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Report No. 6

RESEARCH ON ELECTROCHEMICAL ENERGY CONVERSION SYSTEMS

Interim Technical Report

By

R. T. FOLEY, D. H. BOMKAMP,

and W. R. BAIRD

February 1969

To

U. S. ARMY MOBILITY

EQUIPMENT RESEARCH AND DEVELOPMENT CENTER

Fort Belvoir, Virginia

Prepared By

The American University

Washington, D. C.

Contract No. DA-44-009-AMC-1386(T)

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SUMMARY

The investigation of electrochemical energy conversion systems has involved two specific tasks. The first has dealt with measurements of the solubility of oxygen in organic liquids which might provide the basis for high energy batteries. The solubility of oxygen in γ-butyrolactone is 5.5 ml/100 ml, in propylene carbonate, 1.7, in dimethyl sulfoxide, 3.7, and in N-nitrosodimethylamine, 6.6. The physical method used for these determinations gives results about 2.7% low when compared with literature values for the solubility of oxygen in water. No change in solubility was observed in butyrolactone due to the presence of added electrolyte - up to 0.8 M lithium perchlorate.

The second task deals with the mathematical analysis of electrochemical energy conversion devices. Attention was given to the solution of kinetic equations describing the hydrogen-deuterium exchange of an hydrocarbon on a catalytic surface saturated with deuterium. Kinetic expressions for a five step successive reaction for methane are solved by matrix techniques. These techniques should be conveniently handled by a digital computer and the expressions can be corrected for temperature, flow rates, and other experimental parameters.

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series of solvents. This plot is nearly linear and shows the relationship between log L and γ (3). This relationship has been expressed by Uhlig (4) as:

$$\log L = -\frac{4\pi r^2 \sigma + E}{2.303\,kT}$$

or, the energy required to form a cavity in a liquid surface is proportional to the product of the surface tension and the area of the cavity. This expression holds for simple one component solvent systems but fails for more complex systems.

The solubility has also been correlated as a function of solvent internal pressure $(\partial E/\partial V)_T$, with the higher internal pressure being associated with the lower gas solubility (5).

From an empirical standpoint it has been observed that the solubility of a gas will increase as a function of its molecular weight and size. For simple mono- and diatomic gases the order is He, H_2, N_2, CO, O_2, and Ar.

C. Methods for Determining Solubility of Gases in Liquids.

Many methods are reported in the literature and generally they may be placed in one of the following three categories:

a) chemical

b) electrochemical

c) physical.

The most common chemical method for the determination of oxygen in solution is the Winkler method (6). [illegible] the determination of oxygen [illegible] sulfuric [illegible]

List of Tables

I. INTRODUCTION

This is the sixth semi-annual report of research on high-energy electrochemical energy conversion systems. Up until now the overall program has been divided into seven tasks:

1. Determination of open circuit potentials of a series of couples in various electrolytes, and at appropriate temperatures;

2. Determination of the reversibility of these couples;

3. Electrochemical studies of high-energy couples leading to evaluation of these couples as materials for construction of high-energy electrically rechargeable storage systems;

4. Determination of kinetic parameters and evaluation of the rate limiting factors of selected reactions of electrochemical couples at appropriate electrodes;

5. Determination of kinetic parameters of selected reactions at catalytic electrodes;

6. Investigation of ion transport processes in membranes and/or electrolytes at elevated temperatures, and

7. Mathematical analysis of performance characteristics of electrochemical energy conversion devices.

The first five semi-annual progress reports described work on Tasks 1, 2, 3, 4, 6, and 7. During this reporting period work continued on Tasks 4 and 7.

II. TASK FOUR - OXYGEN ELECTRODE IN PROPYLENE CARBONATE

A. Objective

In the third progress report (1) on this project the concept and theoretical advantages of the air electrode were discussed. To interpret the experimental results from mass transport considerations it is necessary to know the solubility of O_2 in propylene carbonate. To correlate our results with those obtained in other systems it is required to know the solubility of oxygen in organic solvents such as γ-butyrolactone, dimethyl sulfoxide, dimethyl formamide, and N-nitrosodimethylamine. A survey of the literature failed to yield the pertinent data on the solubility of O_2 in these solvents. For these reasons the solubility of O_2 was measured in a number of organic solvents.

B. Solubility of Gases in Liquids

There have been many approaches to the explanation of gas solubility in liquids including various ways of treating the experimental data. Some of these are discussed in the monograph by Hildebrand and Scott (2). None of the approaches have been universally applicable.

