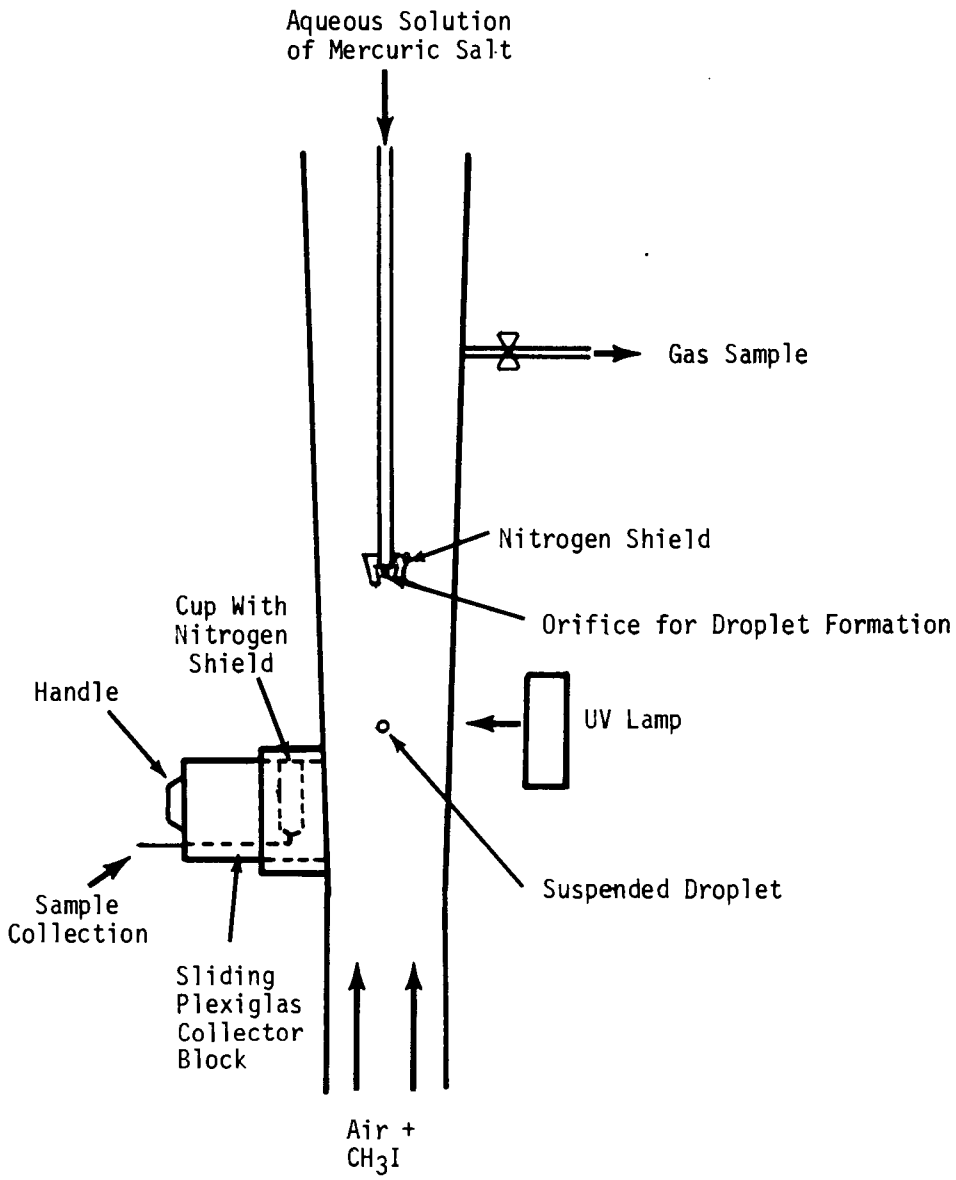
The specific objectives of the study were to determine the mass transfer and kinetics of methyl iodide to aqueous drops containing mercuric sulfate or chloride. The independent parameters investigated were: drop exposure time, mercury concentration, and pH of the aqueous drop.

3. APPARATUS AND PROCEDURE

3.1 Wind Tunnel Apparatus

A diagram of the vertical wind tunnel apparatus is shown in Fig. 1. A Harvard Infusion-Withdrawal Syringe Pump (Model 901) introduced the aqueous solutions through the center tube at a rate of 0.2 - 0.8 cc/min. While the drop was formed at the orifice, it was prevented from reaction by a shield of nitrogen gas which was introduced through a tube concentric to the droplet supply tube. The drops were stabilized in the air flow by making slight adjustments in the tunnel gas flow rate and by changing the shape of the calming section (a wire screen). Drops were collected for analysis by inserting the sliding Plexiglas collector block into the tunnel, thus interrupting the air flow and allowing the droplet to fall into the collector cup where it was again shielded from further reaction by nitrogen gas. The collector was inserted from 1 to 10 sec intervals after the drops had been formed so that drops with varying exposure could be analyzed. The collector was inserted as many as 100 times for a given exposure to obtain 1 cc of drops required for the various analyses. It was assumed that no further reaction occurred after the drop was removed from the tunnel and shielded from ultraviolet light.

Ultraviolet light for photolysis was supplied by an external lamp (long wave UV filter, Model SL-3660). Glass windows were installed in the Plexiglas walls of the wind tunnel to permit better light transmission (passage of light with wavelengths of 3300 Å or greater).



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WIND TUNNEL APPARATUS

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Methyl iodide was introduced into the air stream with another Harvard Infusion-Withdrawal Syringe Pump. All gases were recycled, but a small injection rate (0.1 cc/min) of methyl iodide was maintained during experiments, effectively compensating for any losses from the tunnel. Tunnel gas samples were collected with evacuated glass sample bulbs equipped with vacuum stopcocks. Gas samples were taken one to three times per run depending on run duration.

A summary of the experimental runs is given in Table 1. The solutions were made acidic with nitric acid and basic with ammonium hydroxide. The pH was measured with a Photovolt Digicord pH meter. The concentrations of $HgCl_2$ varied from 0.1 to 1000 ppm, while the $HgSO_4$ concentrations were in the range 0.0015 to 15 ppm. Run S served as a control since it was performed using water droplets free of mercury salts. The pH for this control was 5.84, a typical pH representative of most runs.

Droplet diameter for all experiments was 0.43 cm and was calculated by capturing and weighing 100 droplets of the desired solution. The drop size did not vary because the liquid properties remained fairly constant and the same orifice was used for all experiments. All experiments were performed at room temperature, 24 $\pm$ 1°C.

3.2 Gas Chromatographic Analysis of Droplets

The liquid samples collected at various exposure times were analyzed for methyl iodide with a Varian Aerograph Model 1520 gas chromatograph (GC) (electron capture detector). The chromatograph column (5-ft-long and 0.25-in.-OD glass) was packed with Chromosorb W on which a liquid phase partitioning agent, 20% SE 52, was adsorbed.

The procedure for analysis consisted of extracting 0.2 ml of the aqueous sample with an equal volume of benzene, and then directly injecting either 2 or 5 μℓ liquid aliquots of the organic phase into the column. (Extraction was necessary because water fouled the tritium foil of the electron capture detector.) The column temperature was 59 to 60°C, and the N_2 carrier gas flow rate was about 90 cc/min (supply pressure = 65 psig, column rotameter setting = 90-95; no calibration of flow rate was made). The GC output generally consisted of three peaks: a 25-sec peak resulting from pressure variation caused by injection, an 80-sec CH_3I peak, and a 205-sec benzene peak. The chromatograph was calibrated for CH_3I with a set of standards ranging from 10^{-5} to 10^{-9} M. The calibration curves are shown in Appendix 8.4.

3.3 Other Analytical Techniques

Several other instrumental analyses were used by the Analytical Chemistry Division to identify the content of the gas and liquid samples. Methyl iodide concentration in the tunnel gases was routinely determined

Table 1. Summary of Experiments

Run	Form of Hg in Droplet	Hg Concentration (M)	Average CH_3I Concentration in Gas (M)	Droplet Exposure Times (sec)	pH of Hg Solution
A	$HgSO_4$	5×10^{-9}	2.68×10^{-7}	1, 2, 3, 5, 10	5.85
B	$HgSO_4$	5×10^{-8}	2.35×10^{-7}	1, 2, 3, 5, 10	5.75
D	$HgSO_4$	5×10^{-5}	2.54×10^{-7}	1, 2, 3, 5, 10	3.18
E	$HgSO_4$	5×10^{-6}	2.28×10^{-7}	1, 2, 3, 5, 10	4.30
F	$HgCl_2$	3.7×10^{-7}	3.18×10^{-7}	1, 2, 3, 5, 10	5.85
G	$HgCl_2$	3.7×10^{-6}	3.31×10^{-7}	1, 2, 3, 5, 10	5.50
H	$HgCl_2$	3.7×10^{-5}	3.54×10^{-7}	1, 2, 3, 5, 10	5.35
J	$HgCl_2$	3.7×10^{-4}	3.31×10^{-7}	1, 2, 3, 5, 10	4.50
K	$HgCl_2$	3.7×10^{-3}	3.52×10^{-7}	1, 2, 3, 5, 10	4.27
L	$HgCl_2$	3.7×10^{-3}	3.45×10^{-7}	1, 2, 3, 5, 10	4.27
M	$HgCl_2$	3.7×10^{-3}	5.71×10^{-7}	1, 2, 3, 5, 10	4.27
N	$HgCl_2$	3.7×10^{-5}	7.05×10^{-7}	1, 2, 3, 5	2.20
P	$HgCl_2$	3.7×10^{-5}	6.41×10^{-7}	1, 2, 3, 5	5.48
Q	$HgCl_2$	3.7×10^{-5}	6.48×10^{-7}	1, 2, 3, 5	9.85
S	none	none	6.41×10^{-7}	1, 2, 3, 5, 10	5.84

using gas chromatography. Total iodine content of the liquid drop was specified by neutron activation. Gas chromatography and mass spectrometry of the samples were used to identify any reaction products. Organic components in the drop were extracted with hexane to prepare them for the mass spectrometry. An attempt was made to determine the mercury content of the samples using flameless atomic absorption.

4. RESULTS AND DISCUSSION OF RESULTS

4.1 Mass Transfer Studies

To obtain intrinsic mass transfer data (without chemical reaction of CH_3I with mercury), the wind tunnel system was operated using distilled water drops containing no mercury salts, but the photolysis conditions were identical to those used in the kinetic study. The mass transfer coefficient for the methyl iodide (CH_3I) to the drop was calculated as a function of drop exposure time for tunnel gas CH_3I concentration of 6.4×10^{-7} M. The drop concentrations were measured by a gas chromatograph. This curve has two distinct regions. For exposure times up to 3 sec there is a rapid absorption of the CH_3I into the drop. For larger times the rate of absorption decreases and the slope of the line approaches zero.

