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## **A Study of the Reactions of Alkali Metals With Alcohol in Liquid Ammonia**

Eugene Joseph Kelly  
*University of Tennessee - Knoxville*

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To the Graduate Council:

I am submitting herewith a dissertation written by Eugene Joseph Kelly entitled "A Study of the Reactions of Alkali Metals With Alcohol in Liquid Ammonia." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Jerome F. Eastham, Major Professor

We have read this dissertation and recommend its acceptance:

Charles W. Kennan, Hilton A. Smith, William E. Bull, D. D. Mueller

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

February 28, 1959

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Major Professor

We have read this dissertation  
and recommend its acceptance:

Carl Kelner

Hilton A. Smith

William E. Bull

D. D. Uicker

Accepted for the Council:

Ralph Hawthorn  
Dean of the Graduate School

A STUDY OF THE REACTIONS OF ALKALI METALS WITH  
ALCOHOL IN LIQUID AMMONIA

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A DISSERTATION

Submitted to  
The Graduate Council  
of  
The University of Tennessee  
in  
Partial Fulfillment of the Requirements  
for the Degree of  
Doctor of Philosophy

---

by

Eugene Joseph Kelly

March, 1959



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## CHAPTER I

### NATURE OF THE PROBLEM

#### A. Introduction

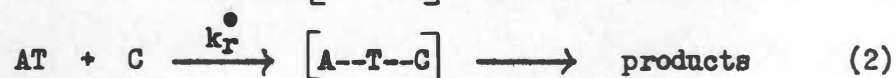
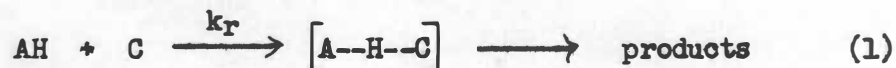
This thesis embodies the results of research performed under a contract between the University of Tennessee and the United States Atomic Energy Commission, the contract calling for an examination of certain chemical separation factors for the isotopes of hydrogen.

The investigation was centered on a study of the fractionation of the isotopes protium (hereafter called hydrogen) and tritium through the reaction of a weak acid with a metal. The reactions were carried out in a homogeneous system with liquid ammonia serving as solvent for the reactants.

#### B. Isotope Effects

##### 1. General Considerations

Consider the following pair of reactions



for which  $k_{\text{r}}$  and  $k_{\text{r}}^{\bullet}$  represent the specific rate constants for the reactions involving hydrogen and tritium (or deuterium) atoms respectively. As a result of the differences in the reactivities of bonds to hydrogen, deuterium, and tritium, the specific rate constants  $k_{\text{r}}$  and  $k_{\text{r}}^{\bullet}$  will differ

in magnitude.<sup>1,2,3</sup> The term "isotope effect" used to describe this phenomenon is properly defined by the expression

$$\beta\alpha = \frac{k_r}{k_r^\bullet} \quad (3)$$

where  $\beta$  is a term involving only symmetry numbers and  $\alpha$  is the "isotope effect." The exact nature of  $\beta$  and  $\alpha$  will be made clear in the following discussion.

According to the absolute theory of reaction rates, the specific rate constant for any reaction is given by the equation

$$k_r = \frac{kT}{h} \exp (-\Delta F_\ddagger / RT) \quad (4)$$

in which the symbols  $k_r$ ,  $k$ ,  $T$ ,  $h$ , and  $R$  represent the specific rate constant, the Boltzmann constant, the absolute temperature, the Planck constant, and the gas constant, respectively, and  $\Delta F_\ddagger$  is the free energy of activation for the reaction.<sup>4</sup> Since the factor  $\frac{kT}{h}$  is independent of the nature of the reaction, it follows that the specific rate constant for any reaction at a given temperature, is determined only by the free energy of activation. Consequently, the isotope effect is governed by the change in the free energy of activation resulting from isotopic substitution. This is shown by substituting the value of  $k_r$  as given by equation (4) into equation (3),

$$\beta\alpha = \exp (\Delta F_\ddagger^\bullet - \Delta F_\ddagger) / RT \quad (5)$$

where the dot refers to the heavier isotopic species, a convention to be followed throughout this discussion.

Again, according to the absolute theory of reaction rates, the specific rate constant may be expressed by the equation

$$k_r = K \frac{Q_{\ddagger}}{\prod Q(\text{reactants})} \left( \frac{kT}{2\pi m_{\ddagger}} \right)^{\frac{1}{2}} \frac{1}{d} \quad (6)$$

where  $K$  is the transmission coefficient,  $d$  is the length along the reaction coordinate representing the transition state,  $m_{\ddagger}$  is the effective mass of the activated complex (i.e., the reduced mass for the mode of vibration leading to reaction), and  $Q$  is the complete partition function per unit volume. The other symbols have their previously indicated meanings, and the symbol  $\ddagger$  refers to the activated complex. Combining equations (3) and (6), it is seen that, for reactions (1) and (2)

$$\beta\alpha = \frac{k_r}{k_r^{\bullet}} = \frac{Q_{\ddagger}^{\bullet}}{Q_{\ddagger} Q} \left( \frac{m_{\ddagger}^{\bullet}}{m_{\ddagger}} \right)^{\frac{1}{2}} \quad (7)$$

In equation (7) it has been assumed that the transmission coefficients and the length of the transition states,  $K$  and  $d$  respectively, are identical for the two reactions. Making the further assumption that the various forms of molecular energy are independent, the complete partition function for each species may be written as a product of the individual partition functions for each form of energy. Since only the ratio of complete partition functions is required, the nuclear spin partition functions will cancel out. The same is true of the electronic partition functions if it is assumed, as is generally true, that only ground states are occupied. Therefore one may write

$$\frac{Q^{\bullet}}{Q} = \frac{Q_T^{\bullet} Q_R^{\bullet} Q_V^{\bullet} Q_Z^{\bullet}}{Q_T Q_R Q_V Q_Z} \quad (8)$$

where  $Q_T$ ,  $Q_R$ ,  $Q_V$ , and  $Q_Z$  represent the translational, rotational, vibrational, and zero-point partition functions, respectively, as defined by the equations

$$Q_T = \frac{(2\pi m kT)^{3/2}}{h^3} \quad (9)$$

$$Q_R = \frac{8\pi^2 (8\pi^3 ABC)^{1/2} (kT)^{3/2}}{\sigma h^3} \quad (10)$$

$$Q_V = \prod_i [1 - \exp(-h\nu_i/kT)]^{-1} \quad (11)$$

$$Q_Z = \prod_i \exp(-h\nu_i/2kT) \quad (12)$$

in which  $\sigma$  is a symmetry number, A, B, and C are moments of inertia,  $\nu_i$  is the frequency of the  $i^{\text{th}}$  mode of vibration, and the other symbols are as previously defined. It should be noted that the rotational partition function given by equation (10) is for a non-linear molecule, and assumes classical rotation. This latter assumption is invalid for reactions involving hydrogen molecules or reactions at very low temperatures. Also, no correction was made for anharmonicity in equations (11) and (12).

Substituting values for the individual partition functions (9-12) into equation (8), one obtains equation (13).

$$\frac{Q^\bullet}{Q} = \frac{\sigma}{\sigma^\bullet} \left(\frac{m^\bullet}{m}\right)^{3/2} \left(\frac{ABC^\bullet}{ABC}\right)^{1/2} \frac{\prod_i [1 - \exp(-u_i^\bullet)]^{-1} \exp(-\frac{u_1^\bullet}{2})}{\prod_i [1 - \exp(-u_i)]^{-1} \exp(-\frac{u_1}{2})} \quad (13)$$

By using the Teller-Redlich theorem, i.e.,

$$\left(\frac{m^\bullet}{m}\right)^{3/2} \left(\frac{ABC^\bullet}{ABC}\right)^{1/2} = \left(\frac{\bar{m}^\bullet}{\bar{m}}\right) \frac{\prod_i u_i^\bullet}{\prod_i u_i} \quad (14)$$

equation (13) becomes

$$\frac{Q^\bullet}{Q} = \frac{\sigma \bar{m}^\bullet \prod_i u_i^\bullet [1 - \exp(-u_i^\bullet)]^{-1} \exp(-\frac{u_1^\bullet}{2})}{\sigma^\bullet \bar{m} \prod_i u_i [1 - \exp(-u_i)]^{-1} \exp(-\frac{u_1}{2})} \quad (15)$$

in which  $\bar{m}^\bullet$  and  $\bar{m}$  represent the masses of isotopic atoms and, for convenience in writing,  $u_1$  represents  $h\nu_1/kT$ . An equation of the form of equation (15) can also be written for  $Q_+/Q_+^\bullet$ . Insertion of both partition function ratios into equation (7) yields equation (16).

$$\beta\alpha = \frac{k_R}{k_R^\bullet} = \frac{\sigma_+^\bullet \sigma_-}{\sigma_+ \sigma_-^\bullet} \left( \frac{m_+^\bullet}{m_+} \right)^{\frac{1}{2}} \frac{\left\{ \prod_i u_{i1} [1 - \exp(-u_{i1}^\bullet)]^{-1} \exp(-\frac{u_{i1}^\bullet}{2}) \right\}_+ \left\{ \prod_i u_{i1} [1 - \exp(-u_{i1})]^{-1} \exp(-\frac{u_{i1}}{2}) \right\}_+}{\left\{ \prod_i u_{i1} [1 - \exp(-u_{i1})]^{-1} \exp(-\frac{u_{i1}}{2}) \right\}_+ \left\{ \prod_i u_{i1}^\bullet [1 - \exp(-u_{i1}^\bullet)]^{-1} \exp(-\frac{u_{i1}^\bullet}{2}) \right\}_+} \quad (16)$$

In connection with equation (3),  $\beta$  was said to involve only symmetry numbers. In fact,  $\beta$  is so defined that it always cancels the factor involving symmetry numbers of equation (16) and  $\alpha$  is equal to all other factors on the right side of equation (16).

$$\beta = \frac{\sigma_+^\bullet \sigma_-}{\sigma_+ \sigma_-^\bullet} \quad (17)$$

Since equation (16) requires experimentally unattainable knowledge, vibrational frequencies of activated complexes, its practical value is rather limited. Nevertheless, it does enable one to draw several qualitative conclusions regarding the isotope effect and its utilization.<sup>5</sup>

It should be emphasized that the isotope effect ( $\alpha$ ) will be observed only if a bond to the isotope is ruptured or formed in the rate-determining step of a reaction. It is assumed then that the isotope is less tightly bound in the activated complex than in the reactant molecule. In the limiting case, there is no bond to the isotope in the activated complex, and  $\alpha$  can be calculated from equation (16) since only the vibrational frequencies of normal molecules are required.

$$\alpha = \left( \frac{m_{\pm}^{\bullet}}{m_{\pm}} \right)^{\frac{1}{2}} \prod_1 \frac{v_1^{\bullet} [1 - \exp(-u_1)]}{v_1 [1 - \exp(-u_1^{\bullet})]} \exp \left( \frac{u_1 - u_1^{\bullet}}{2} \right) \quad (18)$$

As a first approximation, the ratio  $[1 - \exp(-u_1)] / [1 - \exp(-u_1^{\bullet})]$  is equal to unity up to 400-500°C, and also the first and second factors of equation (18) cancel. Then equation (19) holds,

$$\alpha = \prod_1 \exp \left( \frac{u_1 - u_1^{\bullet}}{2} \right) \quad (19)$$

and the isotope effect depends only on the difference in the zero-point energies of the normal molecules.

Since the zero-point energy of a bond to a lighter isotope is greater than that of the bond to a heavier isotope,  $\alpha$  will exceed unity. As bonding in the activated complex increases,  $\alpha$  will decrease. Except for light isotopes, such as those of hydrogen, the difference in the zero-point energies of the bonds to the isotopic atoms will normally dictate the magnitude of the isotope effect as given by equation (16). For the isotopes of hydrogen, the effect of the term involving the ratio of the effective masses of the activated complexes becomes significant. At higher temperatures, all of the terms in equation (16) will cancel except the mass term. In this case,  $\alpha$  becomes equal to  $(\bar{m}^{\bullet}/\bar{m})^{\frac{1}{2}}$ , i.e., the square root of the ratio of the masses of the isotopic atoms. In general, the ratio  $m_{\pm}^{\bullet}/m_{\pm}$  is very close to the ratio  $\bar{m}^{\bullet}/\bar{m}$ , and the significance of the mass term in the hydrogen isotope effect becomes apparent.

## 2. Fractionation and Equilibrium Reactions

For the reactions shown in equations (1) and (2), involving a mixture of molecules containing hydrogen (AH) and its radioactive isotope

(AT), the specific activity of the reactants ( $S_{R,f}$ ) at a fraction ( $f$ ) of reaction is related to that at zero fraction of reaction ( $S_{R,o}$ ) by equation (20).<sup>6,7</sup>

$$S_{R,f}/S_{R,o} = (1 - f)^{\frac{1}{\alpha}} - 1 \quad (20)$$

Similarly, the specific activity of a small increment of the product ( $S_{P,Y}$ ) collected over an interval of reaction ( $Y$ ) between  $f$  and  $(f + \Delta f)$  is given by equation (21).

$$S_{P,Y}/S_{R,o} = \frac{1}{\alpha} (1 - Y)^{\frac{1}{\alpha}} - 1 \quad (21)$$

When  $Y$  is small,  $S_{P,Y}$  is approximately equal to the specific activity of the product for the fraction of reaction  $f$ . Since  $\alpha$  will always exceed unity, the specific activities of the reactants and successive fractions of the product will continuously increase at an ever accelerating rate as the reaction proceeds to completion, a fact which serves as the basis for the enrichment of an isotopic mixture by means of irreversible reactions.