One of the more successful treatments of solubility data utilizes a plot of log L (Ostwald absorption coefficient*) against σ (solvent surface tension) for a given gas in a

---

* $L = v_g/V_s$ where v_g is volume of gas absorbed and V_s is volume of solvent absorbing.

series of solvents. This plot is smoothly linear and shows clearly the relationship between log L and γ (3). This relationship has been expressed by Uhlig (4) as:

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The most common chemical method for the determination of gases in liquids is the Winkler method (6). [illegible] the determination of oxygen in [illegible] [illegible] sulfuric [illegible]

fication of the apparatus used by Morrison and Billett (9). This method was deemed sufficient to furnish results of the desired accuracy, i.e. about 1%. The equipment was constructed relatively easily using commercially available glassware. It was possible to connect the apparatus to the existing vacuum distillation system so that an organic liquid could be degassed by vacuum distillation and the receiver for the distillate could become the reservoir for the gas solubility apparatus. Other modifications to the apparatus were possible to yield greater accuracy but the increased expense and difficulty of operation could not be justified.

The apparatus is schematically shown in figure 1 and is pictured along with the vacuum distillation apparatus in figure 2. This apparatus consists of two calibrated gas burettes joined at their bottoms. One of the burettes is attached to a rough liquid manometer to allow for maintenance of atmospheric pressure in one-half of the system. A large glass spiral is mounted on top of the other burette and provides a large area for gas absorption. As the degassed liquid is dripped from the reservoir into the spiral the liquid will flow down through the spiral as a thin film.

A maximum surface area for absorption will then be presented to the gas. The gas in the two burettes is separated by a U-shaped column of liquid so that there is a decrease of pressure in the absorption burette as liquid enters the spiral, while atmospheric pressure is maintained in the other column. The amount of gas absorbed is equal to the volume differential correcting for the vapor pressure of the solvent.

The experimental procedure is carried out as follows:

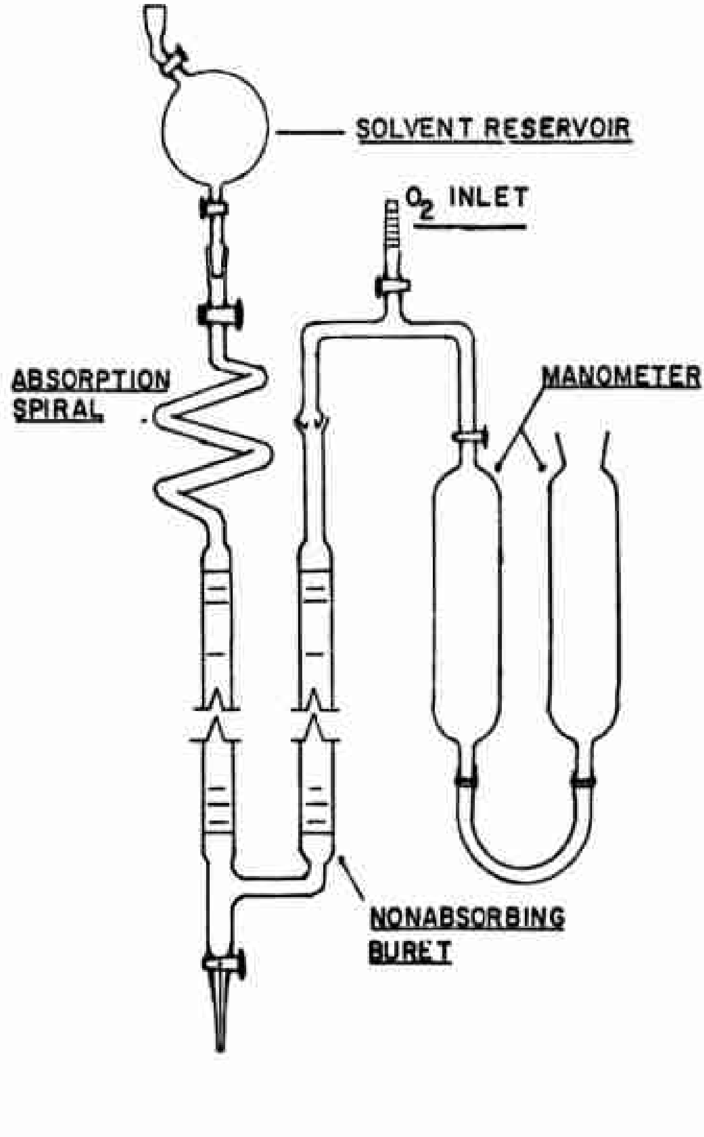


Figure 1. [illegible] and [illegible] apparatus.