It is felt that the data point at t = 5 sec deviates significantly from the primary trend due to the operator collecting the drops. A drop forming on the inlet tube above the collector was at times shaken loose prematurely, dropping into the collection cup unexposed, thereby diluting the concentrations of the droplet sample. This problem varied in its frequency of occurrence with different tunnel operators and techniques of collection (see discussion in Appendix 8.3).

From the data in Fig. 2 the mass transfer coefficients, K_D, for the transport of CH_3I to the water drop was calculated as follows:

$$\frac{d[CH_3I]_d}{dt} = \frac{K_D A_D}{V_D}([CH_3I]_{d,s} - [CH_3I]_d) \qquad (2)$$

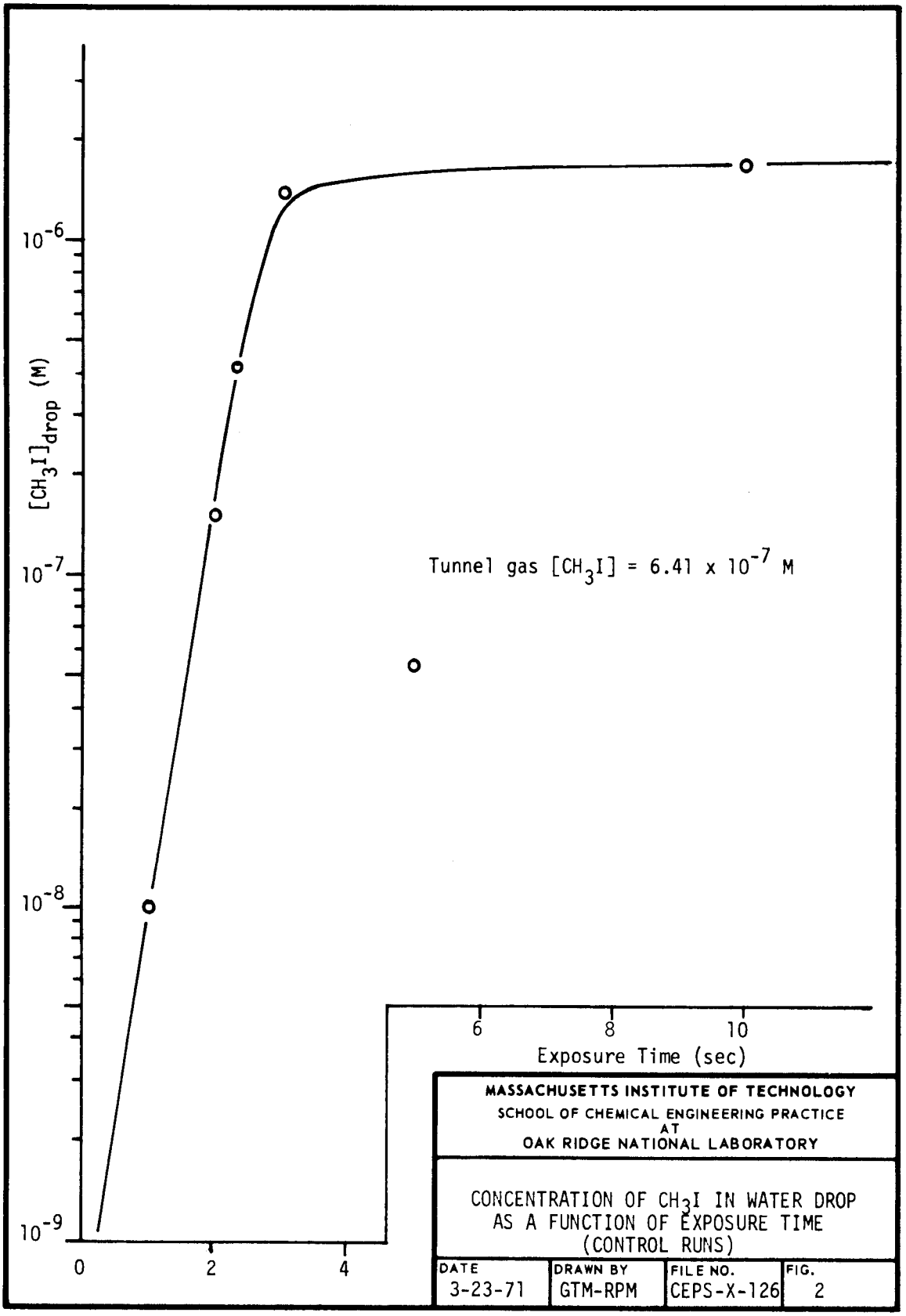
where:

$[CH_3I]_d$ = methyl iodide concentration in the drop at any time t, gmole/ℓ

$[CH_3I]_{d,s}$ = methyl iodide concentration in the drop when it is saturated with CH_3I, gmole/ℓ

A_D = mass transfer area of drop, cm^2

K_D = CH_3I mass transfer coefficient, cm/sec


10^{-6}
10^{-7}
10^{-8}
10^{-9}
$[CH_3I]_{drop}$ (M)
Tunnel gas $[CH_3I] = 6.41 \times 10^{-7}$ M
0
2
4
6
8
10
Exposure Time (sec)
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CONCENTRATION OF CH_3I IN WATER DROP
AS A FUNCTION OF EXPOSURE TIME
(CONTROL RUNS)
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FIG.
2

V_D = volume of drop, cm^3

t = exposure time, sec

The saturation CH_3I drop concentration was calculated from the relation,

$$[CH_3I]_{d,s} = D^*[CH_3I]_g \tag{3}$$

where:

$[CH_3I]_g$ = tunnel gas CH_3I concentration, gmole/ℓ

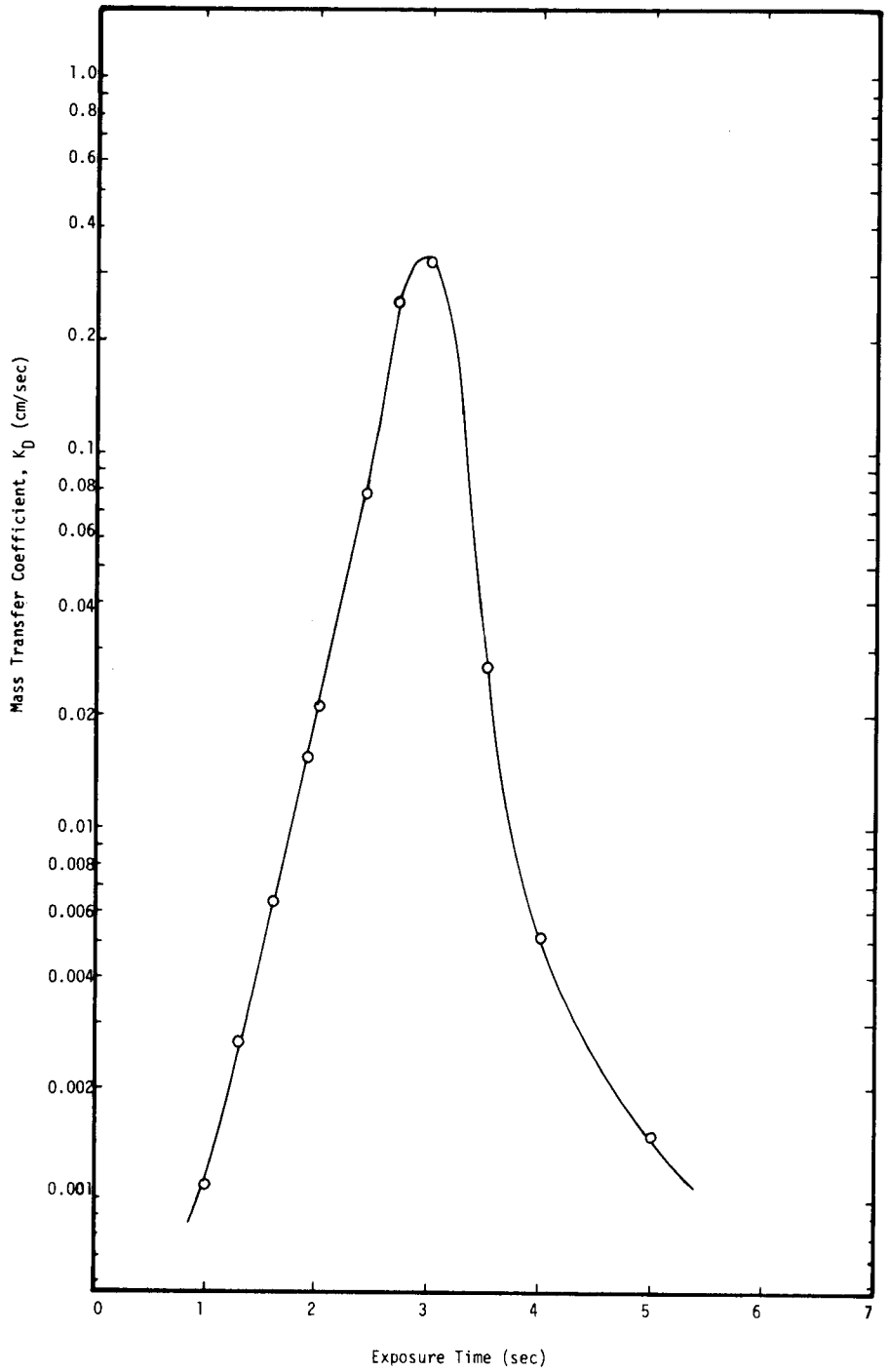
D^* = partition coefficient for methyl iodide in water

The partition coefficient was calculated as the ratio of the concentrations of CH_3I in the droplet and tunnel gas after 10 sec exposure time. A value of 2.81 was obtained (see Appendix 8.1) which is comparable to the value of 3.0 reported by Hasty (2) and 2.8 to 2.9 as found by Soldano (5). Hence Eq. (2) becomes

$$\frac{d[CH_3I]_d}{dt} = \frac{K_D A_D}{V_D}(2.81[CH_3I]_g - [CH_3I]_d) \tag{4}$$

From Fig. 2 the $[CH_3I]_d$ and $d[CH_3I]_d/dt$ were calculated for various exposure times. Since the drop size was known, a mass transfer coefficient was evaluated (see Appendix 8.1 for details). Figure 3 is a plot of the mass transfer coefficient, K_D, as a function of exposure time. The K_D begins at zero initially and rises rapidly to a maximum value of 0.34 cm/sec for an exposure of 2.9 sec. Further increase in the time causes K_D to drop significantly and at $t > 5.5$ sec, K_D is below 0.001 cm/sec. Within the accuracy of the analytical and experimental techniques, it is felt that K_D values below 0.001 cm/sec are subject to very large errors; therefore as a first approximation for $t > 6$ sec, the molecular diffusivity has been used for the evaluation of the kinetic data. The general shape of the curve in Fig. 3 is determined by circulation patterns within the drop which are initially quite vigorous due to drop oscillation and rotation caused by formation of the drop in the wind tunnel. Garner and Lane (1) have reported a similar variation in K_D with exposure time for the absorption of carbon dioxide to water drops in a wind tunnel.