As was previously stated, calculation of an isotope effect by means of equation (16) requires experimentally unattainable vibrational frequencies of activated complexes. This handicap is not present when the isotope effect occurs in an isotopic exchange reaction.<sup>8</sup> For the reaction



the equilibrium constant,  $K$ , is given by

$$K = \frac{Q_{AT}Q_{BH}}{Q_{AH}Q_{BT}} \quad (23)$$

where the  $Q$  again refers to complete partition functions. Using the values of the partition functions given by equations (9) through (12), and proceeding in the same manner used to obtain equation (16), one obtains equation (24).

$$K = \left( \frac{\sigma_{AH} \sigma_{BT}}{\sigma_{AT} \sigma_{BH}} \right) \frac{\left\{ \prod_i u_i [1 - \exp(-u_i)]^{-1} \exp\left(-\frac{u_i}{2}\right) \right\}_{AT} \left\{ \prod_i u_i [1 - \exp(-u_i)]^{-1} \exp\left(-\frac{u_i}{2}\right) \right\}_{BH}}{\left\{ \prod_i u_i [1 - \exp(-u_i)]^{-1} \exp\left(-\frac{u_i}{2}\right) \right\}_{AH} \left\{ \prod_i u_i [1 - \exp(-u_i)]^{-1} \exp\left(-\frac{u_i}{2}\right) \right\}_{BT}} \quad (24)$$

Equation (24) is of much more value than equation (16) since only the vibrational frequencies of normal molecules are required to calculate the equilibrium constant. The right side of equation (24) has one factor ( $\beta$ ) which involves symmetry numbers and one ( $\alpha$ ) which represents the isotope effect on the exchange reaction, i.e.,

$$\beta\alpha = K \quad (25)$$

For heavy isotopes,  $\alpha$  is very nearly equal to unity, and therefore, the equilibrium constant is determined solely by symmetry numbers. In this case, no isotopic enrichment can be achieved by the exchange reaction.

It is to be noted that, except for the mass term and the term involving symmetry numbers, equation (24) is the same as equation (16) if one considers BH and BT as representing the two isotopic forms of the activated complexes. Thus, the factors influencing the isotope effect discussed in connection with equation (16) apply also to equation (24). Here, however, one can no longer assume that the isotopic atoms are bound



less firmly in BH and BT than in AH and AT. The magnitude of the isotope effect in an isotopic exchange reaction is dictated by the difference in the differences of the zero-point energies of the bonds of the isotopic atoms to A and B. Consequently, the isotope effect may be greater than, equal to, or less than unity depending upon the degree to which the difference in the zero-point energies of the bonds of the isotopic atoms to B cancels that difference for A. In general, the isotope effect will be small and will cause the heavy isotope to concentrate in the molecule in which the bond to hydrogen is the strongest. At higher temperatures, the isotope effect approaches unity and all of the terms on the right side of equation (24) will cancel except the symmetry factor.

Equations (16) and (24) refer to gas phase reactions and should be corrected when utilized for liquid phase reactions. This correction involves multiplying the right hand side of the equations by the proper ratio of activity coefficients. This correction is of theoretical interest, but is one which has had little practical application.

### C. Liquid Ammonia

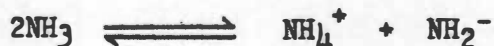
The history of liquid ammonia as a solvent is a fascinating subject. Beginning with the sporadic investigations of Weyl, Joannis and others during the latter half of the nineteenth century, through the systematic studies of Cody, Franklin and Kraus in the early part of this century, and up to the present time, interest in liquid ammonia has mounted continuously. Today, liquid ammonia stands as the most comprehensively studied non-aqueous solvent. As might be expected, the litera-

ture on this subject has become voluminous and complex. Fortunately, several excellent books and review articles are available.<sup>9-18</sup>

### 1. General Properties

The nitrogen atom has three unpaired p electrons available for bonding. Consequently, one might expect the ammonia molecule to have a pyramidal structure with the three bond angles at  $90^\circ$  to one another. Coulomb repulsion of the hydrogen atoms due to their partial ionic character, and an inherent tendency to  $sp^3$  hybridization, result in the bond angles being closer to  $109^\circ$  than  $90^\circ$ . The ammonia molecule, therefore, may be regarded as having a tetrahedral structure with the nitrogen atom at the center and the four corners of the tetrahedron occupied by the three hydrogen atoms and the  $2s^2$  electrons. Many of the intrinsic properties of liquid ammonia can be correlated with this structure.

Liquid ammonia is one of the most "water-like" of the non-aqueous solvents, a fact made apparent by comparing the physical properties of the two solvents presented in Table I. The abnormally high melting points, boiling points, heats of vaporization and fusion, and dielectric constants of the two solvents are cited as evidence of molecular association through hydrogen bonding, with the hydrogen bond in liquid ammonia being somewhat weaker than the hydrogen bond in water. The autoionization of liquid ammonia, which is represented by the equilibrium



occurs to a very limited extent; the dissociation constant is  $1.9 \times 10^{-33}$  (at  $-50^\circ\text{C}$ ) as compared to  $1 \times 10^{-14}$  (at  $25^\circ\text{C}$ ) for water. According to

TABLE I

## PHYSICAL PROPERTIES OF WATER AND AMMONIA

Property	Value for Water	Value for Ammonia
Molecular Weight	18.016	17.032
Density (gms./ml.)	0.958 (100°C)	0.683 (-33.4°C)
Melting Point (°C)	0	-77.7
Boiling Point (°C)	100	-33.4
Critical Temperature (°C)	374.1	132.4
Critical Pressure (Atm.)	217.7	112
Heat of Fusion (kcal./mole)	1.435	1.43
Heat of Vaporization (kcal./mole)	9.719	5.64
Equivalent Conductance (ohm <sup>-1</sup> )	$6 \times 10^{-8}$ (25°C)	$5 \times 10^{-9}$ (-33.4°C)
Dielectric Constant	81.1	22
Viscosity (dyne sec./cm. <sup>-2</sup> )	0.00959 (25°C)	0.00265 (-33.5°C)
Dipole Moment (D $\times 10^{18}$ )	1.85	1.47

the Bronsted-Lowry theory of acids and bases, the ammonium and amide ions are the strongest acid and base, respectively, capable of existence in liquid ammonia. Liquid ammonia is the most basic of the common solvents and, consequently, compounds such as alcohols, enols and even water behave as acids in this solvent. Ammonia is a poorer electrolytic solvent than water because of its lower dielectric constant, but it is a better solvent for organic materials, its solvent properties in this respect being more similar to a lower alcohol than to water.

## 2. Metal-Ammonia Solutions

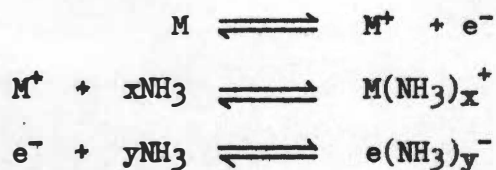
The outstanding difference between liquid ammonia and water as solvents is the ability of the former to dissolve, without chemical reaction, those metals which are strongly reducing in character. The alkali metals are the most soluble and can be recovered from their ammonia solutions by evaporation of the solvent. The alkaline earth metals are less soluble. Upon evaporation of the solvent, the latter yield ammoniates of the type  $M(NH_3)_6$ . Magnesium and aluminum are only very slightly soluble in ammonia.

The exact nature of the metal solutions in liquid ammonia is not yet known. In many respects, these solutions are intermediate between pure metals and electrolytic solutions. The metal-ammonia solutions possess a characteristic blue color in dilute solutions, and a metallic bronze color in concentrated solutions. The absorption spectra, at any given concentration and temperature, are identical for all of the alkali metal solutions. The electrical conductances of the bronze solutions approach values typical of pure metals, whereas the dilute solutions

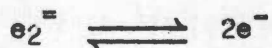
exhibit electrolytic conductances. In all solutions, the negative carrier is the same and is associated with only solvent molecules. At infinite dilution, the equivalent conductance of the sodium solution is about  $1040 \text{ cm.}^2 \text{ equiv.}^{-1} \text{ ohm}^{-1}$ . The ionic conductance of the sodium ion in liquid ammonia is only  $130 \text{ cm.}^2 \text{ equiv.}^{-1} \text{ ohm}^{-1}$ . The fact that the negative carrier must, therefore, have an ionic conductance of  $910 \text{ cm.}^2 \text{ equiv.}^{-1} \text{ ohm}^{-1}$  suggests its having sub-atomic dimensions.

The dilute metal-ammonia solutions are strongly paramagnetic, and have densities less than the density of the pure solvent. In fact, metal-ammonia solutions comprise the lightest liquids known, the saturated solutions of sodium and potassium having densities of  $0.54 \text{ gm./ml.}$  and  $0.63 \text{ gm./ml.}$ , respectively, at  $-33.8^\circ\text{C.}$

In an attempt to explain the preceding observations, Kraus suggested that the metal-ammonia solutions consist of the free metal in equilibrium with metal cations and free electrons.<sup>19</sup> The cations and electrons are then subject to reversible solvation by the ammonia molecules. Such a system is represented by the following equations:



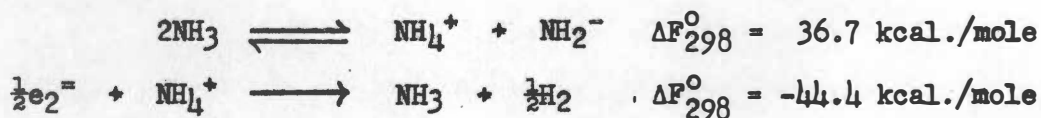
Studies on the absorption spectra and electrical conductances of the metal-ammonia solutions at various temperatures and concentrations have led Ogg to suggest that the electrons exist as single electrons and electron pairs trapped in cavities which they create in the solvent.<sup>20-22</sup> The single electrons and the electron pairs are postulated as being in



equilibrium, with the electron pairs favored by high metal concentrations and low temperatures. This theory satisfactorily accounts for the increase in paramagnetism of the solutions accompanying an increase in their temperature or a decrease in their metal concentration. The heat of reaction for the proposed dimerization of electrons in ammonia has been measured and is approximately equal to 3.0 kcal./equiv.,<sup>23</sup> a value which agrees well with that calculated by Ogg. Bingel has extended Ogg's theory to allow for the effect of the metal cations on the single and paired electrons.<sup>24</sup>

The ability to dissolve the alkali metals is not limited solely to liquid ammonia. Relatively stable solutions of the alkali metals are also formed in methylamine and ethylamine. Solutions of potassium in methanol, ethanol, and even water have been reported, but these solutions, which possess the blue color characteristic of the dilute metal-ammonia solutions, rapidly decay with the evolution of hydrogen.<sup>25</sup>

It should be pointed out that metal-ammonia solutions are thermodynamically unstable,<sup>23</sup> as shown by the free energy changes for the following reactions:



The relative stability of the metal-ammonia solutions, in spite of the net standard free energy change of -7.7 kcal./mole for the evolution of hydrogen, can probably be attributed to the extremely small auto-ionization constant of liquid ammonia. When carefully prepared, alkali

metal-ammonia solutions, particularly of the less active metals, can be kept for months without appreciable decomposition. There are many substances which are known to catalyze the decomposition, so traces of impurities must be avoided.

#### D. Purpose of the Research

The primary objective of this research was to examine the chemical fractionation of isotopes of hydrogen through the reaction of a weak acid with a metal as represented by equation (26). Several investigators pre-

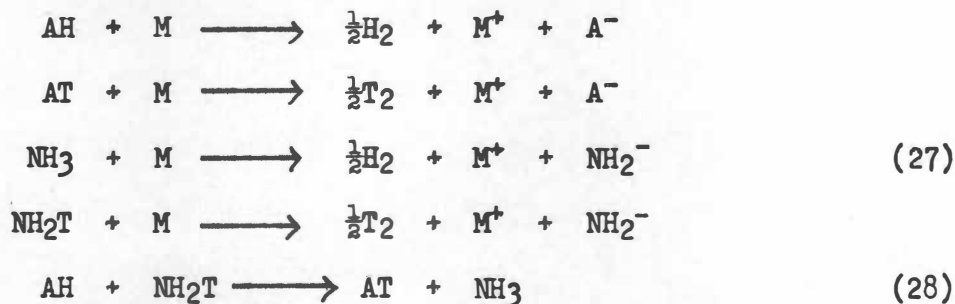


viously studied the chemical separation of isotopes of hydrogen by the addition of metals to water and to various acids and bases.<sup>26,27</sup> Lack of reproducibility of results and lack of agreement amongst the various investigators can be attributed to the fact that these studies dealt with heterogeneous reactions, a fact which is also responsible for the difficulty encountered in interpreting the results. However, it has been established that the magnitude of the separation factor depends strongly on the metal employed.

It is of interest to compare the chemical separation of the isotopes of hydrogen with the separation via electrolysis of water. The electrolytic separation has been subjected to intensive study by many investigators, most of whom agree that the nature of the metal employed as the electrode dictates the magnitude of the separation factor.<sup>28-30</sup> Again, the heterogeneous nature of the systems studied has caused difficulty in interpreting and in reproducing results.

In order to overcome the difficulties inherent in the studies of heterogeneous systems, it was proposed that the reaction represented by equation (26) be studied in liquid ammonia. As pointed out in the previous section, liquid ammonia serves as a suitable solvent for alkali metals and for many weak acids, such as water, alcohol and phenol. This investigation was limited to those systems wherein the metal employed was lithium, potassium or sodium, and the weak acid was an alcohol (mainly ethanol) or the solvent itself. Further, although preparations were completed for the study of the separation of hydrogen and deuterium, only the separation of the hydrogen and tritium isotopes was studied.

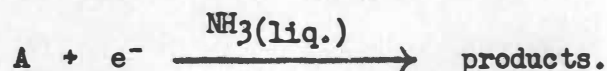
The reaction system involved in this study may be represented by the following set of equations in which AH represents the alcohol and T



represents tritium. The preceding equations serve to emphasize the fact that a satisfactory solution to the stated problem requires knowledge not only of the reaction of an alkali metal with an alcohol in liquid ammonia, but also of the isotopic exchange reaction occurring between the alcohol and the solvent, and of the effect of any simultaneous reaction occurring between the metal and the solvent. All of these "subsidiary" problems are of interest in their own right.