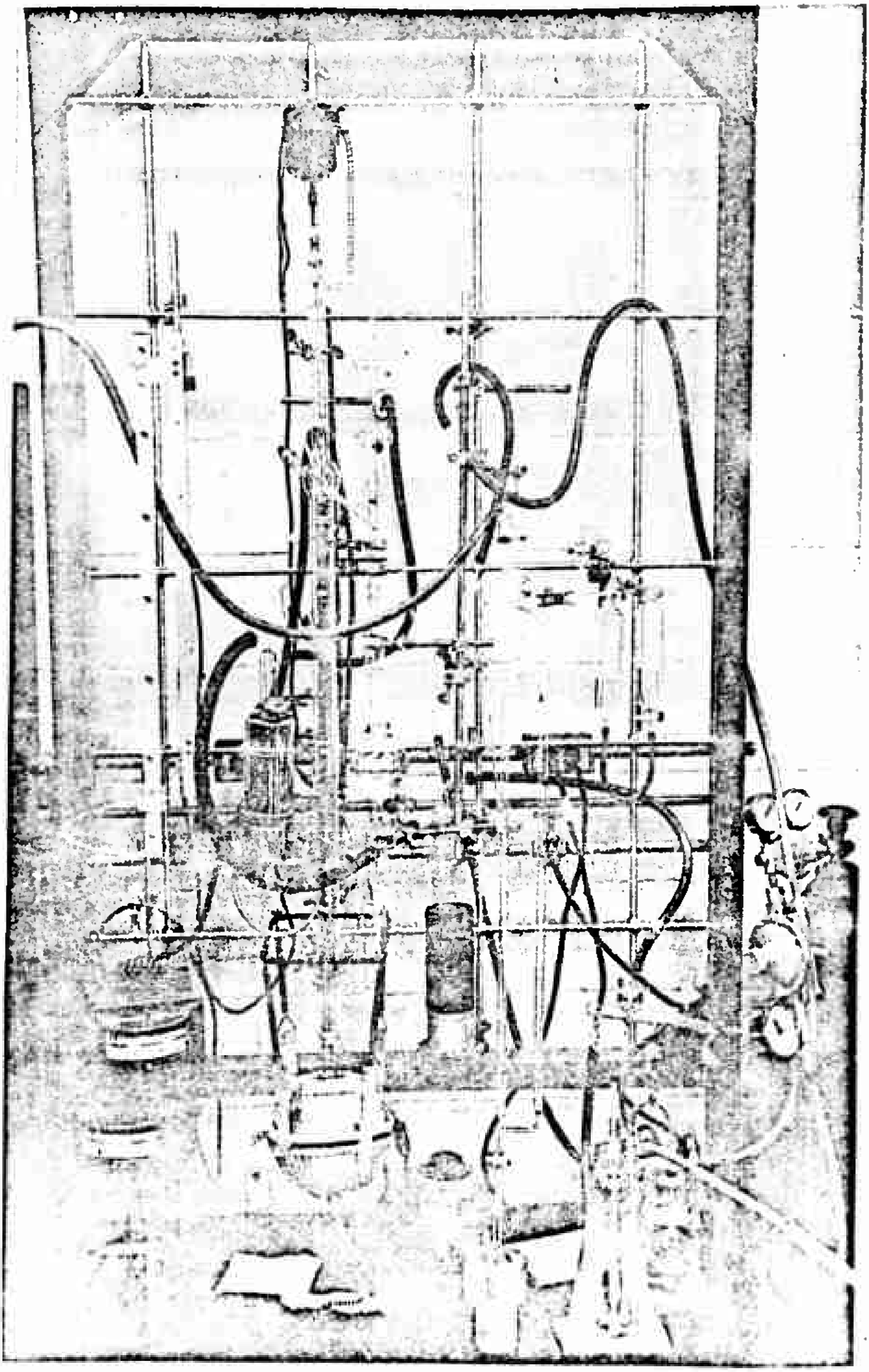


Figure 2. Gas solubility apparatus and vacuum distillation equipment.

1) The solvent is degassed. This is accomplished by vacuum distillation using the Nestor-Faust spinning band distillation column. The distillate is collected in a flask which is then attached to the top of the absorption apparatus via a ground glass fitting.

2) The U-portion connecting the two burettes is filled with pure solvent until the liquid stands at the zero level in both burettes.

3) The oxygen gas is flowed through the two burettes to completely fill them and to saturate the U- portion of solvent.

4) Both columns of gas are returned to atmospheric pressure and all outlets to the atmosphere are closed off.

5) The solvent in the reservoir is slightly pressurized with hydrogen to assume that it will flow into the apparatus. This is done through a gas inlet tube connected to the sample reservoir flask.

6) The solvent is dripped into the absorption spiral at a rate of about 2.5 ml/minute and collected in a volumetric flask as it flows out of the burette at the same rate.

7) After collecting some appropriate volume in the volumetric flask, such as 100 ml, the burettes are drained until the non-absorption side reads 0.0 ml. This indicates that that side is at atmospheric pressure. The amount of solvent above 0.0 in the absorption side is the amount of O_2 absorbed; this must be added to the volume collected.