For the control run the drop samples collected at different exposure times were sent to the Analytical Chemistry Division for total iodine analyses by neutron activation. The results are shown in Fig. 4. The total iodine content follows the same general trend as the CH_3I concentration in the drop, a rapid initial increase followed by a gradual leveling off. This is consistent with mass absorption from the bulk gas phase; however, the



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MASS TRANSFER COEFFICIENT AS A FUNCTION OF EXPOSURE TIME

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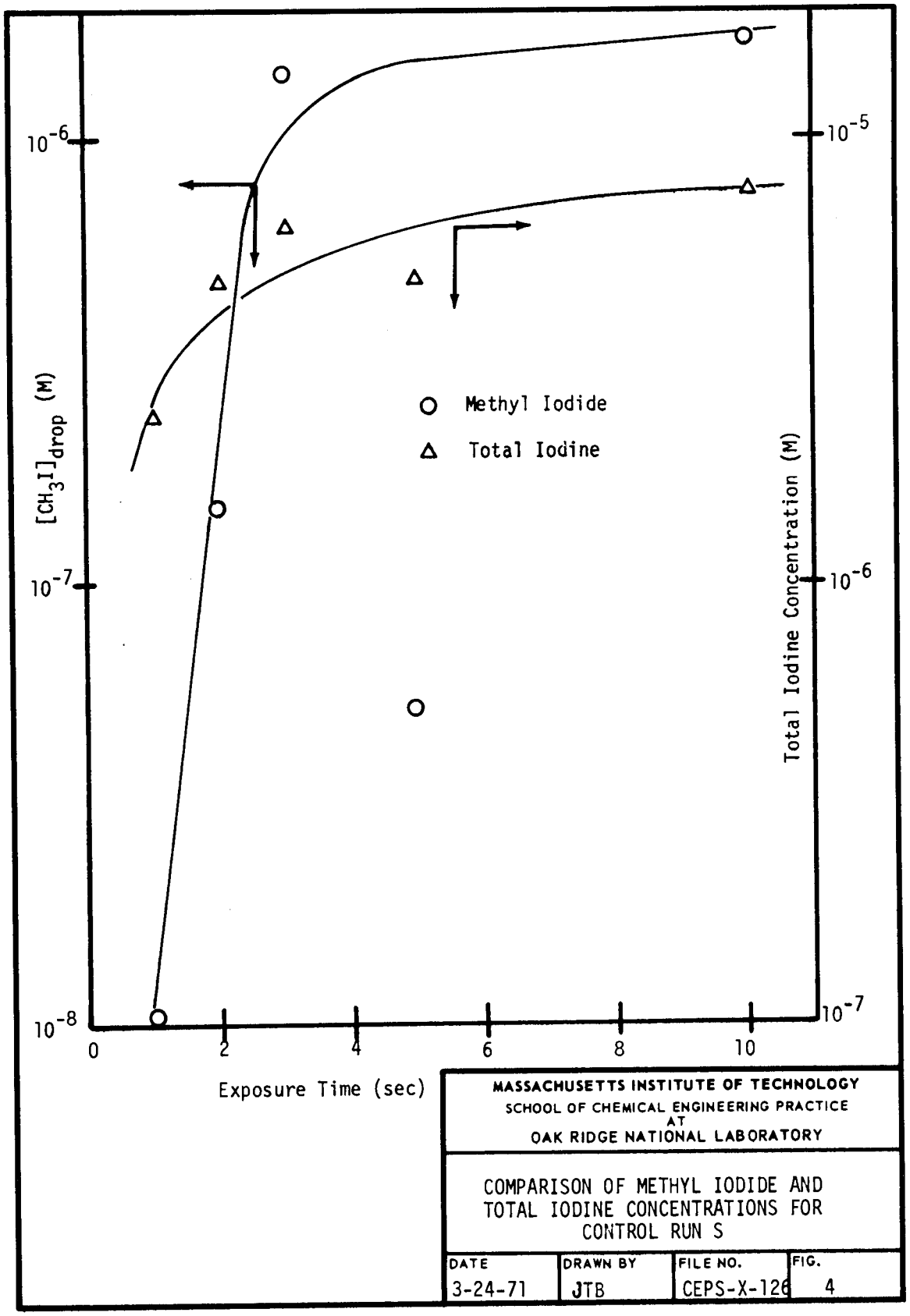
10^{-6}
10^{-7}
10^{-8}
$[CH_3I]_{drop}$ (M)
10^{-5}
10^{-6}
10^{-7}
Total Iodine Concentration (M)
Methyl Iodide
Total Iodine
0
2
4
6
8
10
Exposure Time (sec)
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COMPARISON OF METHYL IODIDE AND
TOTAL IODINE CONCENTRATIONS FOR
CONTROL RUN S
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FIG.
4

total iodine in the drop is approximately 5 to 10 times the CH_3I drop concentration. This may be explained by a possible photolysis of the CH_3I to form I_2 or the existence of iodine complexes in the water phase. Unfortunately only CH_3I was detected in the liquid phase for the control run, and hence the presence of iodine complexes must remain conjecture.

4.2 Kinetic Studies

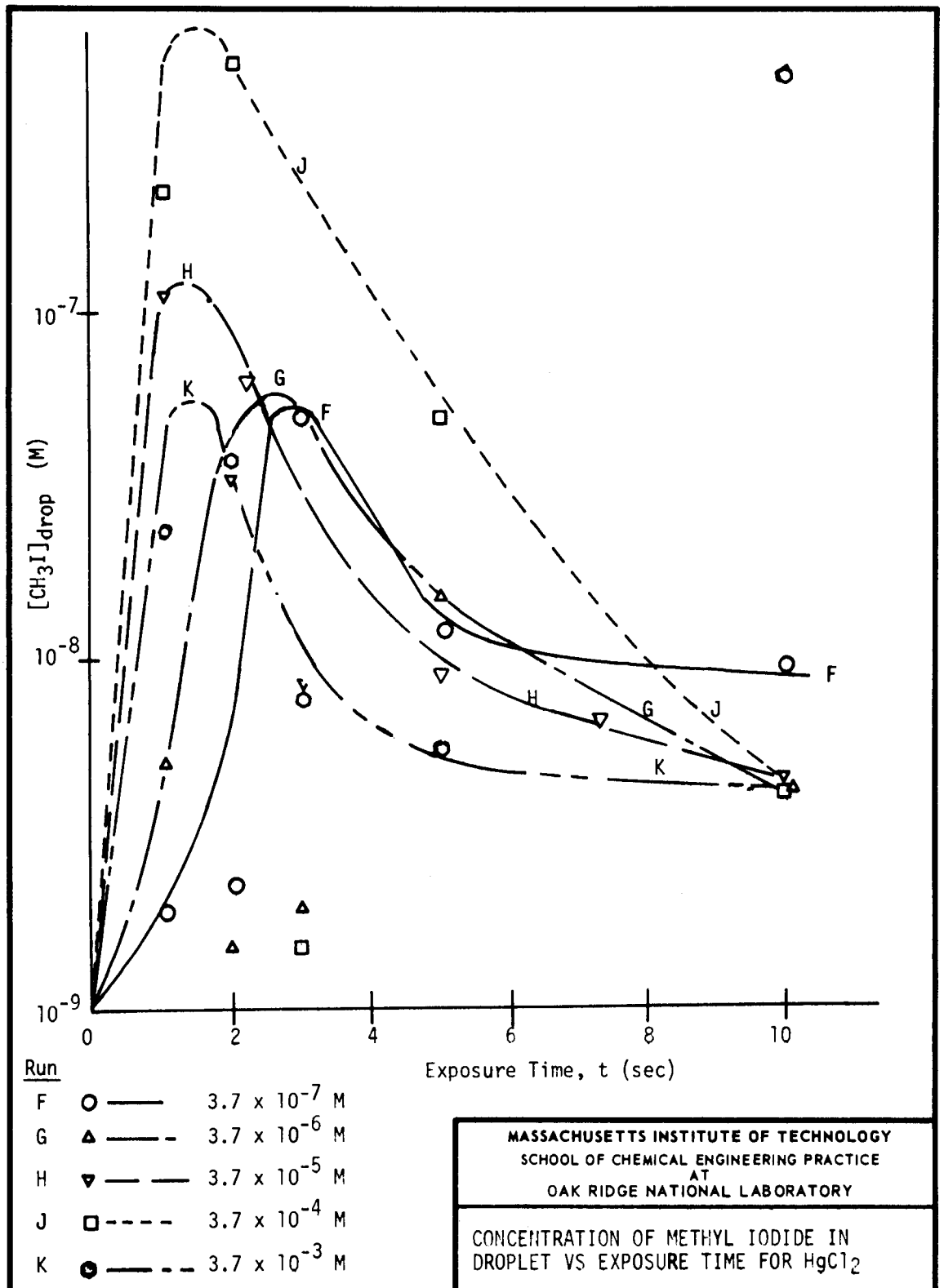
The two mercury salts used were $HgCl_2$ and $HgSO_4$. Drops containing the mercury compounds were suspended in the wind tunnel, and CH_3I concentration in the drop was determined as a function of exposure time. The results for the $HgCl_2$ and $HgSO_4$ are shown in Figs. 5 and 6, respectively. In each case the mercury concentration was altered (see Table 1) while the pH was kept approximately constant.

The results in Figs. 5 and 6 unlike that for the control run are characterized by three distinct regions: (1) a rapidly increasing CH_3I concentration from t = 0 to about 2 sec, (2) a decline in the concentration from t = 2.9 to t = 6 sec, and (3) a gradual decrease in the concentration to some steady state level. Although the precise definition of each of the lines was undoubtedly poor, the same general trend was clearly obvious for all the 14 runs conducted (all are not indicated in Figs. 5 and 6). Within the accuracy of the data no marked effect on the response was observed with changing Hg concentrations (10^{-3} to 10^{-7} M). This is not surprising since for all runs there was a great excess of Hg in the drop; therefore the kinetics observed corresponded to a pseudo reaction rate in the presence of excess mercury. A closer examination of Fig. 5 does indicate the maximum CH_3I concentration occurs at earlier times in the lifetime of the drop as the mercury concentration was increased. Part of the scatter in Fig. 5 could arise from the pH effect (see Sect. 4.3). Runs F, G, and H were within a close pH range of 5.35 to 5.85 and hence these agree fairly closely. Runs J and K had a pH of 4.50 and 4.27, respectively, and these show some anomalous behavior with mercury concentration.

For the $HgSO_4$ solutions very little methyl iodide was observed in the samples as is shown in Fig. 6. Run D with 5×10^{-5} M $HgSO_4$ yielded no observable methyl iodide. This absence of methyl iodide is explained by a 19-day delay in analyzing these samples because of an inoperative gas chromatograph. A similar loss of all observable methyl iodide from standard solutions of 10^{-7}, 10^{-8}, and 10^{-9} M CH_3I was observed after only 9 days. However, from Fig. 6 one can note that the shape of the curves is qualitatively similar to those for drops containing $HgCl_2$.