A knowledge of the rate of the isotopic exchange reaction between the alcohol and the solvent is of interest in connection with the general theory of hydrogen isotope exchange reactions proposed by Brodsky.<sup>31</sup> The elucidation of the mechanism of the reaction of an alkali metal with an alcohol in liquid ammonia should be of considerable value in view of the widespread use of this system in reduction reactions.<sup>32</sup> Consider the reduction of a compound by electrons in liquid ammonia either in the presence or absence of a proton donor, i.e.,



The question has been raised as to how the nature of the product obtained, and the kinetics for a given reaction may depend upon the particular alkali metal supplying the electrons.<sup>33</sup> It was hoped that some light might be shed on this problem during the course of this investigation.

Finally, it was believed that if the experimental difficulties inherent in this problem could be surmounted, the results might serve to pave the way for others to make kinetic studies in liquid ammonia and to use tritium to elucidate the mechanisms of other reactions. In the historical discussion which follows, each of these subsidiary objectives will be discussed.

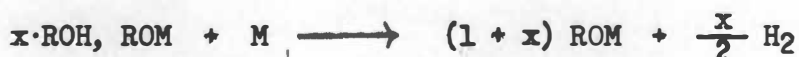
## E. Historical

A survey of the literature has failed to reveal a single instance wherein a quantitative kinetic investigation has been made on a homogeneous metal-ammonia system.

Chablay<sup>34</sup> studied the reactions of various metal-ammonia solutions with several alcohols, and obtained the results shown in Table II. For the monohydric alcohols, the reactions correspond to the equation



Providing the ratio of ammonia to alcohol was very high, the methoxides and ethoxides, being "insoluble" in liquid ammonia, were reported to have precipitated as the reactions proceeded to completion. However, these alkoxides are soluble in the alcohols, and it was observed that when the ratio of ammonia to alcohol was decreased, the alkoxides formed during the early stages of the reaction did not precipitate immediately. Eventually, upon saturation of the reaction solution, an alcoholate precipitated. The alcoholates were given the formula  $x \cdot \text{ROH}, \text{ROM}$ . The insoluble alcoholate was then attacked by the metal-ammonia solutions in the manner represented by the equation



With respect to the stoichiometry of the reactions of the polyhydric alcohols, the interesting observation was made that lithium behaved in a manner intermediate between the other alkali metals and the alkaline-earth metals (see Table II). It was also noted that calcium and lithium reacted more vigorously than the other alkali metals. Although no specific data was given, Chablay stated that the rate of reaction varied with the nature of the alcohol in the order: primary > secondary > tertiary.

Kraus and White studied the reaction of sodium with ethyl alcohol in liquid ammonia.<sup>35</sup> They found that the reaction proceeded with the

TABLE II

 REACTIONS OF ALKALI AND ALKALINE  
 EARTH METALS WITH ALCOHOLS

Alcohol	Products	
$\text{CH}_3\text{OH}$	$\text{CH}_3\text{OM}$ $(\text{CH}_3\text{O})_2\text{M}'$	$\text{M} = \text{Na}, \text{K}, \text{Li}$ $\text{M}' = \text{Ca}, \text{Sr}, \text{Ba}$
$\text{C}_2\text{H}_5\text{OH}$	$\text{C}_2\text{H}_5\text{OM}$ $(\text{C}_2\text{H}_5\text{O})_2\text{M}'$	$\text{M} = \text{Na}, \text{K}, \text{Li}$ $\text{M}' = \text{Ca}, \text{Sr}, \text{Ba}$
$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	$(\text{CH}_3)_2\text{CHCH}_2\text{OM}$	$\text{M} = \text{Na}, \text{K}, \text{Li}$
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH}$	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OM}$ $[(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{O}]_2\text{M}'$	$\text{M} = \text{Na}, \text{K}, \text{Li}$ $\text{M}' = \text{Ca}$
$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OM} \\   \\ \text{CH}_2\text{OH} \end{array}$ $\begin{array}{c} \text{CH}_2\text{O} \\   \\ \text{CH}_2\text{O} \end{array} \text{M}'$	$\text{M} = \text{Na}, \text{K}, \text{Li}$ $\text{M}' = \text{Ca}$
$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ (\text{CHOH})_2 \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OM} \\   \\ (\text{CHOH})_2 \\   \\ \text{CH}_2\text{OH} \end{array}$ $\begin{array}{c} \text{CH}_2\text{OM}' \\   \\ (\text{CHOH})_2 \\   \\ \text{CH}_2\text{OM}' \end{array}$	$\text{M} = \text{Na}, \text{K}$ $\text{M}' = \text{Li}$

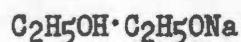
TABLE II

REACTIONS OF ALKALI AND ALKALINE  
EARTH METALS WITH ALCOHOLS  
(Continued)

Alcohol	Products
$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ (\text{CHOH})_2 \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{ccc} \text{CH}_2\text{O} & \diagdown & \\   & & \\ (\text{CHOH})_2 & \text{M}'' & \\   & \diagup & \\ \text{CH}_2\text{O} & & \end{array} \quad \text{M}'' = \text{Ca}$
$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ (\text{CHOH})_4 \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{ccc} \text{CH}_2\text{OM} \\   \\ (\text{CHOH})_4 \\   \\ \text{CH}_2\text{OH} \end{array} \quad \text{M} = \text{Na, K}$
	$\begin{array}{ccc} \text{CH}_2\text{OM}' \\   \\ (\text{CHOH})_4 \\   \\ \text{CH}_2\text{OM}' \end{array} \quad \text{M}' = \text{Li}$

evolution of hydrogen and the formation of an "alcoholate", identified simply as sodium ethylate. The reaction was "vigorous" at first, but rapidly slowed down with the result that after two and one-half hours, the reaction had gone to only 75 per cent completion. This retardation was attributed to the "mushy" condition of their reaction mixture.

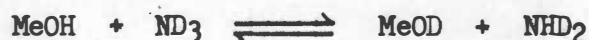
White, Morrison and Anderson<sup>36</sup> also studied the reaction of sodium with ethanol in ammonia and came to the conclusion that during the course of the reaction an alcoholate having the formula



was formed. This compound was reported to precipitate from solution and to undergo no further attack by alkali metal. Hence, the reactions "never" went to completion.

It should be noted that the work of Chablay was far more comprehensive and convincing than that of the other authors, but that all of the work was of a qualitative nature.

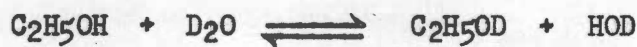
The isotopic exchange reaction (equation 28) between ethanol and liquid ammonia has not been previously studied. However, this type of isotopic exchange has been studied with other species containing active hydrogen. For example, the exchange



has been studied in liquid ammonia by Shatenshtein who reported<sup>37</sup> the reaction to be "instantaneous."\* Similarly, the reactions

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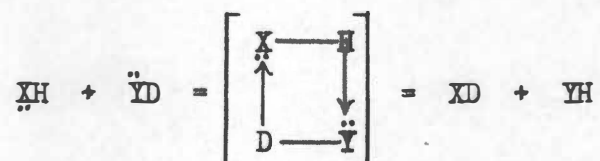
\*The ambiguous term "instantaneous" is commonly applied to a reaction which has gone to completion within the time required for measuring the extent of the reaction. For the particular case of exchange reactions between active hydrogen and ammonia, the time required for measurement has been reduced to less than  $10^{-2}$  sec.<sup>38,39</sup>



and



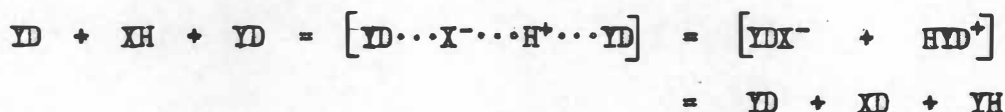
are reported<sup>38,39</sup> to be instantaneous. Many of the exchange reactions of the ammonium ion, in contrast with ammonia, have measurable rates.<sup>31,39,40</sup> Consideration of the above results along with a host of other experimental observations led Brodsky to suggest<sup>31</sup> that all hydrogen isotope exchange reactions can be placed in one of two categories, those reactions which are instantaneous and those which have slow rates or fail to exchange at all. The instantaneous exchange reactions are characterized by the presence of one or more unshared pairs of electrons on the atom bound to the exchanging hydrogen atom, a situation frequently encountered in N-H, O-H and S-H bonds and sometimes in C-H bonds. Brodsky considers that these reactions proceed through an associative mechanism represented as follows:



This symmetrical one-step process does not require activation energy aside from that expended on achieving a favorable orientation of the exchanging molecules and on equalizing the interatomic distances of the X-H and Y-D bonds. Such reactions should proceed rapidly at any temperature without a catalyst. Brodsky considers the rate of the exchange to be completely independent of the acid strength of the exchanging molecules.

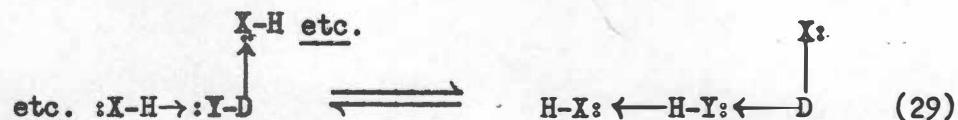
Exchange reactions of the slow type are characterized by the lack of unshared electron pairs on the atom to which the exchanging hydrogen

atom is bound. Brodsky considers these exchange reactions to occur via a 3-body electrolytic dissociation mechanism,

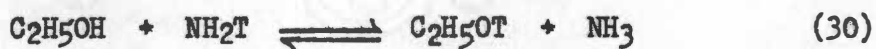


The activation energy of such a reaction depends on the properties of the scissionable X-H bond and on the energy of the interaction of the solvent with the ions  $X^-$  and  $H^+$ . In general, the activation energy should be significant and the rate of the exchange slow. The fact that the exchange rate for slow type exchange reactions is a function of the acid strength of the exchanging species has proven very useful in comparing the strengths of weak acids, particularly hydrocarbons.<sup>37</sup>

A recent critical discussion of Brodsky's theory suggests that the theory may not be definitive in that certain fast exchange reactions may occur via a dissociative mechanism.<sup>41</sup> Furthermore, Brodsky's theory might be extended to include several other mechanisms. For example, certain exchange reactions could proceed through a mechanism (equation 29) of



the type used to account for the abnormally high proton transfer in water. By whatever mechanism though, the exchange reaction of interest in this study (equation 30) would be expected to proceed very rapidly.



Knowledge concerning mechanistic details of the reaction (equation 27) occurring between an alkali metal and liquid ammonia is limited. It does not seem possible that the reaction proceeds via the autoionization



of the ammonia (equation 31 and 32) because of the very low autoionization



constant of ammonia. It is generally accepted that the greater the purity of the metal-ammonia system, the less the rate of its reaction, and that the susceptibility of the metals to this reaction increases in the order lithium, sodium, potassium.

The ammonia-alkali metal reaction (equation 27) is extremely susceptible to catalysis by a variety of materials, particularly the transition elements. In fact, the only quantitative studies made on this reaction have been made in the presence of these catalysts. Watt and co-workers found<sup>42</sup> that, in the presence of various transition elements, the rate of formation of sodium amide was less than that of potassium amide. For the latter reaction, the rate was zero order in potassium for potassium concentrations greater than about 0.03 molar and first order in potassium at lower concentrations. Burgess and Kahler, in a similar study,<sup>43</sup> decided that the sodium reaction was slower than the potassium reaction because sodium amide poisoned the catalyst whereas potassium amide did not.

Heterogeneous studies may have little bearing on the interpretation of the homogeneous reaction of an alkali metal with liquid ammonia. Actually, in the present investigation it was desirable to avoid the reaction rather than study it, and in this connection the suggestions of Dewald and Lepoutre were of considerable use.<sup>44</sup>

A measurement of chemical separation factors in a system such as the one under consideration in this research project has not been made.



By analogy to measured isotope effects for the exchange reactions occurring between various weak acids and heavy water,<sup>1</sup> and by invoking theoretical principles already discussed, one would anticipate that for the reaction



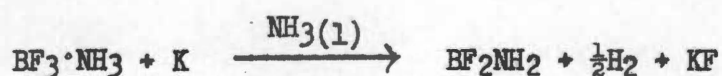
the equilibrium constant should be only slightly less than the statistical factor of 0.33, i.e., there should be a slight concentration of the heavy isotope in the weaker acid, ammonia.

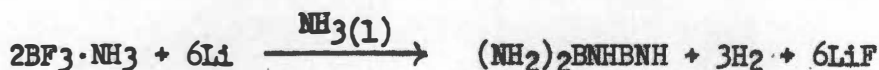
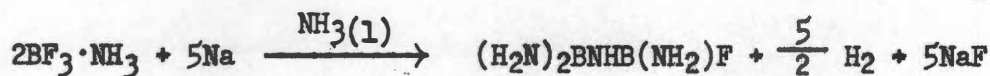
Little can be said concerning the isotope effects to be expected in the homogeneous reaction



since the previous studies of this reaction have been made on heterogeneous systems only. Theoretical considerations would suggest that the isotope effect for the liberation of the isotopes of hydrogen from ammonia should be considerably greater than that from ethanol, and that the isotope effects for the liberation reactions should eclipse the isotope effects in the isotopic exchange reaction. Consequently, the overall fractionation should concentrate the heavier hydrogen isotope in the ammonia solution.

In studying the reaction of boron trifluoride ammoniate with alkali metal-liquid ammonia solutions, Keenan and McDowell<sup>33</sup> observed that the stoichiometry of the reaction was dictated by the particular alkali metal employed, the results being represented by the following equations.





As previously mentioned, Chablay observed that in reactions of alkali metals with various alcohols in liquid ammonia, lithium behaved more like the alkaline earth metals, forming compounds of the type  $\text{CH}_2\text{OLi}(\text{CHOH})_x\text{CH}_2\text{OLi}$  with certain polyhydric alcohols whereas sodium and potassium always formed compounds of the type  $\text{CH}_2\text{OH}(\text{CHOH})_x\text{CH}_2\text{ONa}$ . He further observed that lithium and calcium reacted more vigorously than sodium or potassium.