E. Results and Discussion

One important modification made in the apparatus over that described by Morrison and Billett (9) involved the use of a slight pressure head to maintain a flow of solvent into absorbing burette. This pressurizing gas will be absorbed to some degree and then will be released into the spiral. This obviously decreases the observed solubility of oxygen in the organic liquid by some magnitude. If the pressurizing gas is oxygen a large negative error would be expected. If the pressurizing gas were N_2, or H_2 a smaller error would be expected and the question was whether the error would be small enough to be tolerated. To investigate this effect and also to study the precision and accuracy of the method, a number of experiments were performed with water as the solvent. These values are reported in Table I. As expected, when O_2 was used as the pressurizing gas the values were quite low--by 58%. Although the pressurizing gas does not saturate the water during the time of exposure in the reservoir, considerable gas is absorbed. A series of experiments with N_2 as the pressurizing gas gave results that were 7.1% too low while H_2 produced an error of - 2.1%. The nitrogen runs are not replicates as certain improvements in technique were introduced as the experimental work progressed. For example, in the early work the elapsed time between degassing the solvent and running the experiment was often several hours. Values closer to the accepted literature value were obtained when the experiment was performed directly after degassing through vacuum distillation. Experiments N3, H1, and H2 were run in this manner and the average coefficient, 0.0277, was lower than the accepted 0.02847 value (8) by 2.7%. The results given below for oxygen solubilities in the organic liquids should then be assumed to be low by about 3% assuming that the solubility behavior in these organic solvents is similar to that in H_2O.

In Table II are given solubilities of oxygen in γ-butyrolactone, propylene carbonate, dimethyl sulfoxide, and N-nitrosodimethylamine.

Table I. Solubility of Oxygen in Water (25 ± 0.5°C)

Exp.	Pressurizing Gas	O_2 absorbed (ml/vol.)	O_2 absorbed (ml/100 ml.)	Atmospheric Pressure (mm. Hg)	c.*
A1	A_2	3.1/[illegible].3	3.0	75[illegible]	0.0[illegible]3
A2	A_2	2.[illegible]/1[illegible]	2.[illegible]	75[illegible]	0.0274
N1	N_2	[illegible].4/295	2.[illegible]5	-	0.02[illegible]
N2	N_2	10.5/390.9	2.7	-	0.0254
N3	N_2	3.0/105	2.9	-	0.0274
N4	N_2	7.0/2[illegible]2.[illegible]	2.4	-	(0.0[illegible]27)
O1	O_2	2/10[illegible]	1.[illegible]	754	0.017[illegible]
O2	O_2	1.3/101	1.[illegible]	75[illegible]	0.0170
O3	O_2	1.[illegible]/15[illegible]	0.67	752	0.0063
O4	O_2	1.1/100	1.1	751	0.0104
O5	O_2	1.7/[illegible]	0.05	753	0.00303
Literature value (25°C)					.0285

* Calculated [illegible]; [illegible] $\frac{V_g}{V} \cdot \frac{273}{T}$ [illegible] V_g [illegible] of O_2 [illegible]

[illegible]

Table II. Solubility of Oxygen in Organic Solvents (25 ± 0.5°C)

Solvent	Solubility (ml/100 ml)	Average α	Literature Value
γ-butyrolactone	5.2	0.0499	
	5.6		
	5.8		
	5.2		
Propylene carbonate	1.7	0.0153	
	1.6		
	1.7		
	1.7		
Dimethyl sulfoxide	3.8	0.0342	0.01g O_2/100g (10)
	3.8		
	3.7		(6.4 ml/100 ml)
	3.6		
N-nitrosodimethylamine	6.6	0.0[illegible]	5 x 10$^{-[illegible]}$ [illegible] (11)
	7.1		(11 ml ± [illegible] ml/100 ml)
	6.0		

there is not much good data in the literature to compare our results, but [illegible] the fact that the literature [illegible] different figures. The solubility of oxygen in propylene carbonate [illegible] about 30% of that in butyrolactone. The solubility of [illegible] at [illegible] nitro[illegible], a solvent in which [illegible]. It would appear that propylene carbonate [illegible] particularly good choice for an organic solvent [illegible] oxygen electrode if solubility is [illegible].

One further [illegible] effect of the particular electrolyte [illegible] in the cell [illegible] for the solubility of oxygen [illegible] various concentrations of lithium perchlorate. [illegible] in figure 2 indicate [illegible] in these electrolytes. [illegible] has very little difference [illegible] nitro[illegible] fluorophosphate, [illegible].