4.2.1 Kinetic Model

The shape of the response curves shown in Figs. 5 and 6 can be explained by postulating a mass transfer-kinetic model. For the first two or three seconds the CH_3I concentration increases due to a very rapid mass transfer from the bulk to the liquid phase. The CH_3I in the aqueous drop begins to



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CONCENTRATION OF METHYL IODIDE IN DROPLET VS EXPOSURE TIME FOR $HgCl_2$

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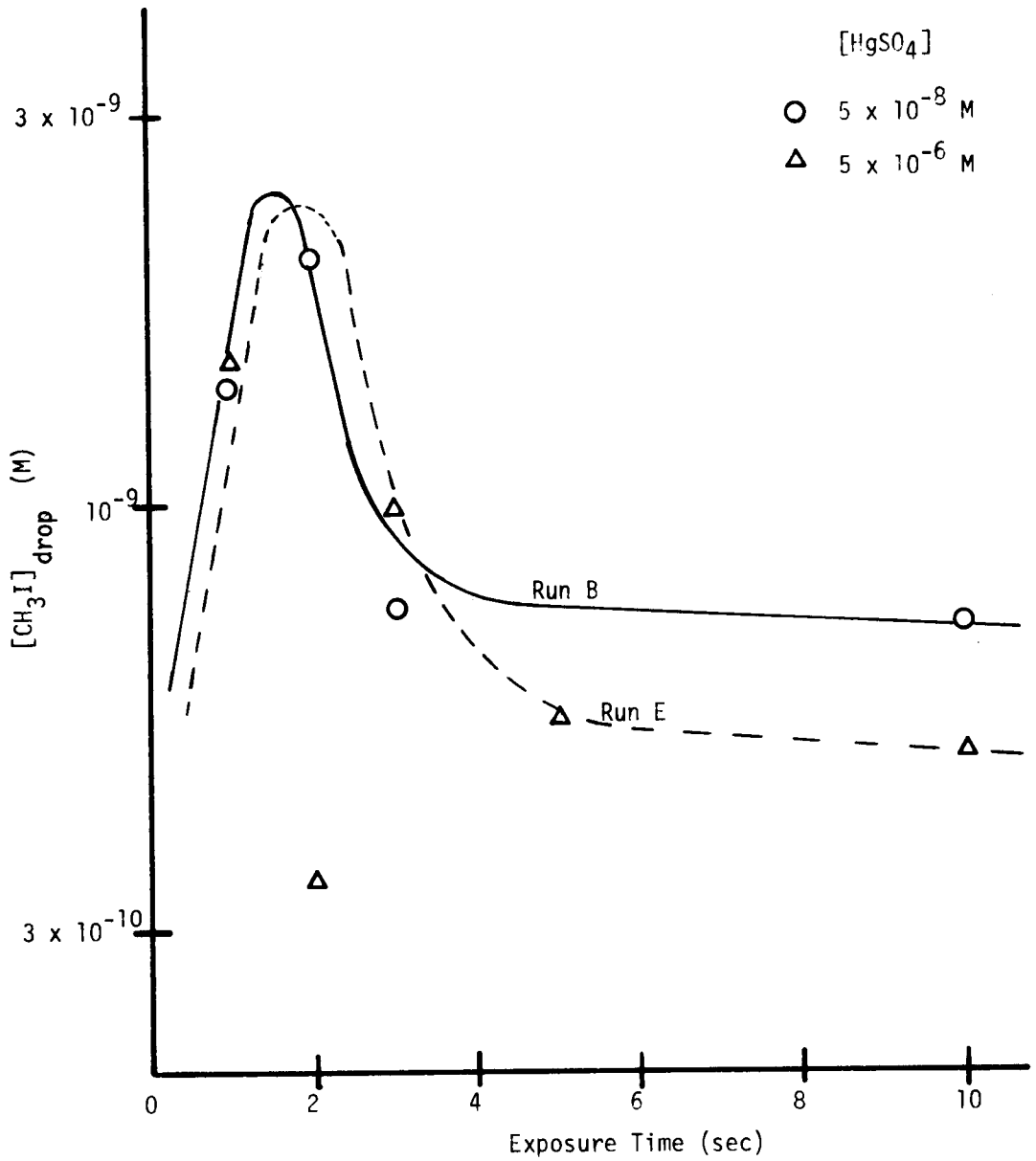

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$[CH_3I]_{drop}$ Vs Exposure Time for $HgSO_4$

DATE	DRAWN BY	FILE NO.	FIG.
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react with the mercury salt to form certain reaction products; and due to the chemical reaction the CH_3I in the drop is now rapidly consumed and the total CH_3I concentration falls. At exposure times greater than about 7 to 8 sec, the CH_3I concentration in the drop is fairly low, and the reaction rate is reduced correspondingly until at some later time there is a dynamic equilibrium between the mass transfer to the drop and the CH_3I consumed by the reaction. When this occurs, the slope of the response curve in Figs. 5 and 6 becomes very small. The above two rate processes can be adequately represented by the following simplified model:

$$aCH_3I + bHgCl_2 \longrightarrow \text{products} \tag{5}$$

and

$$\frac{d[CH_3I]_d}{dt} = -K_1[CH_3I]_d^a\,[HgCl_2]_d^b + \frac{K_D A_D}{V_D}(2.81[CH_3I]_g - [CH_3I]_d) \tag{6}$$

where:

K_1 = reaction rate constant

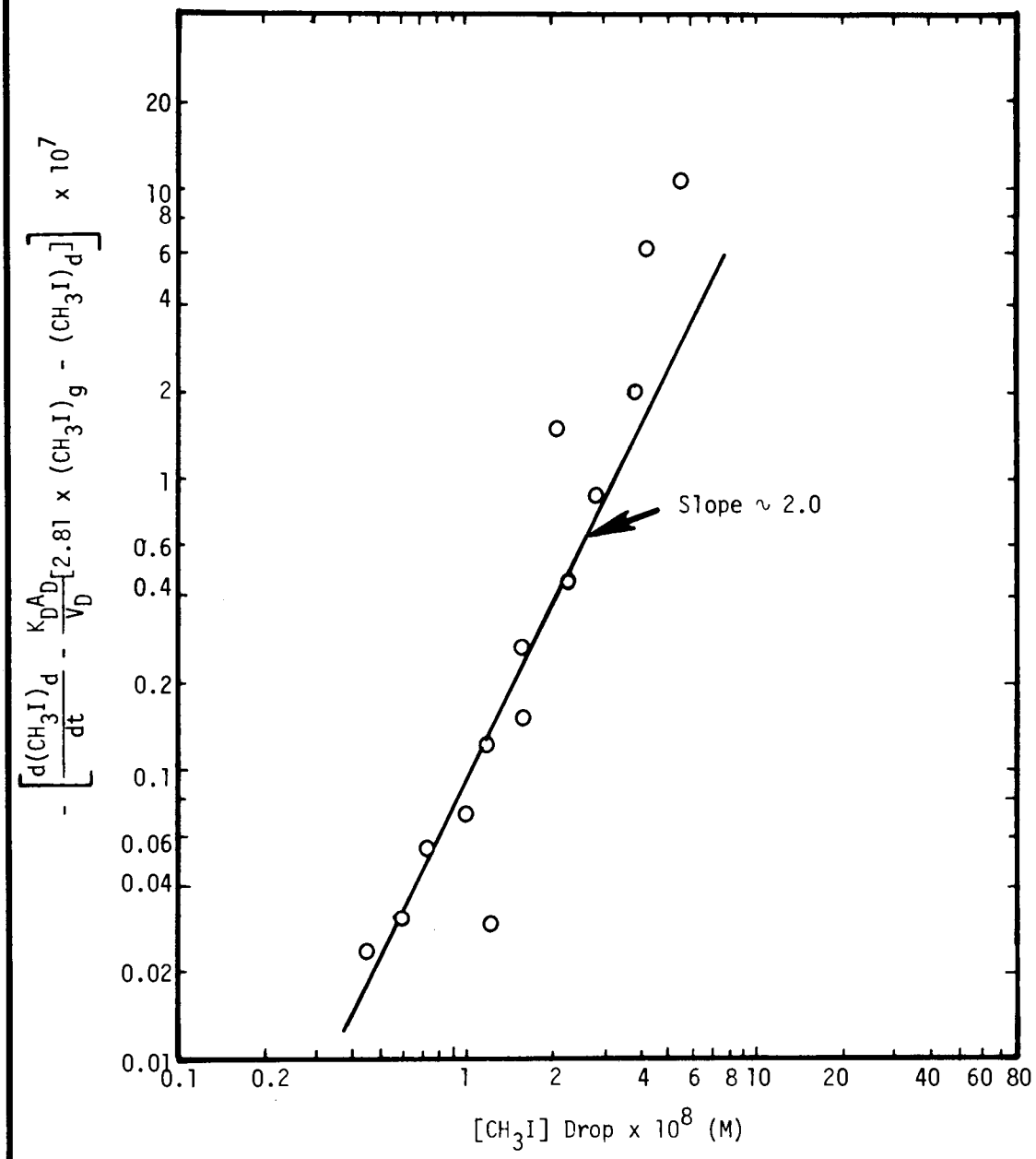
$[HgCl_2]_d$ = $HgCl_2$ concentration in drop at any time t

In the above equation the first term on the right hand side is a reaction rate term which accounts for the CH_3I consumption in the drop.

Since the $HgCl_2$ concentrations were greatly in excess, the change in $HgCl_2$ concentration during a run would indeed be negligible. Hence K_1 and $[HgCl_2]_d^b$ can be combined into a single pseudo reaction rate constant $K[1/sec(\ell/mole)^{a-1}]$, and Eq. (6) simplifies to

$$\frac{d[CH_3I]_d}{dt} = -K[CH_3I]_d^a + \frac{K_D A_D}{V_D}(2.81[CH_3I]_g - [CH_3I]_d) \tag{7}$$

Since it was believed that Runs F, G, and H were the most representative of the data, they were utilized in evaluating the order and rate constant for the chemical reaction (see Appendix 8.2 for details). In Fig. 7 the left hand side of Eq. (1), minus the mass transfer term, is plotted versus the CH_3I drop concentration at any time t. The slope of the curve on log-log coordinates is very close to 2.0 ($\pm$ 5%). In the figure there is some deviation at either very low or very high drop concentrations. At very low CH_3I concentrations in the drop corresponding to either very large or very small exposure times, the evaluation of the mass transfer coefficient is in considerable error due to the experimental and analytical techniques



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EVALUATION OF RATE CONSTANTS AND ORDER OF REACTION

DATE	DRAWN BY	FILE NO.	FIG.
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(see Appendix 8.3). On the other hand, for very large CH_3I concentration (t = 2 to 3 sec), the uncertainty involved in the kinetic data and in drawing the peak CH_3I concentration is considerable. In view of the above, it is concluded that the reaction within the drop is pseudo second order, and the reaction rate constant is 2.58×10^4 ℓ/hr-mole (see Appendix 8.2).