In various organic reduction reactions in liquid ammonia, differences between metals appear in rates of their reactions and in the nature of the products they produce. Again, it is lithium which has often proved to be superior amongst the alkali metals as a reducing agent.<sup>45,46</sup> This led Wilds and Nelson to suggest<sup>46</sup> that "the superiority of lithium as a reducing metal lies in a nearly ideal combination of properties:

- (1) High normal reduction potential
- (2) High solubility and low atomic weight making possible high concentrations and high actual reduction potentials
- (3) The slow rate of reaction with alcohols."

In the reduction of various nickel and silver salts by alkali metals in liquid ammonia, the catalytic activity of the precipitated metals was found to depend on the particular alkali metal employed in the reduction.<sup>47,48</sup> The activity of the reduced metal was greater from potassium reduction than from sodium reduction. When calcium was used, the catalyst's activity was even greater than that from potassium. Watt and Mayfield

suggested<sup>49</sup> that such differences were probably not due to any inherent differences in the nature of the various metal-ammonia solutions, but probably resulted from differential rate factors and solubility relationships. This, of course, leaves unanswered the question as to why the differential rates should exist. For those who would seek an answer in the differences in the thermodynamic functions of the alkali and alkaline earth metals in liquid ammonia, the compilations of thermodynamic data by Jolly<sup>50</sup> and Coulter<sup>51</sup> are of particular value.

## CHAPTER II

### EXPERIMENTAL

#### A. Reactor Systems

The development of a reactor system suitable for the quantitative kinetic investigation of the reaction occurring between an alkali metal and a weak acid in liquid ammonia proved to be a difficult task. Rather than list here the various requirements which had to be met in designing a reactor system, it would seem best to first describe in detail, Reactor System A, the final design which proved to be quite successful. Brief descriptions of other reactor systems which were employed in the preliminary stages of this investigation will then be presented.

##### 1. Reactor System A

This reactor system, shown in Figure 1, consisted of a reactor proper with its auxiliary apparatus, combined with apparatus necessary for the quantitative collection, as a function of time, of hydrogen liberated during the course of a reaction.

Unless otherwise noted, Pyrex glass construction was used throughout. Bulb C (Figure 1) served as the actual reaction chamber. This bulb had a volume of 55 ml., and its neck, terminating at stopcock S<sub>2</sub>, added an additional 45 ml. to give a total chamber volume of 100 ml. A movable jacket for Dry Ice was placed around the neck just below stopcock S<sub>2</sub>.

Bulb C was connected to burettes A and B via a 4 mm., "T-bore" stopcock S<sub>1</sub>. This stopcock was operated by a knob connected to the stop-

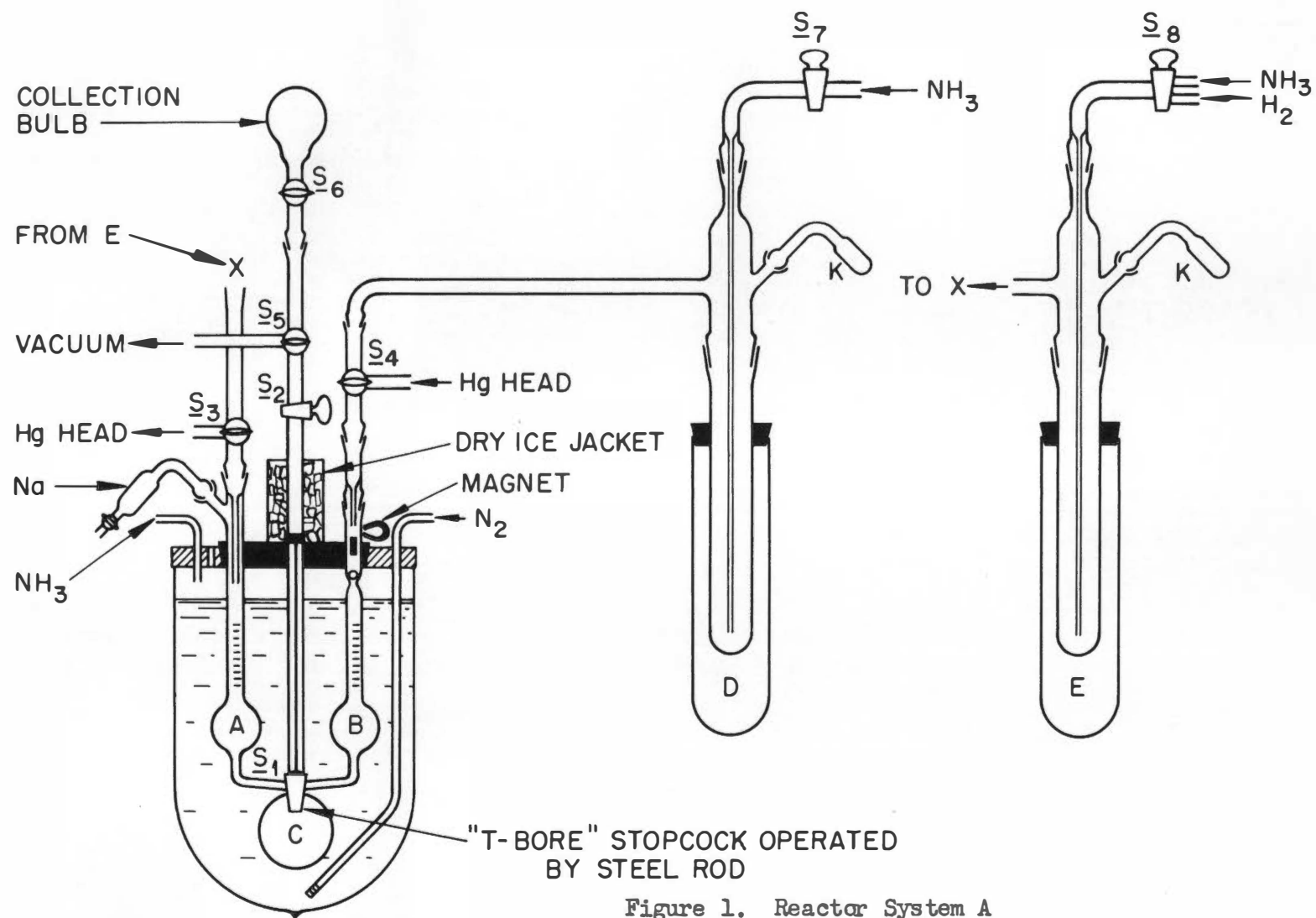


Figure 1. Reactor System A

cock by a stainless steel rod having a diameter of one-eighth inch. The two burettes were fashioned from 25-ml. graduated cylinders, and had a calibrated volume of 25.0 ml. each. Female sections of  $19/38 \overline{\Phi}$  and  $24/40 \overline{\Phi}$  ground glass joints served to extend burettes A and B, respectively, through a No. 15 rubber stopper which had been bored to accomodate these extensions, the neck of the reaction chamber and the connecting rod to stopcock  $S_1$ . The three tubes of the reactor, together with the rubber stopper, thus served to form a closed cycle of considerable mechanical strength.

Burette A was equipped with an addition bulb Na which was fashioned from a  $28/15$  ball and socket joint. Burette B was constricted just above its calibration marks. Two mm. "T-bore" stopcocks  $S_3$  and  $S_4$  connected burettes A and B, via one-fourth inch Tygon tubing, to separate manostats and, via  $12/37 \overline{\Phi}$  ground glass joints, to their ammonia purification reactors D and E. The latter had a volume of 100 ml. each, were constructed from  $34/45 \overline{\Phi}$  ground glass joints, and were equipped with addition bulbs K identical with that attached to burette A.

The manostats enabled the operator to both observe and control pressures in the two burettes. Each manostat was a Y-tube constructed with a 2-mm. capillary tube having a height of 85 cm. for the arm connected to the burette, and with a 17-mm. tube having a height of 25 cm. for the other arm. The bottom of the Y was a stopcock connected to a leveling bulb of mercury.

The 4-mm., "T-bore" stopcock  $S_5$  connected the reaction chamber to a vacuum line and, by means of a  $12/37 \overline{\Phi}$  ground glass joint, to gas col-

lection bulbs. The gas collection bulbs each had a volume of 125 ml. and were used either in trains of four to eight bulbs, or singly (Figure 1), as the occasion demanded. Stopcock S<sub>1</sub>, which operated in liquid ammonia, was lubricated with Dow-Corning "Hy-Vac" silicone lubricant. The other stopcocks and ground glass joints were lubricated with Apiezon-T stopcock lubricant.

The reactor assembly was placed in a large unsilvered Dewar flask which was sealed with a plastic lid cut to take the No. 15 rubber stopper. There were four outlets through the plastic lid, one for the introduction of ammonia, the second for the introduction of nitrogen, the third for the removal of gases, and the fourth for a thermometer. The ammonia purification reactors were placed in smaller unsilvered Dewar flasks.

The following is a description of the actual operational procedure followed with this reaction system. Prior to each experiment, the entire apparatus was disassembled and carefully cleaned. All stopcocks were cleaned with ether and relubricated. A fragile, sealed glass bulb containing a known weight of alcohol was placed on the constriction in burette B. A glass-coated magnetic iron bar was placed on top of the bulb. The entire apparatus was then assembled and "baked-out" under vacuum with infrared lamps. After cooling under vacuum, stopcock S<sub>2</sub> was closed and a stream of ammonia was passed through the system, entering from reactor D through S<sub>4</sub> and leaving through the manostat attached to S<sub>3</sub>.

The mercury head in the manostat attached to S<sub>3</sub> was adjusted to give a positive ammonia pressure in the system of approximately 10 cm.

of mercury. A temporary plug in the side arm on burette A was removed and the addition bulb Na containing alkali metal was quickly attached. The alkali metal had been previously cut and weighed under anhydrous xylene. At the same time, addition bulbs K, containing about 2 gm. of sodium each, were attached to the ammonia purification reactors, D and E. The stream of ammonia gas was stopped by closing stopcock S<sub>7</sub>, and the entire system was evacuated to remove any xylene introduced with the metal and any trace of air which could have entered the system.

Stopcocks S<sub>3</sub> and S<sub>4</sub> were rotated to connect the purification reactors to the manostats only. The purification reactors were immersed in Dry Ice-acetone baths in their respective Dewar flasks, and stopcocks S<sub>7</sub> and S<sub>8</sub> were opened to ammonia tanks. After approximately 30 to 35 ml. of ammonia had condensed into each of the purification reactors, these stopcocks were closed and the addition bulbs were rotated to add sodium to the liquid ammonia. In experiments where tritium-labeled ammonia was used, a stream of hydrogen was passed through the condensed, labeled ammonia during the drying process to remove any traces of contaminating tritium gas. While the purification process was taking place, liquid ammonia was run directly from an inverted tank to fill the large Dewar flask. Stopcocks S<sub>3</sub> and S<sub>4</sub> were opened and any hydrogen left in the system after the purification process was then removed by opening the entire system (A, B, C, D and E) to the vacuum line several times, for a fraction of a second each time. After evacuation, burettes A and B and chamber C were separated from one another by rotating stopcock S<sub>1</sub>.



The Dry Ice-acetone baths were removed from purification reactors and the manostats were observed as the ammonia pressures increased to a positive pressure of 8 to 10 cm. of mercury. Then stopcocks  $\underline{S}_3$  and  $\underline{S}_4$  were opened three ways and condensation of ammonia in the burettes took place. After about 15 ml. of liquid ammonia had condensed in each burette, stopcocks  $\underline{S}_3$  and  $\underline{S}_4$  were rotated to connect the reactors D and E and their manostats only, shutting off the burettes. The addition tube on burette A was rotated to add the alkali metal to the liquid ammonia. The bulb of alcohol in burette B was crushed by repeatedly raising and dropping the magnetic bar with a horseshoe magnet operating through the walls of the burette. After the alkali metal and the alcohol were added to the liquid ammonia, stopcocks  $\underline{S}_3$  and  $\underline{S}_4$  were again opened and the condensation of ammonia continued until each burette contained 25.0 ml. of solution. To prevent further condensation, stopcocks  $\underline{S}_3$  and  $\underline{S}_4$  were then rotated to close the two burettes.

The collection bulb was attached, as shown in the drawing, with stopcocks  $\underline{S}_2$ ,  $\underline{S}_5$  and  $\underline{S}_6$  all open. After vacating the gas collection bulbs and the reaction chamber,  $\underline{S}_6$  and  $\underline{S}_2$  were closed. Stopcock  $\underline{S}_5$  was rotated to connect only the reaction chamber and the gas collection train. Dry Ice was packed in the jacket on the reaction chamber. Stopcocks  $\underline{S}_3$  and  $\underline{S}_4$  were again opened three ways and the mercury levels in the manostats were equalized at approximately 10 cm. of mercury.

Stopcock  $\underline{S}_1$  was then opened three ways, connecting the two burettes with the reaction chamber. In a total time of about 0.1 second, the reactant solutions moved into the reaction chamber, and in passing through stopcock  $\underline{S}_1$ , were efficiently mixed. Stopcock  $\underline{S}_1$  was immediately closed.

To quantitatively remove hydrogen liberated in the closed glass reactor (bulb C) at any desired time, stopcock S<sub>2</sub> was opened and then stopcock S<sub>6</sub> on the evacuated gas collection bulb was opened for a fraction of a second and then closed. Stopcock S<sub>2</sub> was then closed, also. Rather than a single collection bulb, a train of bulbs was employed during the early stages of a reaction to enable fast sampling. The single gas collection bulbs were then used throughout the remainder of the reaction. To replace one bulb with another, stopcock S<sub>5</sub> was closed, the first bulb was removed, and the next put in its place. Stopcock S<sub>6</sub> was opened and the new bulb vacated. The stopcock on the gas collection bulb was closed and S<sub>5</sub> was rotated to open the line from S<sub>2</sub> to the new bulb. Everything was then ready for the next sampling.

Except in the early stages of the reaction when it was left filled constantly, the Dry Ice condenser on the reaction chamber was filled shortly before taking each sample and emptied immediately thereafter.