[illegible]

Table III. Solubility of Oxygen in Lithium Perchlorate - γ-Butyrolacton Solutions

Concentration ($LiClO_4$ (M))	Solubility (ml/100 ml)	c
0.2	5.6	0.0513
0.45	5.8	0.0531
0.6	5.4	0.0495
0.8	5.6	0.0513

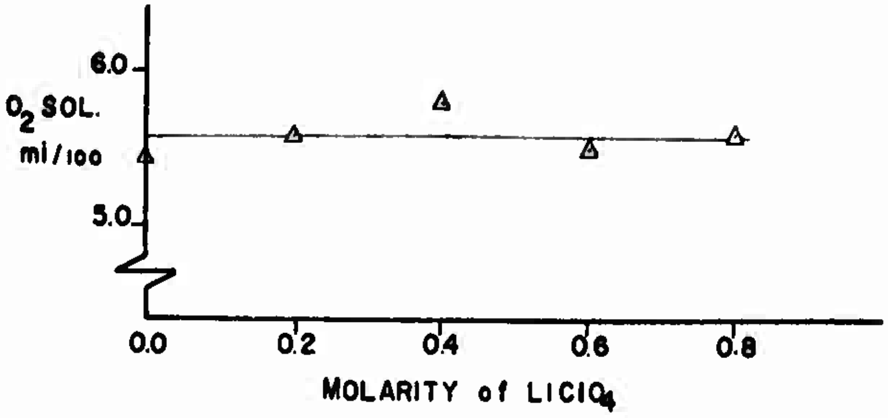


Fig. 3 O_2 SOLUBILITY IN BUTYROLACTONE vs. $LiClO_4$ CONCENTRATION

a solvent that was saturated with oxygen by mechanical stirring or agitation with a gas diffuser would tend to yield high values. This might account for some of the results reported in the literature that appear to be high.

III. TASK SEVEN - MATHEMATICAL ANALYSIS OF ELECTROCHEMICAL ENERGY CONVERSION SYSTEMS

A. Background

The reaction of hydrocarbons on a fuel cell catalyst is being studied by observing the H-D exchange of the hydrocarbon on the surface saturated with D_2. Studying the kinetics of this exchange is complicated by the large number of ways in which deuterated species can be formed, which makes solution of the rate expressions difficult. In this section techniques for solving the rate expressions for the successive deuteration of methane are described. Kinetic expressions for first order successive reactions of the type

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

have been solved for three step irreversible reactions. The rate expressions for the three step successive reaction are:

$$\frac{d[A]}{dt} = -k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B]$$

These expressions can be integrated to the form:

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = [A]_0 \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$[C] = [A]_0 \left\{1 + \frac{1}{k_1 - k_2}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right\}$$

For a five step successive reaction,

$$A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$$

solution of the rate expression by calculus methods would be difficult.

By use of other techniques, these expressions can be solved more efficiently.

B. Discussion

Solution of the rate expressions for a five step successive reaction would be desirable in order to create a model for reactions such as the successive one site exchange of D for H in CH_4. When gaseous CH_4 is passed over a catalytic surface which has been exposed to D_2 such that all available sites are assumed to be occupied and only one exchange of D for H is made with each contact of the molecule with the surface, the reaction is:

$$CH_4 \xrightarrow{k_{01}} CH_3D \xrightarrow{k_{12}} CH_2D_2 \xrightarrow{k_{23}} CHD_3 \xrightarrow{k_{34}} CD_4$$

If it is assumed that the rate of increase of a deuterated species is proportional only to the number of molecules of the lower deuterated species and the probability of transition from one specie to the next higher deuterated specie, first order reaction kinetics can be used for each transition between specie and the rate expressions are:

(1)

$$\frac{d[CH_4]}{dt} = -k_{01}(CH_4)$$

$$\frac{d[CH_3D]}{dt} = k_{01}(CH_4) - k_{12}(CH_3D)$$

$$\frac{d[CH_2D_2]}{dt} = k_{12}(CH_3D) - k_{23}(CH_2D_2)$$

$$\frac{d[CHD_3]}{dt} = k_{23}(CH_2D_2) - k_{34}(CHD_3)$$

$$\frac{d[CD_4]}{dt} = k_{34}(CHD_3)$$

The solutions for these expressions are given in Appendix A and are:

(2)

$$(CH_4) = (CH_4)_0 e^{-k_{01}t}$$

$$(CH_3D) = (CH_4)_0 \frac{k_{01}}{k_{12}-k_{01}}\left(e^{-k_{01}t} - e^{-k_{12}t}\right)$$

$$(CH_2D_2) = (CH_4)_0 \left\{k_{01}k_{12}\left[\frac{e^{-k_{01}t}}{(k_{12}-k_{01})(k_{23}-k_{01})} + \frac{e^{-k_{12}t}}{(k_{01}-k_{12})(k_{23}-k_{12})} + \frac{e^{-k_{23}t}}{(k_{01}-k_{23})(k_{12}-k_{23})}\right]\right\}$$

$(CHD_3) = (CH_4)_0 \{$ [illegible]

$+$ [illegible] $+$ [illegible]

$+$ [illegible] $\}$

$(CD_4) = (CH_4)_0 \{ 1 +$ [illegible]

$+$ [illegible]

$+$ [illegible]

$+$ [illegible] $\}$

Larson and Hall (12) assumed the expressions (1) to be applicable in the H-D exchange of CH_4 on a deuterated silica-alumina surface. In the absence of the solutions to all the rate expressions, the authors solved the first rate expression for the value of k_{01} and assumed that the rate of exchange per hydrogen atom is $(\frac{1}{4})\, k_{01}$, regardless of the molecule reacting, i.e., $k_{12} = 3/4\, k_{01}$, $k_{23} = 1/2\, k_{01}$, $k_{34} = 1/4\, k_{01}$. This assumption implies that the rate of H-D exchange is constant, with a correction made for the number of H's available. This assumption provided k values for the remainder of the rate expressions which were then numerically evaluated from the experimental data. The values calculated by the authors using this technique were consistent with the experimental values.