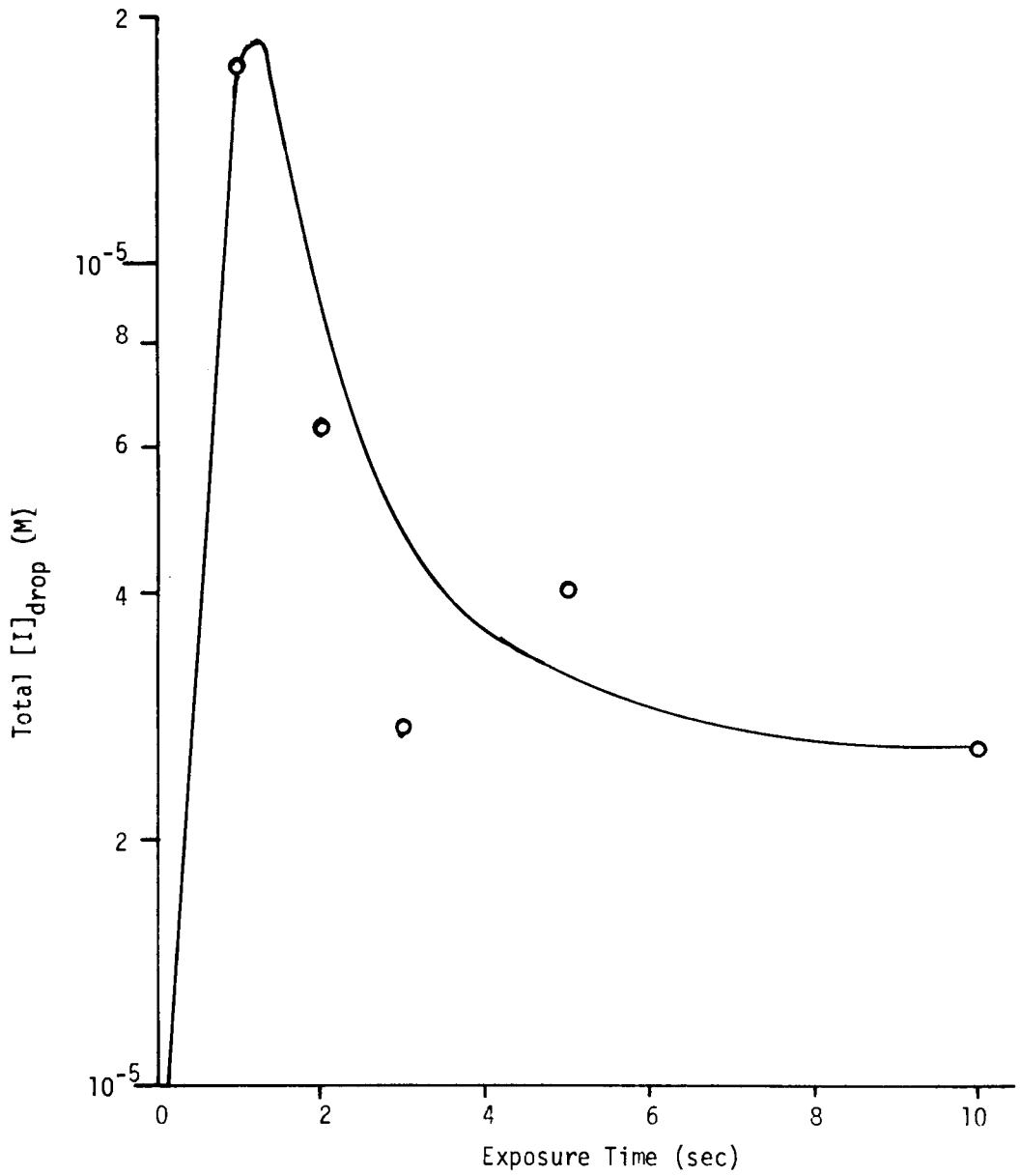
The total iodine content (based on neutron activation) in the aqueous drop containing mercury for Run A (5×10^{-9} M $HgSO_4$, see Table 1) is shown as a function of drop exposure time in Fig. 8. The total iodine content in the drop appears to be higher than the average methyl iodide concentration in the drop by almost an order of magnitude (strict comparison is not possible since Fig. 8 is for mercuric sulfate). This same trend was also observed for the control run (Fig. 4) and could be due to photolysis of CH_3I to I_2 or the presence of unidentified iodine complexes in the drop. This curve exhibits the same characteristically rapid increase in iodine concentration followed by a sharp decay and then a leveling off. This trend is qualitatively consistent with the mass transfer kinetic model discussed earlier. In the initial period total iodine increases due to rapid absorption and mass transfer during the early stages of drop formation and oscillation (see Sect. 4.1). For t > 2 sec the CH_3I reacts rapidly with the mercury salt and the decrease in total iodine in the drop can then be attributed to the volatilization or diffusion of the reaction products from the drop to the bulk gas phase. Ultimately around t > 8 sec a dynamic equilibrium between total iodine entering the drop due to mass transfer and the loss of iodine because of reaction product diffusion is achieved. At this exposure time the curve starts leveling off. Since the general shape of the curve with the mass transfer-kinetic model is so similar, it could be postulated that the unidentified iodine in the drop is not reacting with the mercuric salts. Further quantification from Fig. 8 was not possible since the results are based on $HgSO_4$ for which no reliable liquid sample gas chromatography data were available. However, the qualitative trend adds further credence to the postulated model.

4.3 Effect of pH

The effect of pH on the methyl iodide concentration in the drop as a function of exposure time is shown in Fig. 9. The mercury salt used was $HgCl_2$ of 3.7×10^{-5} M. The pH was varied from 2.2 to 9.9. An increase in drop pH appears to decrease the loss rate of methyl iodide from the drop. Since the fall in CH_3I concentration is due to chemical reaction, it appears from these decay curves that the rate of reaction is higher at a lower pH.

It is important to remember that the form of the mercury in solution is changed by the addition of the acid or base. Ammonium hydroxide was used to adjust pH because ammonia is known to form soluble complexes with mercuric salts as shown below:

$$HgCl_2 + 2NH_3 = Hg(NH_3)_2\,Cl_2 \qquad (8)$$



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TOTAL IODINE IN DROP AS A FUNCTION OF EXPOSURE TIME

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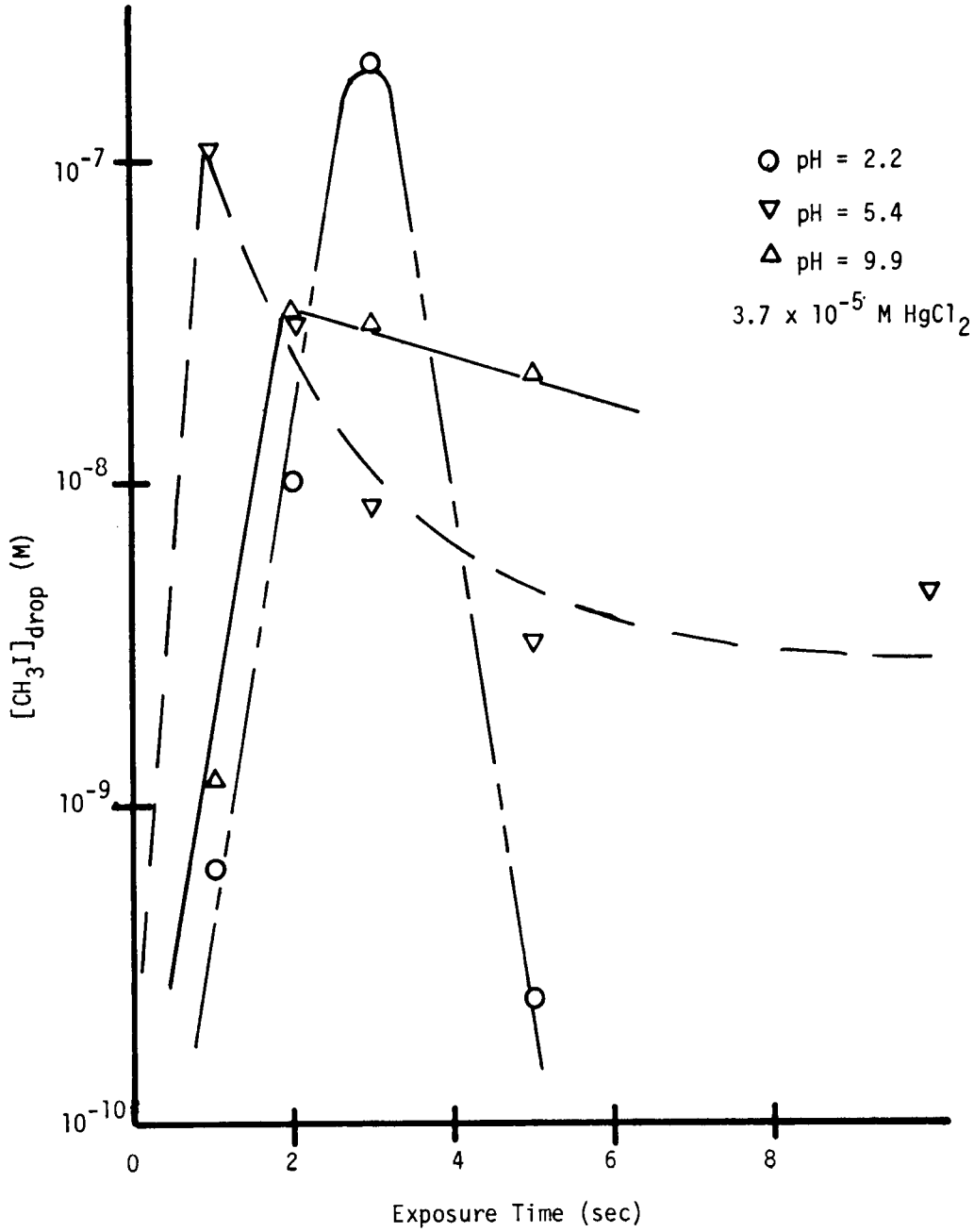

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EFFECT OF pH

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$$HgCl_2 + 2NH_3 = HgNH_2Cl + NH_4Cl \quad (9)$$

$$2HgCl_2 + 4NH_3 + H_2O = Hg_2NCl \cdot H_2O + 3NH_4Cl \quad (10)$$

For the low pH run nitric acid was present in such large quantities that the mercuric salt in the droplets would be more characteristic of mercuric nitrate than mercuric chloride. Nitric acid was used to prevent precipitation of the mercury. (HCl addition would have exceeded the solubility product of $HgCl_2$.) Because of this change in form of the mercury in the drops, it is difficult to attribute the trends observed only to the pH difference.