The customary volume of reaction solution was 50 ml. This left a free space of approximately 50 ml. between the solution and stopcock S<sub>2</sub>. The space between stopcock S<sub>2</sub> and the stopcock on the collection bulbs was negligible since capillary tubing was used there. Therefore, in opening the reactor to a vacated bulb, it might have been anticipated that only  $\frac{125}{125 + 50}$  or roughly 70 per cent of the hydrogen in the reactor would be removed. However, in devising this technique of removing the hydrogen, it was believed that the gas above the solution would rush into the vacated bulb and that additional ammonia would immediately evaporate from the solution and likewise enter the collection bulb until

the bulb was filled with gas at nearly atmospheric pressure. The gas entering after the initial surge would thus serve to completely sweep out any hydrogen left in the reactor. To further insure quantitative removal of the hydrogen, the Dry Ice jacket was put on the top of C and covered the upper 15 ml. of the 50 ml. of free space. This jacket resulted in the preferential accumulation of hydrogen in the upper 15 ml. of space, thus further aiding the hydrogen removal.

The apparatus and technique were thoroughly tested. For example, 50 ml. of liquid ammonia was condensed in tube C and known volumes of hydrogen were introduced into the reactor and then collected in a vacated bulb. The gas was quantitatively removed every time. Also, using two bulbs, a random volume of hydrogen was introduced into the reactor. The reactor was then opened to the first bulb, and then to the second bulb. If the gas was quantitatively removed by the first bulb, no gas should be found in the second bulb. Such was true, even when as much as 40 ml. of hydrogen was introduced into the reactor. Duplication of results on duplicate alcohol-alkali metal reactions substantiated the early tests.

Tests were also made to ascertain that molecular hydrogen, in contact with reaction solution, did not exchange. At the end of a typical (excess) alkali metal-alcohol reaction in labeled ammonia, unlabeled hydrogen was introduced into the reactor and left for several hours. Upon removal, it was found that the hydrogen had gained no activity.

The reaction system just described met several requirements. It provided for the rapid formation of a homogeneous solution containing known initial concentrations of the reactants. The reactions occurred

at the constant boiling point of the solvent ( $-33.4^{\circ}\text{C}$ ), and in an anhydrous, closed system. The system also provided for the rapid quantitative removal of the hydrogen liberated during the course of the reaction. The procedure of collecting the hydrogen in consecutive, discrete increments was dictated by the requirement of performing isotopic analyses on the increments when hydrogen isotopes were employed. In experiments with hydrogen isotopes, use of the twin burettes permitted a choice in the initial location of labeled species.

During the development of Reactor System A, other reaction systems were employed, systems which, while failing by various degrees to meet all of the preceding requirements, were nonetheless useful.

## 2. Other Reactor Systems

Reactor System A employed a three-tube reactor in conjunction with the vacated-bulb method of collecting liberated hydrogen. The reactor systems to be described in this section used a 1-tube reactor coupled with either the vacated-bulb method or one of two water-displacement methods for collecting the hydrogen.

Reactor System B differed from Reactor System A only in the design of the reactor proper; a one-tube reactor (Figure 2) was used in place of the three-tube reactor. The vacated-bulb technique was employed for collecting the hydrogen. The reactor head was made from the outer part of a  $3/4/45$   $\Phi$  ground glass joint sealed off flat just above its shoulder. To this flat head was sealed three outlet tubes. The first outlet, terminating in a  $12/37$   $\Phi$  ground glass joint, provided for the removal of liberated hydrogen via a Dry Ice condenser and the 4 mm. stopcocks S<sub>1</sub>

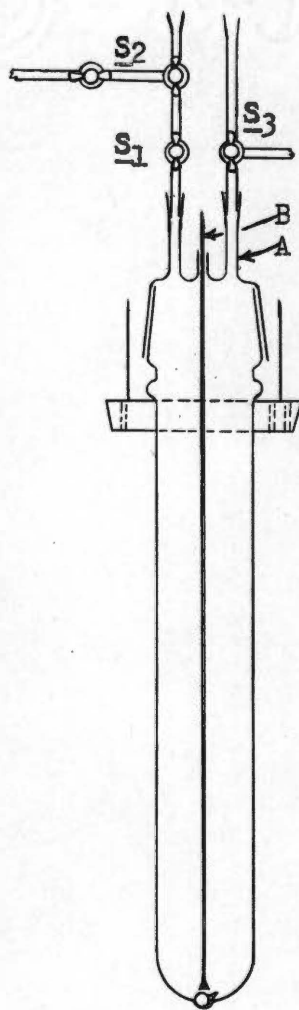


Figure 2. Reactor System B

and  $S_2$  leading to a train of vacated gas collection bulbs. Stopcock  $S_2$  also connected the system to a vacuum line. The second outlet, also terminating in a  $12/37$   $\Phi$  ground glass joint, accommodated a 4-mm. glass ammonia inlet tube A which extended to the bottom of the reactor. The 2-mm. stopcock  $S_3$  on the second outlet led to an ammonia purification reactor and to a manostat. A length of 2-mm. Pyrex rod B, enlarged and flattened on the lower end, extended from the bottom of the reactor up through a gas-tight rubber sleeve on the third opening, through which this rod could be moved up and down. The lower section of the reactor tube was made from the inner part of a  $34/45$   $\Phi$  ground glass joint and had a calibrated volume of 50 ml. The total volume of the reactor tube was 153 ml. The auxiliary apparatus not shown in Figure 2, *i.e.*, ammonia purification reactor, manostat, gas collection bulbs, and Dewar flask for the reactor, was the same as that used with Reactor System A and shown in Figure 1.

After cleaning and drying the Reactor System B, a sealed glass bulb containing a known weight of alcohol was placed at the bottom of the reactor tube. The Pyrex rod B was lowered until it just touched the bulb. A weighed quantity of alkali metal, still coated with xylene, was dropped into the reactor tube and the assembly of the reactor was completed. The reactor was then baked out under vacuum with infrared lamps. By the same procedure used with Reactor System A, purified ammonia was condensed into the reactor tube to give 50 ml. of solution. A gas collection bulb was attached to the reactor head and vacated. The Dry Ice condenser on the reactor head was filled. To initiate the reaction, the

bulb of alcohol was crushed by applying pressure with Pyrex rod B. From that point on, the procedure employed with Reactor System B was identical to that followed with Reactor System A.

The other two reactor systems used in this research employed the l-tube reactor just described, with certain minor modifications, coupled with a water-displacement method for collecting the hydrogen. Reactor System C, an adaptation of the type described by Fernelius and Johnson,<sup>52</sup> is shown in Figure 3. A rubber sleeve was used for the ammonia inlet tube A as well as for the crushing rod B. A piece of Tygon tubing connected the third outlet of the reactor head to an ammonia scrubbing tower C via the mercury manostat D. Up to the moment the bulb of alcohol was crushed, the procedure followed was as described for Reactor System B with the exception that, after the purified ammonia was condensed in the reactor tube, the ammonia inlet tube A was raised so that its tip was just above the surface of the solution. A steady stream of gaseous ammonia was passed from tube A through the reactor to the ammonia scrubber. The ammonia scrubber had a volume of approximately 3 l., of which the 300 ml. directly below stopcock S<sub>1</sub> were calibrated. The scrubber was completely filled with freshly boiled, distilled water prior to each experiment. Reaction in System C was initiated by crushing the bulb of alcohol. The liberated hydrogen was continuously swept from the reactor by the stream of ammonia. The sweep ammonia dissolved in the scrubbing tower while the hydrogen accumulated below stopcock S<sub>1</sub> where its volume was read as the reaction proceeded.

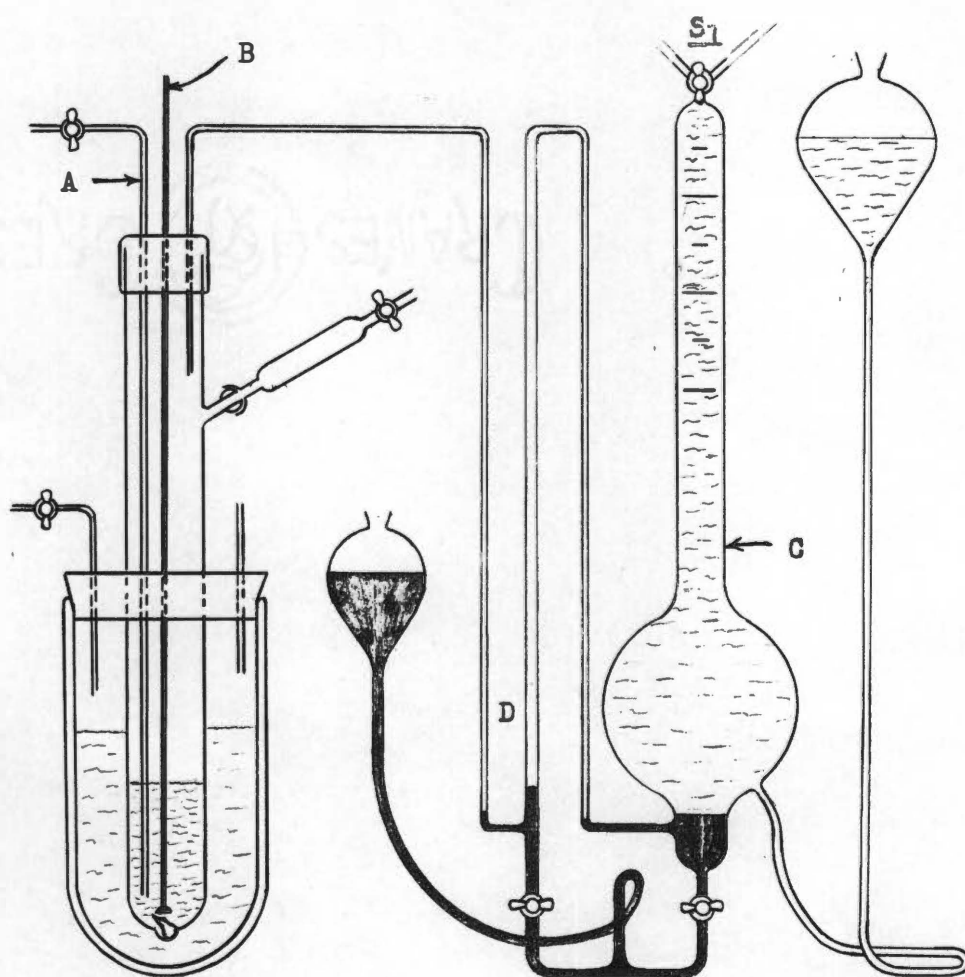


Figure 3. Reactor System C



In a fourth reaction system tested, Reactor System D, everything was identical to Reactor System C with one exception. The tube which had connected manostat D and scrubber tower C (Figure 3) led, not into a scrubber tower, but directly into a large pan of water where its tip pointed upward and served as a delivery tube to water-filled, gas collection bulbs. The latter were fashioned from the outer parts of 24/40  $\text{F}$  ground glass joints and had volumes ranging from 10 to 25 ml. each. As hydrogen displaced the water from one of the bulbs, the sweep ammonia vapor was dissolved, and when the bulb had partially filled with hydrogen, it was quickly replaced by another and was stoppered. Stoppers were made from the inner part of a 24/40  $\text{F}$  ground glass joint, joined just above the shoulder to a 2-mm. stopcock which was terminated with the inner part of a 12/37  $\text{F}$  ground glass joint. Each stopper was filled with water before being used to stopper the hydrogen-filled outer part.

The reactor systems just described led to the development of Reactor System A. It is appropriate, therefore, to discuss briefly their inadequacies in light of the merits or characteristics previously ascribed to the System A.

In the 1-tube reactors, reaction was initiated by crushing a bulb of alcohol in an alkali metal solution in liquid ammonia. From the instant the bulb was crushed, until a homogeneous solution was formed, indeterminate concentration gradients existed in the reaction mixture. Consequently, the hydrogen liberated during this short period of mixing was liberated under conditions other than those assumed for a homogeneous solution. The 1-tube reactor lacked the versatility of the 3-tube reac-

tor, particularly with regard to the choice of the initial location of labeled species when employing isotopes of hydrogen. Whereas the 3-tube reactor enabled one to approach the equilibrium point of an isotopic exchange reaction from either side while employing only labeled liquid ammonia, the 1-tube reactor also required the use of labeled alcohols. Finally, with the 3-tube reactor, the reaction occurred in a completely closed glass chamber, whereas, in the 1-tube reactor, the threat of leakage through the rubber sleeves was always present.

The water-displacement method employed with Reactor System C precluded the use of this system when an isotopic analysis of the hydrogen was required since the hydrogen was not collected in discrete increments. Even when no isotopic analysis was required, the observed volume of hydrogen had to be corrected for the partial pressures of the water and the dissolved ammonia, a correction which could only be approximated since the ammonia concentration of the solution in the scrubber-tower was continually increasing throughout a reaction.

With Reactor System D, the hydrogen was collected in separate increments and the total volume of each increment could be determined. Also, an isotopic analysis on each increment could be obtained. However, the stream of gaseous ammonia required to remove the liberated hydrogen from the reactor was found to exchange with the labeled ammonia solution and lower the activity of the latter.

## B. Analytical Procedures

When the vacated-bulb method was used to collect the hydrogen liberated during a reaction, each gas collection bulb contained a mixture of hydrogen and ammonia, the latter being present in amounts ranging from 80 to 100 per cent by volume. Each bulb of gas was subjected to an analytical procedure wherein the hydrogen was separated from the ammonia, the volume of the hydrogen was measured, and the specific activities of the two gases were determined. The volumetric gas analysis train shown in Figure 4 was used in conjunction with an ionization chamber and a vibrating-reed electrometer for these operations.