As a verification of the concentration expressions (2), the concentration of each of the deuterated species was calculated using the author's calculated value of k_{01} and the assumptions $k_{12} = 3/4\, k_{01}$, $k_{23} = 1/2\, k_{01}$, $k_{34} = 1/4\, k_{01}$. The calculated values agree with the experimental values within experimental errors, indicating that the assumptions regarding the k values are reasonable. However, with the concentration expressions (2), it would not have been necessary to make any assumptions regarding the k values, as each k can be solved for independently using these expressions.

Since the probability of a H-D exchange does appear to be independent of the specie reacting, a binomial distribution of the deuterated species when at equilibrium is suggested where $p = 1/4$ in $P_x = \frac{4!}{x!(4-x)!} p^x (1-p)^{4-x}, x = 0,1,\ldots 4$. The use of the binomial distribution is allowed by inspecting the manner in which each of the deuterated specie is formed. For example, in order to form D_2, there must have been two contacts of the CH_4 molecule with the surface in which an H-D exchange occurred, and two contacts with the surface in which an H-D exchange did not occur. If $p=1/4$ is the probability of any particular H of CH_4 exchanging on the surface, then the probability of two successful exchanges and two unsuccessful exchanges is $p^2(1-p)^2 = (1/4)^2(3/4)^2$. Since the number of ways in which four H atoms taken two at a time can be arranged is $\frac{4!}{2!(4-2)!} = 6$, the total probability of forming D_2 is $P_2 = \frac{4!}{2!\,2!}(1/4)^2(3/4)^2 = .211$.

The calculated values are:

$P_0 = .316$

$P_1 = .422$

$P_2 = .211$

$P_3 = .047$

$P_4 = .004$

The mean number of H atoms exchanged is $4(1/4) = 1$

When these probability values are expressed as a ratio:

(CH_4) cc. 1

(CH_3D) cc. 1.244

(CH_2D_2) cc. .41

(CHD_3) cc. .15

(CD_4) cc. .013

The equilibrium distribution of the deuterated species from ref(12) are:

(CH_4) cc. 1

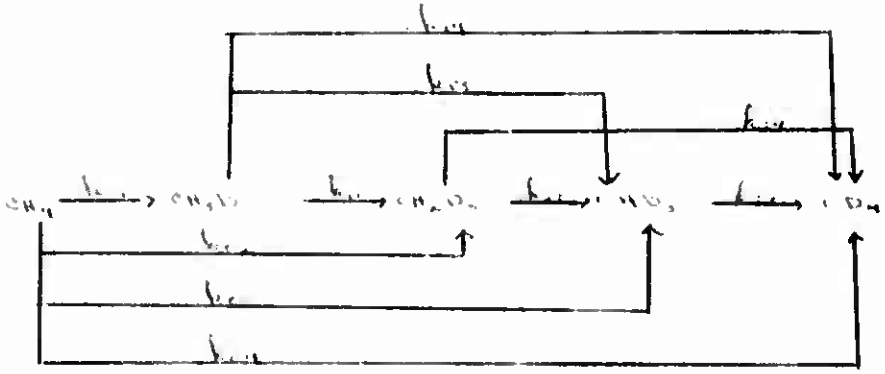
(CH_3D) cc. 1.25

(CH_2D_2) cc. 0.40

(CHD_3) cc. 0.10

(CD_4) cc. 0.013

Thus far it has been assumed that only one H-D exchange can occur when a specie contacts the surface. If more than one H-D exchange can occur on contact with the surface, the following diagram represents the ways in which deuterated species can be formed:



When first order reaction kinetics are assumed, the rate expressions are:

$$\frac{d(CH_4)}{dt} = -(k_{01}+k_{02}+k_{03}+k_{04})(CH_4)$$

$$\frac{d(CH_3D)}{dt} = k_{01}(CH_4) - (k_{12}+k_{13}+k_{14})(CH_3D)$$

$$\frac{d(CH_2D_2)}{dt} = k_{02}(CH_4) + k_{12}(CH_3D) - (k_{23}+k_{24})(CH_2D_2)$$

$$\frac{d(CHD_3)}{dt} = k_{03}(CH_4) + k_{13}(CH_3D) + k_{23}(CH_2D_2) - k_{34}(CHD_3)$$

$$\frac{d(CD_4)}{dt} = k_{04}(CH_4) + k_{14}(CH_3D) + k_{24}(CH_2D_2) + k_{34}(CHD_3)$$