4.4 Identification of Compounds in Drop and Tunnel Gas

An attempt was made to identify the postulated compounds in the liquid drop and tunnel gas. Some of the possible reaction products could have been organo-mercury compounds such as methyl or ethyl mercury iodide, methyl or dimethyl mercury forms, and hydrocarbon gases, e.g., methane, ethane, propane, etc. The liquid drop samples were sent to the Analytical Chemistry Division for mass spectrometry analyses. Mass spectrometry of the organics extracted from the droplets with hexane showed an extremely large number of peaks in the range from 100 to 400 mass numbers. No CH_3HgI was seen in the mass spectrum. One mass spectrum did reveal the presence of ethyl mercury iodide C_2H_5HgI. This could have been formed by the reaction of CH_3I and the mercury salt. It is also worth noting that compounds with volatilities equal to or greater than that of water are lost from the sample during evaporation of hexane prior to injection into the mass spectrometer. Several compounds which may have been lost include the methyl and dimethyl mercury forms.

No results for mercury content of the droplet were obtained using atomic absorption because the methyl iodide in the sample was found to absorb at the same frequency as mercury thereby masking the mercury absorption. Attempted analysis of these same samples for mercury by additional atomic absorption and classical analytical chemistry techniques did not reveal any conclusive evidence since mercury concentrations were small, and there existed a distinct possibility of its adsorption on stainless steel tubes and fittings used in the analysis.

Samples from the tunnel gas were sent for chromatographic analysis by the Analytical Chemistry Division. Two unidentified peaks in addition to the CH_3I peak (see Appendix 8.5) were recorded by the gas chromatograph. Attempts were made to simulate these peaks by injecting methane, ethane, propane, and dimethyl mercury dissolved in ethanol into the gas chromatograph. Methane was observed to have the same retention time as one of the unknown peaks indicating that the tunnel gas did contain some methane. No peak was seen for dimethyl mercury on the gas chromatograph when it was

injected with ethanol. It is possible that the compounds decomposed or were adsorbed on the stainless steel fittings of the chromatograph or that the dimethyl mercury peak was masked by the ethanol peak. Identification of the unknown peaks was also attempted using a combination gas chromatograph-mass spectrometer to no avail. It should be noted that it is possible to decompose the methyl or dimethyl mercury forms to yield radicals in the wind tunnel in the presence of ultraviolet light.

4.5 Environmental Implications

Because only one mercury form was identified in the liquid and tunnel samples, it is only possible to theorize on possible environmental implications. Since some coals contain as much as 300 ppm mercury and one or two percent sulfur, one might postulate the presence of an aqueous drop containing mercuric sulfate. Such a drop in the presence of sunlight and a gaseous hydrocarbon like methane could result in the formation of organo mercury compounds or complexes. These airborne compounds, perhaps methyl, dimethyl, or ethyl forms, may then possibly interchange with the land and water phases of the environment, thereby causing a potential health hazard.

5. CONCLUSIONS

1. The reaction of methyl iodide with aqueous drops containing mercuric chloride under photolysis conditions is of pseudo second order with respect to CH_3I concentration. The pseudo second order rate constant was found to be 2.58×10^4 ℓ/hr-mole or 0.093×10^9 ℓ/mole-sec.

2. The overall mass transfer and kinetics of CH_3I to airborne aqueous drops containing an excess of mercury can be adequately represented by the rate model:

$$\frac{d[CH_3I]_d}{dt} = -0.093 \times 10^9 [CH_3I]_d^2 + \frac{K_D A_D}{V_D}(2.81[CH_3I]_g - [CH_3I]_d) \qquad (1)$$

3. The mass transfer coefficient, K_D, for the CH_3I to the drop at small exposure times was found to be at least two orders of magnitude higher than its steady state molecular diffusivity.

4. Increasing drop pH seemed to lower the rate of the CH_3I-Hg reaction.

5. Mercury salt concentrations from 10^{-3} to 10^{-7} M did not apparently effect the observed kinetics.

6. The total iodine content in the drop was 5 to 10 times higher than the CH_3I concentration in the drop for all exposure times. Methyl iodide was the only form of iodine identified in the drop.

7. Although attempts to identify specific reaction products in the drop and tunnel gas were unsuccessful, C_2H_5HgI and CH_4 were found in the liquid drop and tunnel gas, respectively.

8. Rain drops containing mercury salts can possibly react with hydrocarbons in the atmosphere producing organo mercury compounds.

6. RECOMMENDATIONS

1. Before adequate simulation of environment-mercury interactions can be successfully carried out, it will be necessary to develop several reliable analytical techniques for measuring a variety of mercury forms. The systems recommended for development are:

a) Neutron activation: The sample to be tested must be sealed in a quartz crystal before submission.

b) Gas chromatography (electron capture detector): The system recommended by Wallis et al. (6) for determination of organo-mercury compounds by multiple pass solvent extraction and re-extraction is suggested.

c) Gas chromatography - mass spectroscopy: Useful results may be obtained when the two are used in series.

d) High resolution flameless atomic absorption spectrometry.

2. To facilitate the detection of mercury forms existent in the environment, many organo mercury compounds should be synthesized and routinely identified under laboratory conditions

7. ACKNOWLEDGEMENT

We would like to express our appreciation for the consulting advice of B.A. Soldano of the Reactor Chemistry Division. In addition, we would like to thank Zell Combs for her invaluable assistance in gas chromatography analyses. Thanks are also due R. Matthews of Analytical Chemistry.

8.1 Sample Calculations for Mass Transfer Coefficient

The mass transfer coefficient, K_D, for CH_3I was calculated from the defining equations

$$\frac{d[CH_3I]_d}{dt} = \frac{K_D A_D}{V_D}([CH_3I]_{d,s} - [CH_3I]_d) \qquad (2)$$

$$[CH_3I]_{d,s} = D^*[CH_3I]_g \qquad (3)$$

The partition coefficient, D*, for CH_3I in water was calculated as the ratio of the CH_3I concentrations in the drop and tunnel gas after a 10-sec exposure time. A value of 2.81 was obtained.

average drop volume (100 collections), $V_D = 0.0416\ cm^3$

drop radius $= (V_D \times \frac{3}{4\pi})^{1/3} = 0.43$ cm

$\therefore$ mass transfer surface area per drop, $A_D = 4\pi r^2 = \pi D^2$

$= (4\pi)(0.43)^2 = 0.581\ cm^2$

Equation (2) can now be rewritten as,

$$(K_D)_t = \left(\frac{d[CH_3I]_d}{dt}\right)_t \left(\frac{V_D}{A_D}\right)\left(\frac{1}{2.81[CH_3I]_g - [CH_3I]_d}\right) \qquad (11)$$

For the control run (see Fig. 2), $[CH_3I]_g = 6.41 \times 10^{-7}$ mole/ℓ

$$\therefore \quad (K_D)_t = \frac{0.0716\left(\frac{d[CH_3I]_d}{dt}\right)_t}{18 \times 10^{-7} - [CH_3I]_d} \text{ cm/sec} \qquad (12)$$

$d[CH_3I]_d/dt$ was found from Fig. 2 and the K_D calculated for several exposure times. The results are shown in Table 2.

For t > 6 sec, the K_D values are apparently << 0.001, and a large error in these calculations results. Hence for the kinetic analysis for t > 6 sec, the steady state molecular diffusivity of 0.000268 cm/sec was utilized.

Table 2. Calculation of Mass Transfer Coefficients

Time (sec)	$[CH_3I]_d$	$\left(\frac{d[CH_3I]_d}{dt}\right)_t$	K_D (cm/sec)
0.5	2.15×10^{-9}	6.76×10^{-9}	0.000269
0.7	3.55×10^{-9}	1.159×10^{-8}	0.000462
1.0	7.60×10^{-9}	2.75×10^{-8}	0.00110
1.3	1.8×10^{-8}	6.53×10^{-8}	0.00262
1.6	4.10×10^{-8}	1.55×10^{-7}	0.00631
1.9	9.3×10^{-8}	3.67×10^{-7}	0.0154
2.0	1.25×10^{-7}	4.9×10^{-7}	0.021
2.4	3.6×10^{-7}	1.55×10^{-6}	0.077
2.7	7.5×10^{-7}	3.68×10^{-6}	0.251
3.0	1.38×10^{-6}	1.9×10^{-6}	0.324
3.5	1.45×10^{-6}	1.3×10^{-7}	0.0266
4.0	1.5×10^{-6}	1.27×10^{-7}	0.0051
5.0	1.55×10^{-6}	0.374×10^{-7}	0.0015
6.0	1.6×10^{-6}	0.29×10^{-7}	∿0.0008

8.2 Sample Calculations for Reaction Kinetics

In Sect. 4.2 it was mentioned that Runs F, G, and H were believed to be the most representative of the $HgCl_2$ data. Figure 10 is a sight average response for the three runs based on all data points. This was necessary since individual definition of the separate curves was not possible.

Equation (7), derived in Sect. 4.2, is now used to calculate the order and reaction rate constant.

$$\frac{d[CH_3I]_d}{dt} = -K[CH_3I]_d^a + \frac{K_D A_D}{V_D}(2.81[CH_3I]_g - [CH_3I]_d) \qquad (3)$$

or

$$-\left[\frac{d[CH_3I]_d}{dt} - \frac{K_D A_D}{V_D}(2.81[CH_3I]_g - [CH_3I]_d\right] = K[CH_3I]_d^a \qquad (13)$$

The average CH_3I concentration for the response shown in Fig. 10 was 3.34×10^{-7} gmole/ℓ (average for Runs F, G, and H).

For t = 0.5 sec, $[CH_3I]_d = 1.8 \times 10^{-9}$ gmole/ℓ. From Table 2, K_D = 0.000269 cm/sec.

$$\frac{K_D A_D}{V_D}(2.81[CH_3I]_g - [CH_3I]_d) = \frac{(0.000269)(0.581)}{0.141}[0.281(3.34 \times 10^{-7}) - (1.8 \times 10^{-9})]$$