### 1. Volumetric Gas Analysis

The volumetric gas analysis train consisted of a cold-finger T, a hand-operated Toepler pump P, a gas burette B, a manometer M, and a manostat N. The bulb of the Toepler pump had a volume of approximately 500 ml. A gas trap and a 2-mm. stopcock S<sub>8</sub> were joined to the bottom of this bulb, and led, via Tygon tubing, to a mercury-filled leveling bulb L. The 100-ml. Pyrex gas burette B was calibrated in tenths of a milliliter. A thermometer was inserted between the burette and its air-jacket. The mercury-filled leveling bulb K was attached to the burette by Tygon tubing. The inner tube of the manostat N, extending from the 2-mm. "T-bore" stopcock S<sub>6</sub> to just below the surface of the mercury in its mercury well, had a total length of approximately 85 cm. The manometer M was used only at pressures below 10 cm. of mercury. Stopcocks S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub> and S<sub>4</sub> were all 2 mm. 120° stopcocks. A typical analysis

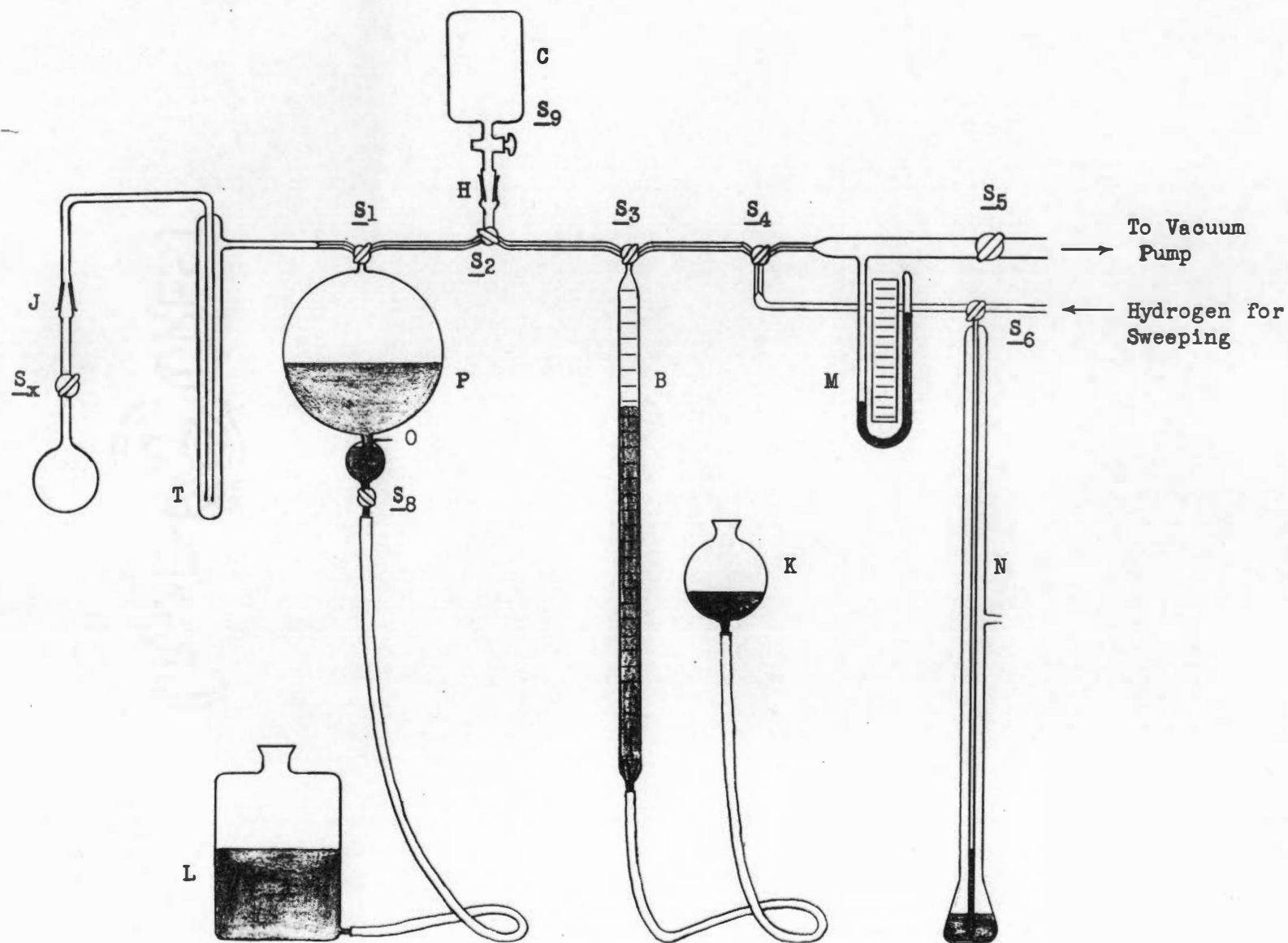


Figure 4. Gas Analysis Train

using this apparatus is described below.

A gas collection bulb, filled with hydrogen and ammonia, and an ionization chamber C were attached to the apparatus by means of 12/37 ground glass joints J and H, respectively. With stopcocks  $S_x$ ,  $S_9$  and  $S_6$  closed, the remaining stopcocks were manipulated in such a manner that the entire system was vacated. Stopcocks  $S_1$  and  $S_3$  were then rotated to connect the horizontal arms, and the Toepler pump and the gas burette were filled with mercury. The cold-finger T was fitted with a Dewar flask, the flask being placed as high as possible on the cold-finger. The Dewar flask was then filled with liquid nitrogen. Stopcock  $S_1$  was turned to connect the Toepler pump to the gas collection bulb, after which stopcock  $S_x$  on the latter was opened. The mercury in the Toepler pump was then slowly drained into the leveling bulb L to fill bulb P with hydrogen and leave ammonia frozen out in the cold-finger. When the mercury level reached the mark 0, stopcock  $S_8$  was closed. After five minutes, stopcocks  $S_1$ ,  $S_2$  and  $S_3$  were set to connect the Toepler pump to the gas burette. The mercury level in the Toepler bulb was raised until the bulb was completely filled and the mercury extended through the capillary manifold and filled the bore of stopcock  $S_3$ . Stopcock  $S_3$  was then closed, and the volume  $V_1$  of hydrogen in the burette was measured. At the same time, room temperature and pressure were recorded. By repeating this operation, a second fraction of the hydrogen in the gas collection bulb was transferred to the gas burette where the total volume  $V_2$  of the two combined fractions of the hydrogen was measured, again at a recorded temperature and pressure. As discussed

later in this section, the total volume of hydrogen originally in the gas collection bulb was calculated from  $V_1$  and  $V_2$ .

Stopcock  $S_4$  was rotated to connect stopcocks  $S_3$  and  $S_6$ , and stopcock  $S_6$  was opened, the latter stopcock being used in conjunction with the valves on a hydrogen tank to regulate hydrogen flow rate into the manifold. With an applied hydrogen pressure of one atmosphere, stopcock  $S_3$  was opened horizontally, thereby forcing the mercury out of the manifold and back into the bulb of the Toeppler pump. Stopcock  $S_8$  was closed again, and the manifold was re-evacuated. Then, the ionization chamber C, which had a volume of 250 ml., was evacuated and filled with tank hydrogen. This was repeated five times to insure the complete removal of all of the gas left in the chamber from any preceding analysis. With the ionization chamber under vacuum, the leveling bulb K was lowered and stopcock  $S_3$  was rotated to connect the chamber and the gas burette. The mercury level in the burette was raised until it was flush with the stopcock  $S_3$ . This left the hydrogen sample, at a low pressure, distributed between the ionization chamber, the bore of stopcock  $S_3$  and the connecting tubing. Stopcock  $S_9$  was closed and stopcock  $S_4$  was rotated to connect stopcock  $S_3$  and  $S_6$ . Stopcock  $S_6$  was opened, allowing a hydrogen flow rate of approximately 50 ml. (STP) per second. Stopcocks  $S_3$  and  $S_9$  were in that order opened and closed alternately seven times each, each time for a fraction of a second. Then, with stopcock  $S_9$  finally left open, stopcock  $S_3$  was opened to the hydrogen line. The mercury level in the inner tube of the manostat N immediately rose under the influence of the partial vacuum in the manifold. As hydrogen swept into the ioniza-

tion chamber, the level of the mercury in the manostat decreased and, finally, hydrogen began to break the surface of the mercury reservoir. This indicated that the chamber was filled with gas at atmospheric pressure, at which time stopcock  $S_9$  was immediately closed. In this manner, a known quantity of hydrogen was transferred to the ionization chamber for isotopic analysis. This chamber, used only with hydrogen, was removed and replaced by another chamber used solely for measuring the specific activity of ammonia.

Previous to analysis of the ammonia's radioactivity, the entire system, including the cold-finger, was again evacuated. With the mercury leveling bulb K lowered, stopcock  $S_3$  was rotated to connect the burette and the cold finger. The Dewar flask was removed. When the ammonia in the cold-finger reached room temperature, an aliquot was measured in the gas burette and transferred to an ionization chamber by the same procedure as that described for hydrogen.

When hydrogen was collected by displacement of water as in Reactor System D, the collection bulb contained, in addition to hydrogen and ammonia, varying amounts of water. For analysis of these bulbs, it was necessary to use a Dry Ice-acetone bath on the bulb itself, as well as a liquid nitrogen trap on the cold finger. Otherwise, the procedure was identical to that just described.

The total amount of hydrogen in each gas collection bulb was calculated from the first two fractions of hydrogen removed from it by the Toepler pump. Let  $V$  and  $\alpha$  represent, respectively, the amount of hydrogen originally in the gas collection bulb, and the fraction of the hy-

drogen transferred to the burette with each identical operation of the Toepler pump. If  $V_1$  represents the volume of the first fraction, and  $V_2$  that of the first and second fractions combined, then equations (1) and (2) may be written.

$$\alpha V = V_1 \quad (1)$$

and 
$$\alpha (V - V_1) = V_2 - V_1 \quad (2)$$

Dividing (1) and (2) and simplifying yields (3).

$$V = \frac{V_1^2}{2V_1 - V_2} \quad (3)$$

All gas volume measurements were corrected to standard temperature and pressure.

For equation (3) to be valid, it was necessary to maintain a constant liquid nitrogen level on the cold-finger T in Figure 4. If the total free space to the left of stopcock  $S_1$  is represented by  $V_B$ , and the volume of the Toepler bulb from the mark M to stopcock  $S_1$  is represented by  $V_P$ , then

$$\alpha = \frac{V_P}{V_P + V_B} \quad (4)$$

if, and only if, the entire free space is at the same temperature. The use of the liquid nitrogen bath on the cold-finger T resulted in a temperature gradient in this free space. However, as long as the liquid nitrogen level was maintained constant, a steady state of thermal equilibrium was maintained. Under these conditions, the value of  $\alpha$  was found to be less than that calculated by equation (4), but the use of equation (3) was still justified. To illustrate the degree of accuracy obtained



in these measurements, and the decrease in  $\alpha$  when the liquid nitrogen trap was used, the following typical experimental results are cited. Without a liquid nitrogen trap, the volume of a sample of hydrogen as calculated from equation (3) was 71.11 ml. The actual value was 71.19 ml. and  $\alpha$  was 0.7266. Using the trap with a constant liquid nitrogen level, the volume of another sample as calculated from equation (3) was 54.72 ml. The actual value was 54.70 ml. and  $\alpha$  was 0.6729.

## 2. Isotopic Gas Analysis

The use of an ionization chamber in conjunction with a vibrating-reed electrometer for the determination of tritium by ion current measurement has been described elsewhere.<sup>53,54</sup> In this work, the "rate-of-charge" method was used to measure the ion current produced by the radiation in the ionization chamber. When using this method, ion current from the ionization chamber is fed to a capacitor in the vibrating-reed electrometer (Applied Physics Corporation, Model 31). The rate at which the charge on the capacitor increases, the measured variable, is directly proportional to the radiation or activity in the chamber, i.e.,

$$\frac{dq}{dt} = ka$$

where  $q$ ,  $a$ , and  $t$  represent charge, activity and time, respectively, and  $k$  is a proportionality constant. It follows that for a constant activity  $a_1$

$$\int_0^q dq = ka_1 \int_0^t dt$$

or

$$a_1 = \frac{q}{kt} \quad (5)$$

When not in use the capacitor is grounded. For a measurement, at zero time, the ground is removed from the capacitor and it is left attached to an electrode in the ionization chamber. The time  $t$  required to produce a charge  $q$  is then measured. The time  $t_q$  that would be required for the same activity  $a_1$  to produce a reference charge  $Q$  is calculated from equation (5), i.e.,

$$t_q = \frac{Q}{q} t$$

Let  $t_m$  represent the time required to produce the charge  $Q$  when the ionization chamber contains  $V_s$  milliliters of a radioactive hydrogen sample plus sufficient non-radioactive hydrogen to give a total pressure of one atmosphere. Then the activity  $A_m$  corresponding to the time  $t_m$  is given by equation (6).

$$A_m = \frac{Q}{k t_m} \quad (6)$$

Let  $t_B$  represent the time that is required to produce the charge  $Q$  when the chamber contains only non-radioactive hydrogen at a pressure of one atmosphere. The activity  $A_B$  corresponding to the time  $t_B$  is the background activity and is given by equation (7).

$$A_B = \frac{Q}{k t_B} \quad (7)$$

The measured activity  $A_m$  is the sum of the background activity  $A_B$  and the activity  $A_s$  resulting from the radioactive hydrogen sample, i.e.,

$$A_m = A_B + A_s \quad (8)$$

Combining equations (6), (7) and (8), it is seen that

$$A_s = \frac{Q}{k} \left( \frac{t_B - t_s}{t_B t_s} \right) \quad (9)$$

and that the ratio of the activities of two different samples is given by

$$\frac{A_s}{A_{s'}} = \frac{t'}{t} \left( \frac{t_B - t}{t_B - t'} \right)$$

Consequently, if only relative activities are required, the value of the proportional constant  $\frac{Q}{k}$  need not be known, and the activities may be expressed in units of reciprocal time. However, it is customary to express activities in terms of millicuries (mc.) or microcuries ( $\mu$ c.). If  $t_0$  represents the time that is required for a standard sample containing  $A_0$  microcuries of tritium to produce the charge  $Q$ , then from equation (9) equation (10) may be written.

$$\frac{Q}{k} = \left( \frac{t_B t_0}{t_B - t_0} \right) A_0 \quad (10)$$

Using this value of  $\frac{Q}{k}$  ( $\mu$ c.·time), the activities calculated by equation (9) are in units of microcuries.