The solutions to these expressions using the techniques described in Appendix A are: where $A = (k_{01}+k_{02}+k_{03}+k_{04})$, $B = (k_{12}+k_{13}+k_{14})$, $C = (k_{23}+k_{24})$.

$$(CH_4) = (CH_4)_0 e^{-At}$$

$$(CH_3D) = (CH_4)_0 \left\{ \frac{k_{01}}{A-B} (e^{-Bt} - e^{-At}) \right\}$$

$$(CH_2D_2) = (CH_4)_0 \left\{ \frac{k_{02}}{A-C} (e^{-Ct} - e^{-At}) + k_{01}k_{12} \left[\frac{e^{-At}}{(C-A)(B-A)} + \frac{e^{-Bt}}{(A-B)(C-B)} + \frac{e^{-Ct}}{(A-C)(B-C)} \right] \right\}$$

$$(CHD_3) = (CH_4)_0 \left\{ \frac{k_{03}}{A-k_{34}} (e^{-k_{34}t} - e^{-At}) \right.$$

[illegible]

[illegible]

When transitions between species other than by one site exchanges are prohibited, the above expressions become identical to the previous expressions.

C. Matrix Solution of Differential Equations

The technique used to solve the differential equations was that of "compartment analysis" as introduced by Beauchamp. (13,14). Each of the five species of the methane reaction is considered to be a "compartment." The number of molecules in each compartment is a function of time and the probability of a transition of a molecule into and from the compartment. At the moment the mechanism of transition between compartments is not important, rather it is desired to create a mathematical model which will explain the experimental values. The model then should describe the number of molecules in each compartment as a function of the above two variables. It follows that this model be exact and rigorous and be based on a minimum number of a priori assumptions. Once the exact model has been determined, assumptions can be made based on physical likelihood, valid approximations, etc. The purpose of the effort is to determine how the experimental data can be explained. The criteria usually being a least square error fit of the experimental values. Once the proper reaction parameters have been determined, mechanisms which are consistent with the parameters can be postulated. If the experimental data can not be explained under any conditions, then the model created is not applicable.

The generalized linear differential equation

$$\frac{d}{dt}x_i = \sum_{j=1}^{N} k_{ij}x_j \qquad i = 1, 2, \cdots, N$$

can be rewritten in matrix notation

$$\frac{d}{dt}\begin{bmatrix} x_1 \\ x_2 \\ \cdot \\ \cdot \\ \cdot \\ x_N \end{bmatrix} = \begin{bmatrix} k_{11} & k_{12} & \cdots & k_{1N} \\ k_{21} & k_{22} & \cdots & k_{2N} \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ k_{N1} & & & k_{NN} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ \cdot \\ \cdot \\ \cdot \\ x_N \end{bmatrix}$$

$$\text{or} \quad \dot{X} = KX$$

The solution of the matrix equation is $X = e^{Kt}X_0$, or

$$\begin{bmatrix} x_1(t) \\ x_2(t) \\ \cdot \\ \cdot \\ \cdot \\ x_N(t) \end{bmatrix} = \begin{bmatrix} e^{k_{11}t} & e^{k_{12}t} & \cdots & e^{k_{1N}t} \\ e^{k_{21}t} & e^{k_{22}t} & \cdots & e^{k_{2N}t} \\ \cdot & & & \\ \cdot & & & \\ e^{k_{N1}t} & & & e^{k_{NN}t} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ \cdot \\ \cdot \\ \cdot \\ x_N \end{bmatrix}_0$$

where the vector X_0 is the value of $x(t)$ at $t=0$.

Saaty (15) shows the solution of the matrix e^{Kt} to be

$$e^{Kt} = \sum_{j=1}^{N} \frac{\prod_{i \neq j} (\lambda_i I - K)}{\prod_{i \neq j} (\lambda_i - \lambda_j)} e^{\lambda_j t}$$

where the λ_i $(i = 1, 2, \cdots, N)$ are the N distinct characteristic roots of the determinant K.

Using this method of solution, [illegible] (16) shows the solution for the reaction $c_1 \xrightarrow{k_{21}} c_2 \xrightarrow{k_{32}} c_3$.