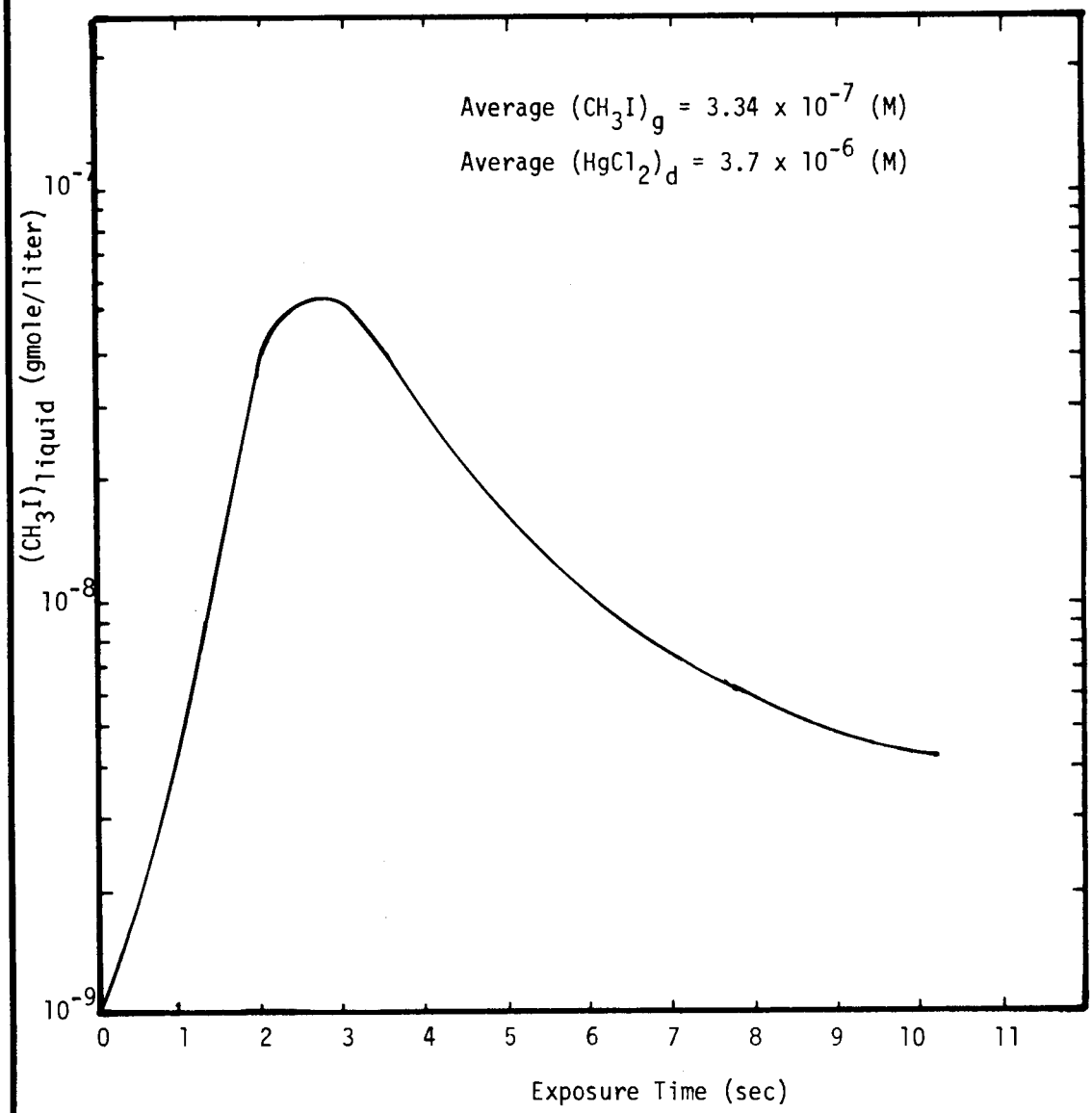
$$= 0.0322 \times 10^{-7} \text{ gmole/ℓ-sec}$$

From Fig. 10,

$$\frac{d[CH_3I]_d}{dt} = 2.32 \times 10^{-9} \text{ mole/ℓ-sec}$$

Upon substitution in Eq. (13),

$$-K[CH_3I]_d^a = 2.32 \times 10^{-9} - 0.0322 \times 10^{-7} = -0.0093 \times 10^{-7}$$



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AVERAGE RESPONSE USED FOR KINETIC ANALYSIS

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Similarly the other calculations were performed for different exposure times. The results are summarized in Table 3. Equation (13) is then plotted on log-log coordinates in Fig. 7. Slope of the line is the pseudo order of the reaction. This was found to be 2.0 (± 5%). The pseudo reaction rate constant (K) was then calculated from Eq. (13). Table 4 summarizes the values for K. The average value is 0.093×10^9 ℓ/mole-sec or 2.58×10^4 ℓ/hr-mole.

Table 4. Evaluation of Pseudo Second Order Rate Constant (K)

$[CH_3I]_d$	Left Hand Side of Eq. (13)	K (ℓ/mole-sec)
1.05×10^{-8}	0.1×10^{-7}	0.0907×10^9
3.25×10^{-8}	1.0×10^{-7}	0.0947×10^9
1.45×10^{-8}	0.2×10^{-7}	0.0951×10^9
2.32×10^{-8}	0.5×10^{-7}	0.0929×10^9
0.66×10^{-8}	0.04×10^{-7}	0.0918×10^9

Hence the overall model which represents the mass transfer and kinetics can be written as,

$$\frac{d[CH_3I]_d}{dt} = -0.093 \times 10^9 [CH_3I]_d^2 + \frac{K_D A_D}{V_D}(2.81[CH_3I]_g - [CH_3I]_d) \tag{1}$$

8.3 Discussion of Errors

Because of the nature of the uncertainties involved, any attempt to quantify the error would have little value. As such, only a brief mention of possible errors is given below.

8.3.1 Drop Collection

Drop exposure times of 1, 2, 3, 5, and 10 sec were used. As these times were based on simultaneous manipulation of an electric timer and the collection mechanism by the experimenter, it is assumed that errors up to 33% of the total time were realized for the 1, 2, and 3-sec times. Additionally, it is possible that unexposed drops on the nozzle head were

Table 3. Summary of Calculations for Kinetic Model

Time (sec)	$[CH_3I]_d$	K_D (cm/sec)	$\left(\frac{d[CH_3I]_d}{dt}\right)_t$	$\frac{d[CH_3I]_d}{dt} - \frac{K_D A_D}{V_d}(2.81[CH_3I]_g - [CH_3I]_d = K[CH_3I]_d^a$
0.5	1.8×10^{-9}	0.000269	2.32×10^{-9}	-0.009×10^{-7}
1.0	4.6×10^{-9}	0.0011	1.18×10^{-8}	-0.024×10^{-7}
1.1	6.0×10^{-9}	0.0018	1.25×10^{-8}	-0.031×10^{-7}
1.4	1.2×10^{-8}	0.0030	2.61×10^{-8}	-0.122×10^{-7}
1.5	1.55×10^{-8}	0.004	3.67×10^{-8}	-0.142×10^{-7}
2.0	3.8×10^{-8}	0.021	6.2×10^{-8}	-1.99×10^{-7}
2.5	5.5×10^{-8}	0.09	1.33×10^{-8}	-10.8×10^{-7}
3.5	4.2×10^{-8}	0.0266	-2.91×10^{-8}	-6.2×10^{-7}
4.0	2.8×10^{-8}	0.0051	-2.08×10^{-8}	-0.848×10^{-8}
4.35	2.3×10^{-8}	0.00280	-1.33×10^{-8}	-0.424×10^{-7}
4.5	2.1×10^{-8}	0.0024	-1.17×10^{-8}	-1.47×10^{-7}
5.0	1.58×10^{-8}	0.0015	-0.75×10^{-8}	-0.266×10^{-7}
5.5	1.22×10^{-8}	0.000268	-0.52×10^{-8}	-0.029×10^{-7}
6.0	1.0×10^{-8}	0.000268	-0.37×10^{-8}	-0.0713×10^{-7}
7.0	7.4×10^{-9}	0.000268	-0.20×10^{-8}	-0.0544×10^{-7}

occasionally knocked loose and dropped into the cup due to the force of insertion of the collector. This would cause lower concentrations (and hence absorption reported) of methyl iodide in the drop.

8.3.2 Impurities

It has repeatedly been shown that trace amounts of impurities in drops can act as surfactants in decreasing the internal circulation rate and in creating a physical barrier to diffusion, thereby decreasing mass transfer (3). As pH was varied throughout our experiment, it is possible that K_D would be effected.

8.3.3 Gas Chromatography

Several sources of error exist in the gas chromatography. CH_3I concentration in the sample collection bottles decays with time. For example, a fresh 10^{-7} M CH_3I solution gives a large, easily detectable peak in gas chromatography analysis but after one week's storage in a sample bottle, it is often no longer detectable. Based on this, nearly all the $HgSO_4$ droplet data were determined to be of doubtful value (it was stored 2.5 wk). The $HgCl_2$ droplet data appeared not to be effected significantly in accuracy as it was run within 48 hr of collection. (Control samples showed only slight decreases in CH_3I concentration over several days duration.) Secondly, extraction of 0.2 ml of aqueous solution with an equal volume of benzene and then injection of the organic phase in aliquots of 2 to 5 μℓ into the gas chromatography would result in small measuring errors. Thirdly, baseline drift and occasional random peak behavior persisted in the gas chromatography output regardless of the numerous adjustments and supposed corrections of the equipment. Errors arise from this, no doubt, though the effects are not distinguishable. Lastly, small errors in area measurements would increase with decreasing peak sizes.

8.3.4 Calculations

Because of the scatter encountered in the data, calculations based on slopes of experimental curves can possibly be in some error. The mass transfer coefficients used to calculate the rate constant were assumed to be the same as those found for the non-reactive water droplets. It was assumed that the presence of the mercury salt does not appreciably change the distribution coefficient of the CH_3I in the liquid (aqueous phase) and gas phases.

8.4 Gas Chromatography

8.4.1 Calibration Curves for Liquid Samples

Calibration curves for CH_3I concentration analysis of liquid samples were prepared by extracting standards of aqueous solutions with benzene, and running them through the gas chromatograph. The standard concentrations of CH_3I are plotted versus relative peak areas (see Figs. 11 and 12) for 2 μℓ and 5 μℓ benzene solution aliquots. Relative peak areas were determined by measurement with a Dietzgen planimeter.