Since  $A_s$  is the activity of  $V_s$  milliliters of the sample, the activity per milliliter or the "specific activity"  $\bar{A}$  ( $\mu$ c./ml.) is simply

$$\bar{A} = \frac{A_s}{V_s} \quad (11)$$

If  $V$  represents the total volume of hydrogen, having a specific activity  $\bar{A}$ , present in a gas collection bulb, then the total activity  $A$  ( $\mu$ c.) of the hydrogen in the bulb is

$$A = V\bar{A} \quad (12)$$

The total activity  $A_T$  ( $\mu\text{c.}$ ) collected by  $n$  consecutive gas collection bulbs during the course of a reaction is then

$$A_T = \sum_{i=0}^{i=n} (A)_i \quad (13)$$

In the next chapter, activity data for hydrogen samples will be expressed in terms of  $\bar{A}$ ,  $A$  and  $A_T$  as defined by equations (11), (12) and (13), respectively. Only specific activities  $\bar{A}$  will be given for radioactive ammonia samples.

A 250-ml. stainless steel, Borkowski ionization chamber was used for measuring tritium activities of hydrogen samples, and a similar brass chamber was used for measuring the tritium activities of ammonia samples. Two complications arose in the determination of the specific activities of the ammonia samples. First, it was observed that the specific activity, as measured in the brass chamber, decreased as the time interval  $\Delta t$  between filling the chamber and making the measurement increased. This effect is illustrated in Figure 5 in which the apparent specific activity  $\bar{A}_{\text{obs.}}$  is plotted as a function of  $\Delta t$ . This effect probably resulted from adsorption of ammonia molecules on the walls of the chamber and its electrode, as evidenced by a significant increase in the background activity of the chamber after each analysis. The high background activities were reduced to normal levels by repeatedly vacating the chamber and flushing with hydrogen. To compensate for this effect, an apparent specific activity vs. time curve (Figure 5) was drawn for each ammonia analysis and extrapolated to zero time for a measured specific activity  $\bar{A}_m$ .

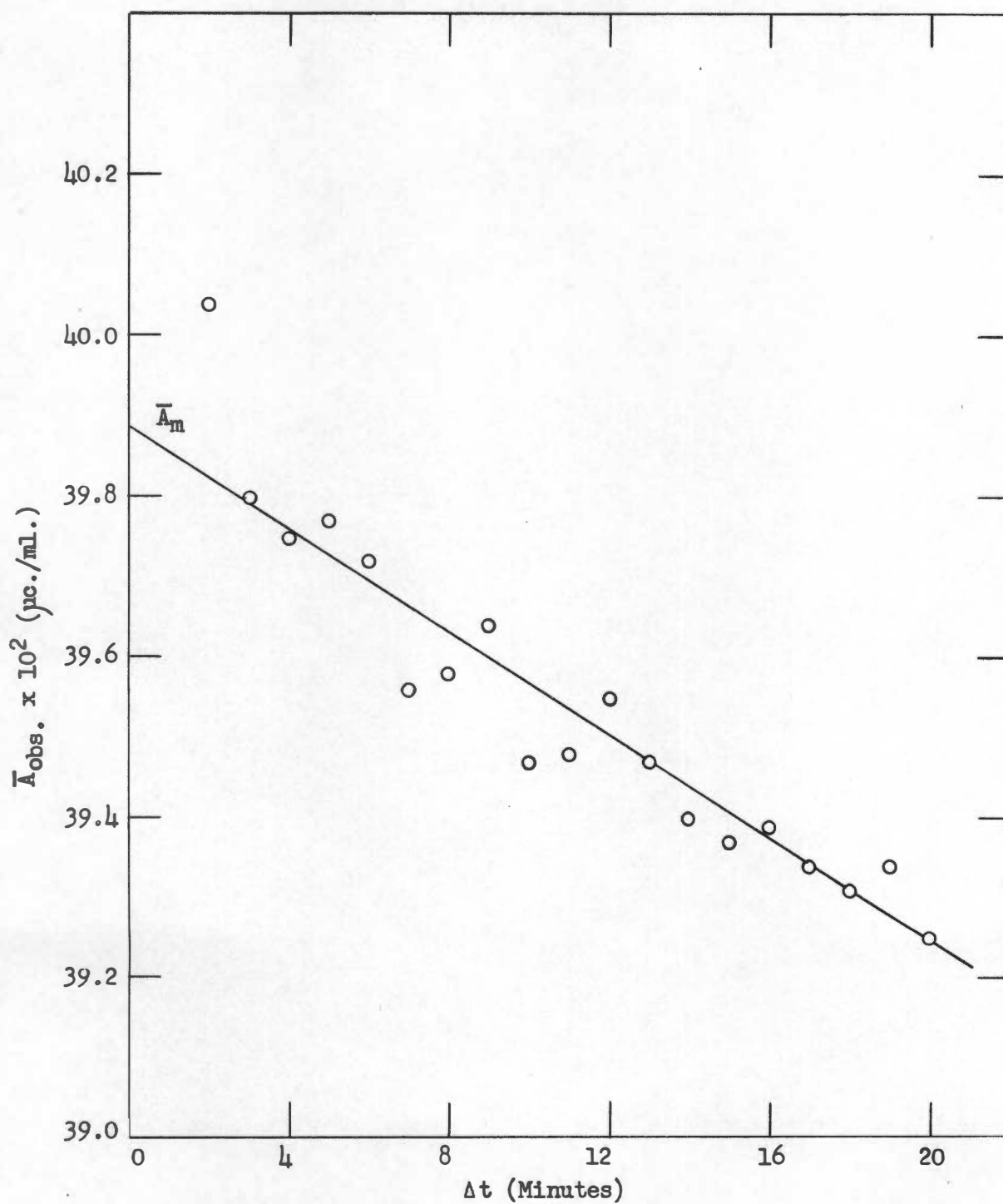


Figure 5. Variation in the Observed Specific Activity of Ammonia with Time.

The second complication with ammonia resulted from a difference in the counting efficiencies of ammonia and hydrogen.<sup>53</sup> It was observed that the measured specific activity of an ammonia sample was a linear function of the volume ( $V_S$ ) of the ammonia in the chamber. This effect is shown in Figure 6, where measured specific activity  $\bar{A}_m$  is plotted as a function of the volume of ammonia. It is seen that for the volume range covered the measured specific activity  $\bar{A}_m$  was a linear function of the volume  $V_S$ , i.e.,

$$\bar{A}_m = \beta V_S + \bar{A} \quad (14)$$

where  $\bar{A}$  corresponds to the specific activity that the ammonia would have if the counting efficiency of ammonia was the same as the counting efficiency of hydrogen. It was further observed that the slope  $\beta$  in equation (14) exhibited a linear dependence on  $\bar{A}$ , i.e.,

$$\beta = \gamma \bar{A} . \quad (15)$$

The experimentally determined value of  $\gamma$  was  $0.00465 \text{ ml.}^{-1}$ . By combining equations (14) and (15), one obtains equation (16),

$$\bar{A} = \frac{\bar{A}_m}{0.00465 V_S + 1} \quad (16)$$

with which all values of  $\bar{A}_m$  for ammonia were corrected.

### C. Reagents

#### 1. Alkali Metals

The alkali metals employed in this investigation, sodium, potassium, and lithium, were reagent grade metals obtained in lump form, stored under mineral oil, from the General Chemical Division of the Allied Chemi-

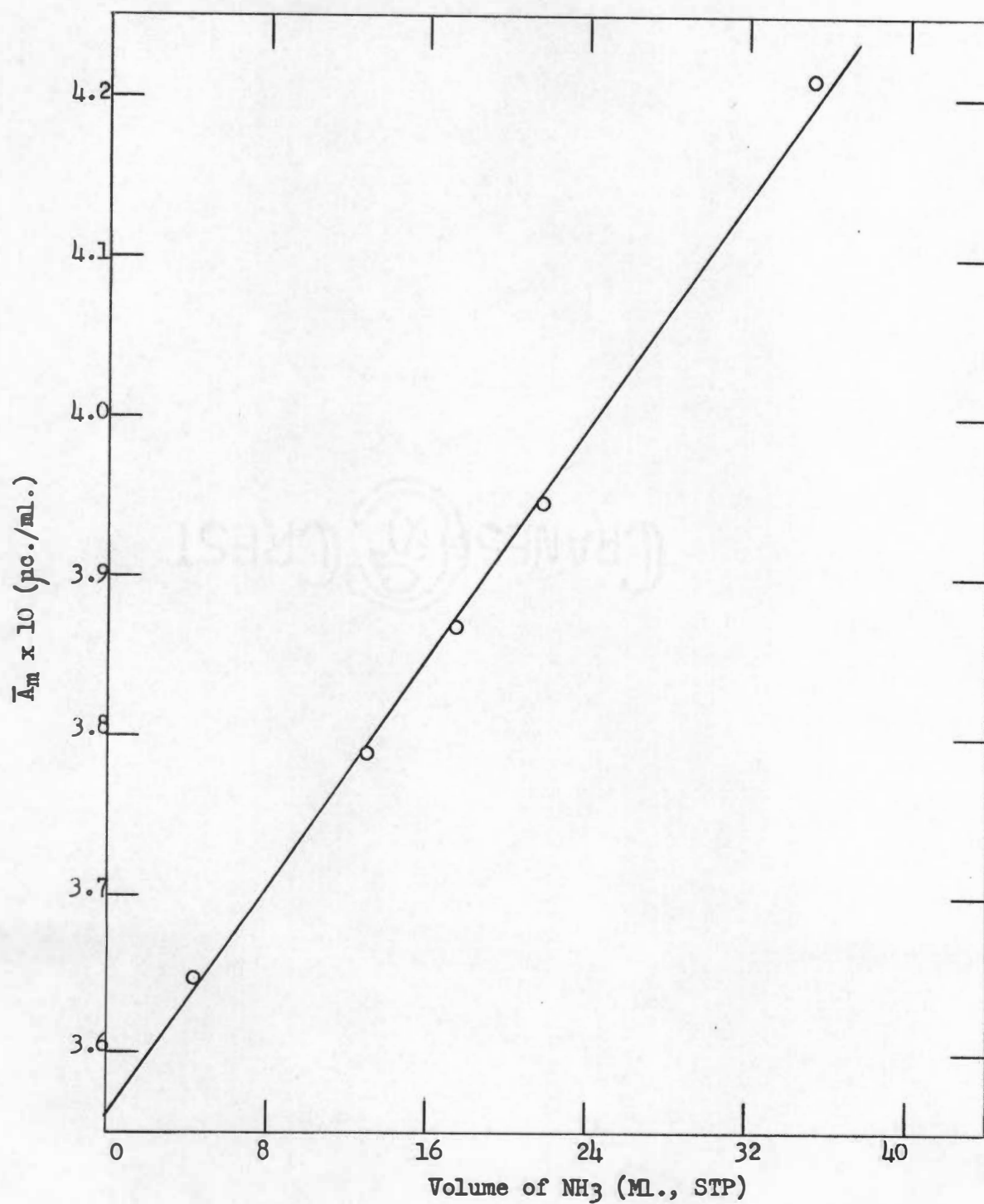


Figure 6. Variation in the Measured Specific Activity of Ammonia with the Volume of Ammonia Counted.

cal and Dye Corporation. In order to prepare a sample, a lump of the metal was cut under mineral oil into small cubes weighing approximately 0.1 gm. each. The desired weight of the alkali metal sample was approximated by transferring an appropriate number of the cubes, still coated with mineral oil, to a weighing bottle containing dry xylene. The weight of the weighing bottle and its contents, determined before and after the addition of the metal, gave a rough estimate of the weight of the metal. Due to the presence of mineral oil on the metal, the estimate was usually about 10 per cent low. The alkali metal addition tube on burette A of the reactor (Figure 1) was carefully cleaned and dried in a vacuum dessicator. The tube was then stoppered, vacated, and weighed. The cubes of alkali metal were then transferred from the weighing bottle to the addition tube. The tube was again vacated, to remove the xylene carried over with the metal, and weighed. The difference in the weight of the tube before and after adding the metal gave an accurate value for the weight of the metal sample. The addition tube containing the metal was then filled with gaseous ammonia and attached to the reactor.

## 2. Alcohols

The alcohols used in this investigation were anhydrous ethanol and anhydrous isopropyl alcohol. Commercial Solvents Corporation absolute ethanol was further dried by treatment with magnesium, following the procedure described by Vogel.<sup>55</sup> The isopropyl alcohol, labeled with tritium in the hydroxyl hydrogen position and triply distilled from calcium oxide, was obtained from the Oak Ridge National Laboratory.



The apparatus used for preparing samples of known weight of anhydrous alcohol is shown in Figure 7. The apparatus consisted of a three-way, 2-mm., 120° capillary stopcock, S<sub>1</sub>, sealed to a 2-ml. burette, B, calibrated in hundredths of a milliliter, and to a 150-ml. flask, A. Calcium chloride drying tubes, D<sub>1</sub> and D<sub>2</sub>, and stopcocks, S<sub>2</sub> through S<sub>5</sub>, were used to stopper A and B, respectively. The third or vertical arm of the stopcock was drawn to a fine capillary tip, F, and fitted with a glass jacket, E, as shown in the figure.

After being dried, the alcohol was distilled directly into the reservoir A. The entire apparatus shown in Figure 7 had been previously dried under vacuum. The capillary delivery tube, F, was inserted into the neck of an empty glass bulb, C, having a long thin neck and a capacity of only slightly more than the volume of alcohol desired. Stopcock S<sub>1</sub> was rotated to connect A and B. By manipulating stopcocks S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub>, and S<sub>5</sub>, the alcohol drained from A into B. When the level of the alcohol in B reached the zero calibration mark, stopcock S<sub>1</sub> was rotated to connect B and F. When the desired volume of alcohol had drained into bulb C, the bulb was sealed with a torch. During this process, dry nitrogen was introduced through the side arm on the jacket, E. A rather accurate estimate of the weight of the alcohol sample was obtained from the volume of alcohol delivered and the density of the alcohol. The exact weight was obtained by weighing the bulb C before and after filling with alcohol. The sample containers, C, were very thin-walled bulbs blown from 4-mm. Pyrex tubing. Prior to both weighings, they were dried in a vacuum dessicator.