The rate differential equations are:

$$\frac{dc_1}{dt} = -k_{11}c_1$$

$$\frac{dc_2}{dt} = k_{21}c_1 - k_{22}c_2$$

$$\frac{dc_3}{dt} = k_{32}c_2$$

In matrix notation, $\dot{c} = Kc$

the solution being $c(t) = e^{Kt}c$

where $$K = \begin{bmatrix} -k_{11} & 0 & 0 \\ k_{21} & -k_{22} & 0 \\ 0 & k_{32} & 0 \end{bmatrix}$$

The characteristic roots of K are given by the roots of the determinant $|\lambda I - K| = 0$

$$\begin{vmatrix} \lambda + k_{11} & 0 & 0 \\ -k_{21} & \lambda + k_{22} & 0 \\ 0 & -k_{32} & \lambda \end{vmatrix} = 0$$

The characteristic roots are $\lambda_1 = -k_{11}$, $\lambda_2 = -k_{22}$, $\lambda_3 = 0$.

The solution of [illegible] is then:

$$c(t) = \sum_{j=1}^{3} \frac{\prod (\lambda_j I - K)}{\prod_{i \neq j} (\lambda_j - \lambda_i)} e^{\lambda_j t}$$

evaluating the matrix products for e^{Kt},

$$e^{Kt} = \frac{(K-\lambda_2 I)(K-\lambda_3 I)}{(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)}e^{\lambda_1 t} + \frac{(K-\lambda_1 I)(K-\lambda_3 I)}{(\lambda_2-\lambda_1)(\lambda_2-\lambda_3)}e^{\lambda_2 t} + \frac{(\lambda_1 I-K)(\lambda_2 I-K)}{(\lambda_1-\lambda_3)(\lambda_2-\lambda_3)}e^{\lambda_3 t}$$

when these products are formed and addition made by matrix addition.

$$e^{Kt} = \begin{bmatrix} e^{-k_{21}t} & 0 & 0 \\ \frac{k_{21}}{k_{21}-k_{32}}\left(e^{-k_{32}t}-e^{-k_{21}t}\right) & e^{-k_{32}t} & 0 \\ 1+\frac{1}{k_{32}-k_{21}}\left(k_{21}e^{-k_{32}t}-k_{32}e^{-k_{21}t}\right) & 1-e^{-k_{32}t} & 1 \end{bmatrix}$$

Substituting e^{Kt} into $C(t) = e^{Kt}C_0$

$$\begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix} = \begin{bmatrix} e^{-k_{21}t} & 0 & 0 \\ \frac{k_{21}}{k_{21}-k_{32}}\left(e^{-k_{32}t}-e^{-k_{21}t}\right) & e^{-k_{32}t} & 0 \\ 1+\frac{1}{k_{32}-k_{21}}\left(k_{21}e^{-k_{32}t}-k_{32}e^{-k_{21}t}\right) & 1-e^{-k_{32}t} & 1 \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix}_0$$

In instances where the initial concentrations are zero except for (C_1), where at $t = 0$, $C(0) = C_1(0)$, only the first column of the matrix e^{Kt} need be formed, which considerably reduces the work required in multiplying matrices.

The above technique [illegible] for single [illegible]. In the latter [illegible] rate constants, [illegible] (k_{21}, k_{32}, [illegible]).

D. Conclusions

Exact expressions have been derived for H-D exchange of methane on a surface of adsorbed deuterium. While the expressions are awkward to handle, valid approximations are available which will ease calculations.

From the symmetry of the expressions for the multiple site exchange, it appears that the expressions for other molecules can be deduced with a minimum of calculations.

There are several advantages to this method of solving kinetic expressions over calculus methods. In particular the matrix operations can be conveniently handled by a digital computer, not only to derive the concentration expressions but also to substitute experimental values into the rate expressions. Also in the matrix form, perturbation matrices can be included to apply any necessary corrections for temperature, flow rates, etc., without disturbing the original rate constant expressions.

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1 ORIGINATING ACTIVITY (Corporate author) The American University, Washington, D.C.	2a REPORT SECURITY CLASSIFICATION Unclassified 2b GROUP
3 REPORT TITLE [illegible]	
4 DESCRIPTIVE NOTES (Type of report and inclusive dates) [illegible]	
5 AUTHOR(S) (Last name, first name, initial) [illegible]	

6 REPORT DATE February 1969	7a TOTAL NO OF PAGES 26 + [illegible]	7b NO OF REFS [illegible]

8a CONTRACT OR GRANT NO DA-44-[illegible]-1595 (?) b PROJECT NO [illegible] c d	9a ORIGINATOR'S REPORT NUMBER(S) 9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
10 AVAILABILITY LIMITATION NOTICES Foreign announcement and dissemination of this report by DDC is not authorized. Not releasable to foreign nationals	
11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY U.S. Army Mobility Equipment Research and Development Center Fort Belvoir, Virginia

13 ABSTRACT

[illegible] investigation of electrolyte [illegible] involved two specific tasks. The first [illegible] solubility of oxygen in organic liquids [illegible] energy batteries. The solubilities of oxygen in [illegible] 5.5 ul/ml, in propylene carbonate, 1.7, in [illegible], 3.7, and in [illegible] [illegible]. [illegible] of oxygen in [illegible] due to the presence of [illegible] carbonate. [illegible]

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