8.4.2 Sample Output from Tunnel Gas Analysis

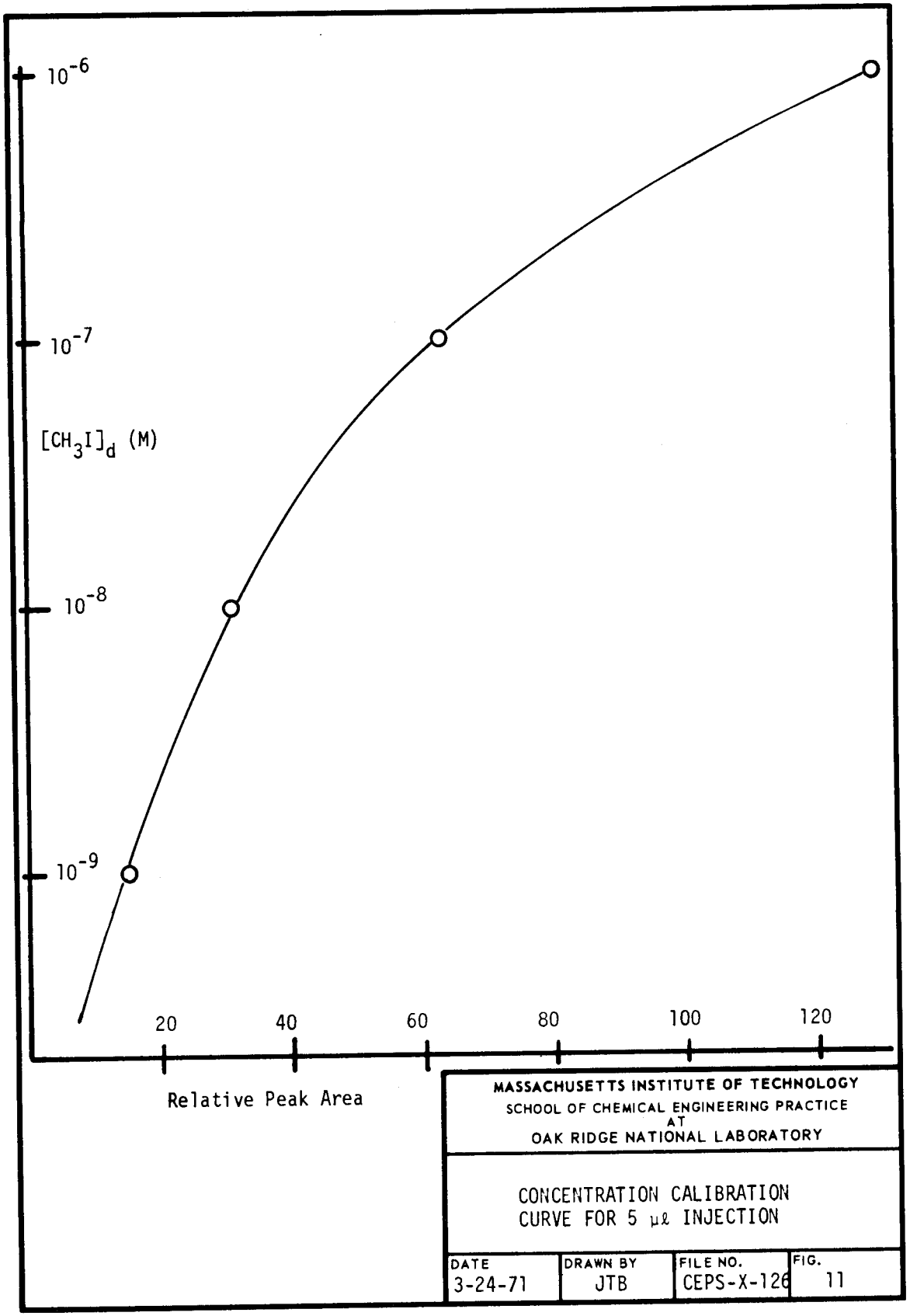
A sample chart showing the output from the tunnel gas analysis is given in Fig. 13.

8.5 Location of Original Data

All laboratory data were recorded in ORNL Databook A-5508-G, pp. 32-52, on file at the M.I.T. School of Chemical Engineering Practice, Bldg. 1000, ORNL.

8.6 Nomenclature

a,b	order of the reaction with respect to CH_3I and $HgCl_2$, respectively
A_D	mass transfer surface area/drop, cm^2
$[CH_3I]$	methyl iodide concentration, gmole/ℓ
D*	CH_3I partition coefficient
K	pseudo reaction rate constant, gmole/ℓ-hr
K_D	mass transfer coefficient, cm/sec
K_1	general reaction rate constant, $1/hr(\ell/gmole)^{a-1}$
M	molarity, gmole/ℓ
t	exposure time, sec
V_D	volume of drop, cm^3


10^{-6}
10^{-7}
$[CH_3I]_d$ (M)
10^{-8}
10^{-9}
20
40
60
80
100
120
Relative Peak Area
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CONCENTRATION CALIBRATION
CURVE FOR 5 μℓ INJECTION
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FIG.
11

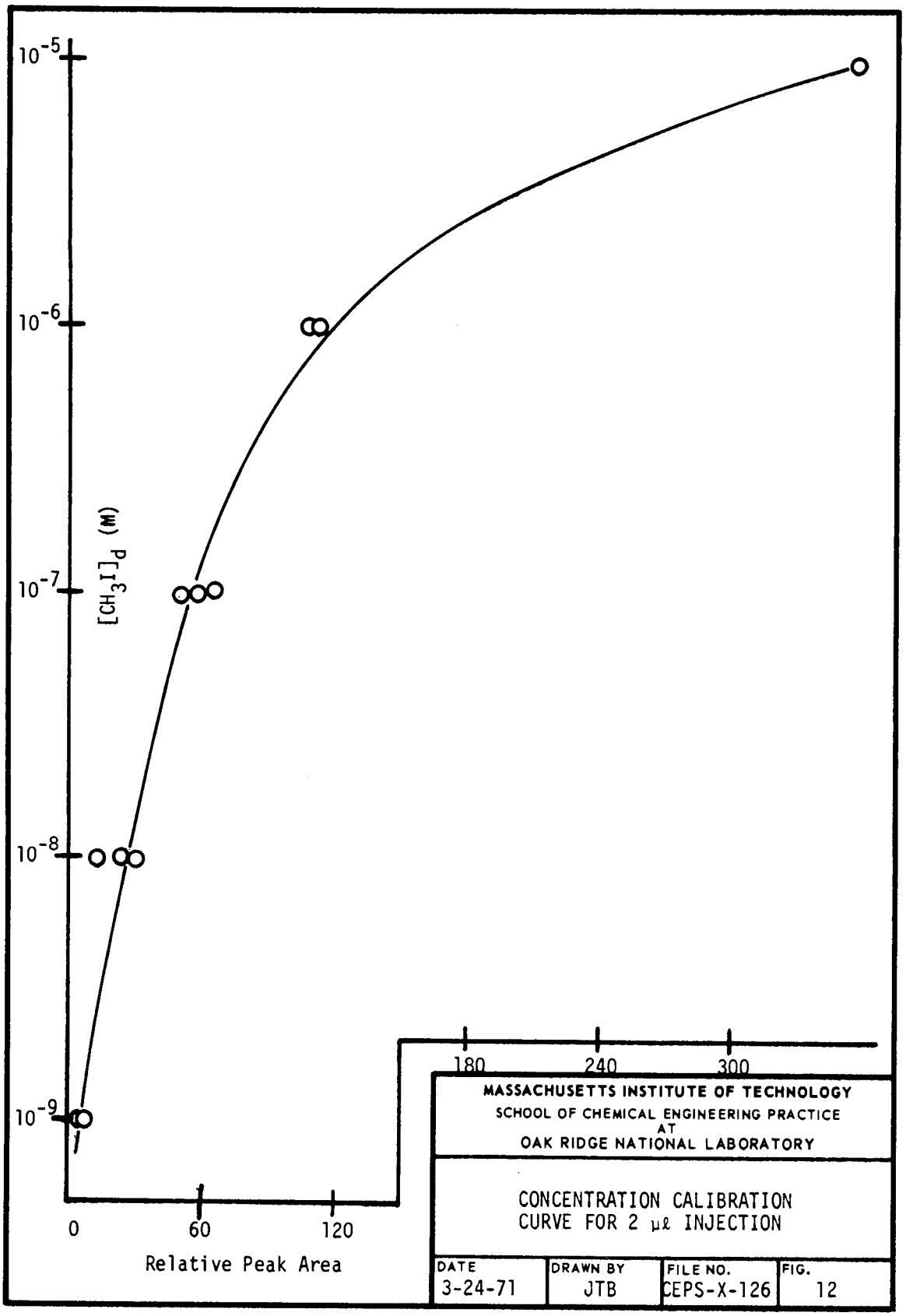
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
$[CH_3I]_d$ (M)
0
60
120
180
240
300
Relative Peak Area
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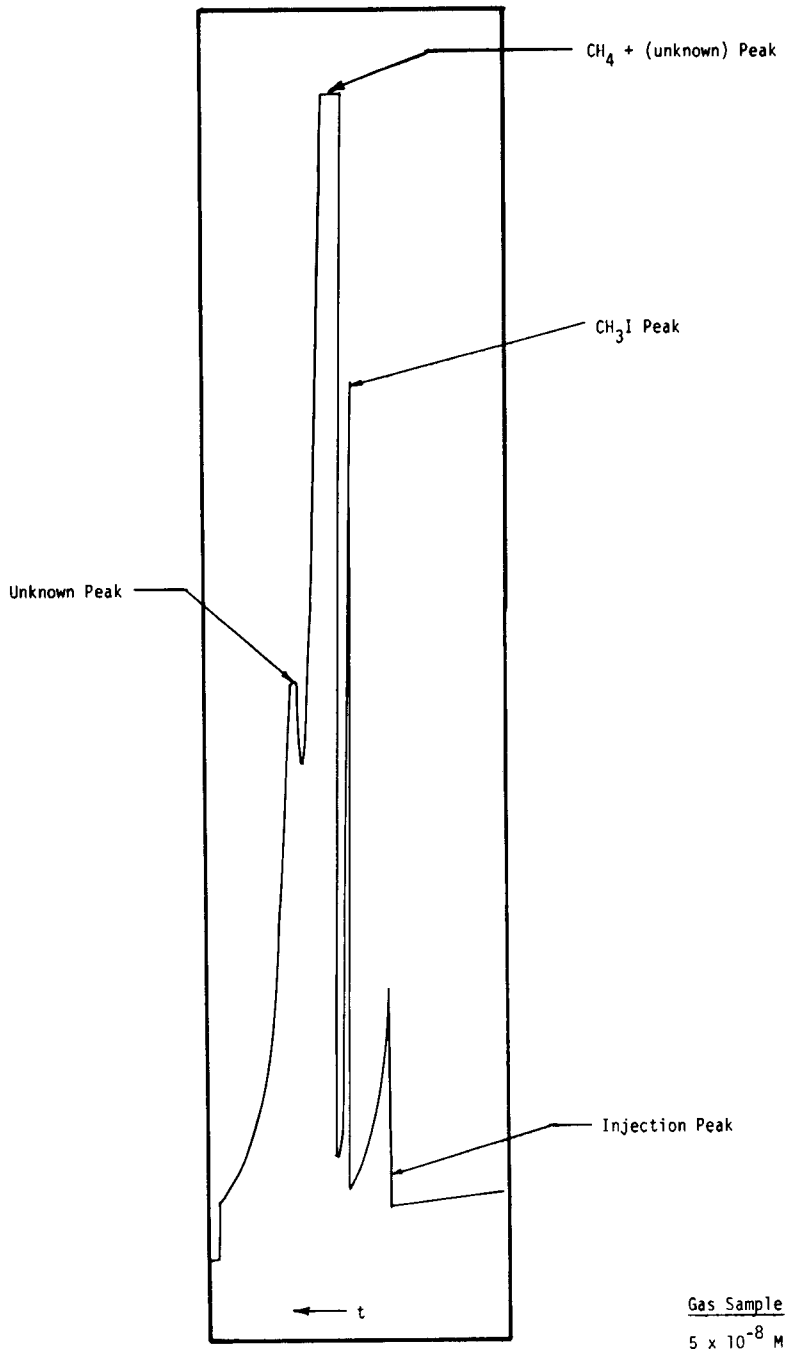
FIG.
12



Gas Sample

5×10^{-8} M $HgSO_4$

1 sec drop exposure

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GAS CHROMATOGRAPHY OUTPUT FOR TUNNEL GAS

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3-23-71	PHW	CEPS-X-126	13

Subscripts

d,D	drop
g	gas
S	drop saturated with methyl iodide
t	any time t

8.7 Literature References

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