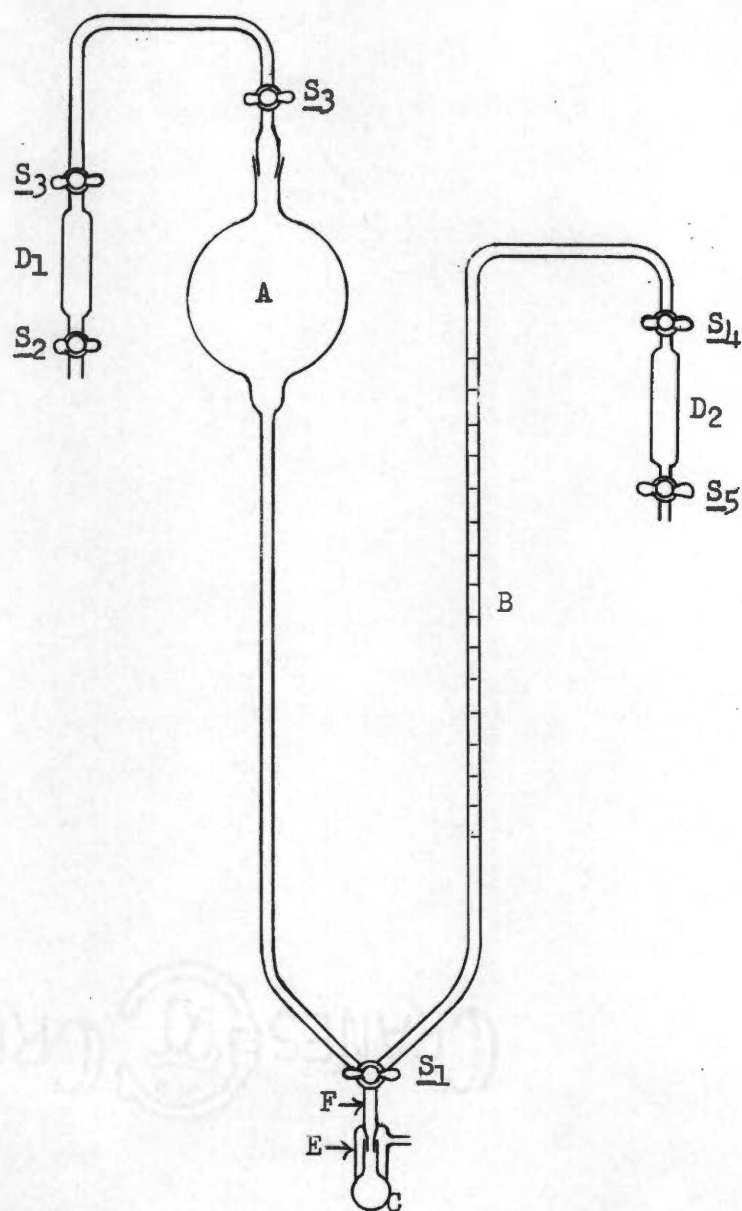


Figure 7. Apparatus for Preparation of Alcohol Samples

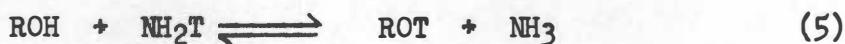
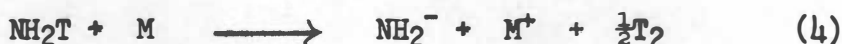
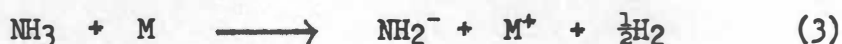
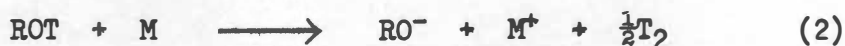
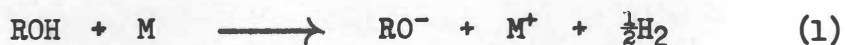
### 3. Ammonia

The ammonia used was E. I. DuPont de Nemours Company highest purity (99.8 per cent) anhydrous grade ammonia. Before use, the ammonia was twice distilled, once from sodium, in the manner described in the previous section of this chapter. Tritium labeled ammonia was obtained from the Oak Ridge National Laboratory, and after dilution with unlabeled ammonia, was purified by the same techniques used with the unlabeled ammonia and by being purged with gaseous hydrogen as described in the previous section of this chapter.

### CHAPTER III

#### EXPERIMENTAL RESULTS AND DISCUSSION

It was pointed out in Chapter I (page 16) that the reaction system involved in this study could be represented, at least from an overall stoichiometric viewpoint, by the following set of equations in which ROH, M, and T represent an alcohol, an alkali metal, and tritium, respectively.



All of these reactions occur simultaneously upon mixing an alkali metal and an alcohol in liquid ammonia. However, as was indicated in Chapter II, the measured variables included only the initial concentrations and activities of the reactants, and the volume and activity of the liberated hydrogen as a function of time. Consequently, in order to make a quantitative kinetic investigation of the primary reactions represented by equations (1) and (2), it was first necessary to determine the effect of the other reactions, i.e., the reaction of the metal with the labeled solvent (equations (3) and (4)) and the isotopic exchange reaction occurring between the alcohol and the solvent (equation (5)), on the measured volume and activity data. In the following presentation, first consideration will be given to those competing or secondary reactions.

### A. Metal-Ammonia Reaction

Using Reactor System A (Figure 1), the data shown in Table III was obtained for the reaction of potassium with labeled liquid ammonia (equations (3) and (4)). In this particular experiment, burette A contained  $4.056 \times 10^{-2}$  gm. atoms of potassium dissolved in labeled liquid ammonia to give 25.0 ml. of solution. Burette B contained 25.0 ml. of unlabeled ammonia. The resultant solution was, therefore, 0.81 M in potassium.

Column II of Table III gives the time,  $t$ , as measured from the start of the reaction,  $t^0$ , at which the evolved hydrogen was removed from the reactor by the gas collection bulb whose number appears in column I. The volume ( $V_{\text{ml.}, \text{STP}}$ ), specific activity ( $\bar{A}_{\mu\text{c.}/\text{ml.}}$ ), and the total activity ( $A_{\mu\text{c.}}$ ) of the hydrogen contained in each gas collection bulb are listed in columns III, IV, and V, respectively. Columns VI and VII list the total volume ( $V_T \text{ ml.}, \text{STP}$ ) and total activity ( $A_T \mu\text{c.}$ ) of the hydrogen liberated during the time interval from  $t^0$  through  $t$ , i.e., the summations of the values listed in columns III and V. Since the tritium was present only in tracer quantities, its contribution to the values of  $V$  and  $V_T$  was insignificant. The specific activity ( $\bar{A}_{\text{NH}_3} \mu\text{c.}/\text{ml.}$ ) obtained by analysis of the ammonia contained in each gas collection bulb is listed in column VIII.

Referring to bulbs 2 through 5, the lack of a sufficient quantity of hydrogen precluded the determination of its specific activity. It is apparent from the data in column IV, bulbs 8 through 12, that the specific activity of the evolved hydrogen was essentially constant throughout the

TABLE III

## POTASSIUM-AMMONIA REACTION

Reactor System A							
Reactants: Burette A: 1.5858 gm. (0.0406 gm. atoms) of potassium plus $\text{NH}_2\text{T}$ to give 25.0 ml. of solution							
Burette B: 25.0 ml. of $\text{NH}_3$							
I	II	III	IV	V	VI	VII	VIII
Sample Number	Time from $t^0$	V (ml.)	$\bar{A} \times 10^3$ (mc./ml.)	$A \times 10^3$ (mc.)	$V_T$ (ml.)	$A_T \times 10^2$ (mc.)	$\bar{A}_{\text{NH}_3} \times 10^2$ (mc./ml.)
1	15 sec.	1.91	218.0	41.64	1.91	41.64	7.63
2	50 sec.	0.05	- - -	- - -	1.96	- - -	4.12
3	97 sec.	0.05	- - -	- - -	2.01	- - -	4.14
4	3 min.	0.06	- - -	- - -	2.07	- - -	4.02
5	10 min.	0.31	- - -	- - -	2.38	- - -	3.67
6	30 min.	1.23	1.24	1.53	3.61	41.79	3.82
7	1 hr.	1.69	1.57	2.66	5.30	42.06	3.98
8	5 hrs.	12.74	1.84	23.37	18.04	44.40	3.92
9	10.75 hrs.	19.56	1.92	37.50	37.60	48.15	4.00
10	16 hrs.	10.59	1.97	20.86	48.19	50.23	4.04
11	22 hrs.	9.62	1.89	18.19	57.81	52.05	3.70
12	28 hrs.	12.36	1.96	24.19	70.17	54.47	4.19

experiment. The low specific activities recorded for bulbs 6 and 7 can be attributed to the lack of sufficient hydrogen for an accurate analysis. However, it is seen that the specific activity of the hydrogen contained in the first bulb was approximately 110 times greater than that of the succeeding samples. This difference obviously could not be attributed to experimental inaccuracies. The data in column VIII shows that the specific activity of the ammonia in bulbs 2 through 12 was essentially constant, but here too the specific activity of the first sample was abnormally high. The volume of ammonia counted for each case was 13.0 ml. at STP.

It was concluded from the above experiment, that the labeled liquid ammonia was contaminated with molecular tritium, which was removed by the first collection bulb. After this discovery, the labeled liquid ammonia was preswept with tank hydrogen while being dried over sodium. This treatment was found to remove the contaminant. It must be noted, however, that some of the experiments reported herein were performed before the presence of the "hot" contaminant was suspected. In such cases, this fact will be noted.

Since only 15 per cent of the potassium and an insignificant fraction of the solvent reacted during the period of observation, twenty-eight hours, it was impossible to determine the order of the reaction with respect to the reactants. It seems likely, cf. Chapter I (page 23), that the rate of the reaction was dictated by impurities which served as catalysts. From columns II and III, it is seen that the average rate at which hydrogen was evolved was approximately 2 ml./hr.

In another experiment, using a single-tube reactor (Figure 2), the initial potassium concentration was reduced to 0.31 M. The data for this experiment is shown in Table IV. The volume of hydrogen liberated in one hundred ten hours was only 12.78 ml., corresponding to a rate of 0.17 ml./hr. The addition of an iron nail to the solution in the reactor after one hundred ten hours increased the rate to about 12 ml./hr.

Experiments of the type just described were carried out using sodium and lithium in place of potassium. Again, the results indicated that the reaction was under catalytic control. In one experiment, Table IV, the initial sodium concentration was 0.83 M and the average rate of hydrogen evolutions was 0.11 ml./hr. In a second experiment, the initial sodium concentration was reduced to 0.31 M. The total volume of hydrogen liberated in one hundred ten hours was 2.65 ml., the rate being only 0.024 ml./hr. After one hundred ten hours, an iron nail was added to the solution and the rate increased to 2.03 ml./hr. In the case of lithium, Table IV, a solution having an initial lithium concentration of 0.35 M evolved 1.02 ml. of hydrogen in one hundred ten hours for a rate of 0.0093 ml./hr. The addition of an iron nail to the solution after the one hundred ten hours increased the rate of hydrogen evolution to 0.49 ml./hr.

It had been hoped that by carefully cleaning the reactor system, purifying the reactants, and excluding impurities from the reactor, the reaction between the alkali metal and liquid ammonia could be eliminated. This hope was never realized; in the experiments just described, the metal-ammonia solutions were prepared with fastidious care. In general, the



TABLE IV

## ALKALI METAL-AMMONIA REACTIONS

System*	Time (Hrs.)	V (ML.)	$\frac{\Delta V}{\Delta t}$ (ML./Hr.)
0.31 M Potassium	110	12.78	0.1166
0.31 M Potassium plus iron nail	1	11.97	11.97
0.83 M Sodium	8	0.833	0.1042
0.83 M Sodium	8	0.856	0.1070
0.31 M Sodium	110	2.65	0.0241
0.31 M Sodium plus iron nail	1	2.03	2.03
0.31 M Lithium	110	1.02	0.0093
0.31 M Lithium plus iron nail	1	0.49	0.49

\*Reactor System B used in all experiments.

rates of the reaction decreased in the order, potassium:sodium:lithium, with the rate being quite appreciable in the case of potassium and almost insignificant in the case of lithium. This same trend was observed, as will be shown in subsequent sections of this chapter, in the alkali metal-alcohol-liquid ammonia systems. In these systems, the rate of metal-ammonia reaction varied from 0.25 ml./hr to 5.0 ml./hr. for potassium, from 0.05 ml./hr. to 0.53 ml./hr. for sodium, and from 0.07 ml./hr. to 0.10 ml./hr. for lithium. These rates were of such a magnitude as to necessitate a correction of the volume and activity data obtained in the metal-alcohol-ammonia systems for the metal-ammonia reaction in order to study the metal-alcohol reaction. The method of effecting this correction will now be discussed.

For illustrative purposes, suppose that the rate expression for the evolution of hydrogen by the metal-ammonia reaction could be represented by the equation

$$\frac{d[H_2]}{dt} = k[M]^a [NH_3]^b \quad (6)$$

Similarly,

$$\frac{d[T_2]}{dt} = k^\bullet [M]^a [NH_2T]^b \quad (7)$$

Then, dividing equation (6) by equation (7),

$$\frac{d[H_2]}{d[T_2]} = \frac{k}{k^\bullet} \left( \frac{[NH_3]}{[NH_2T]} \right)^b \quad (8)$$

However, since only a very small fraction of the solvent reacted in any experiment in this work, the ratio  $[NH_3]/[NH_2T]$  remained essentially constant in spite of any isotope effect on the reaction. Under these con-

ditions, equation (8) becomes

$$d[H_2] = c d[T_2] \quad (9)$$

which, upon integration gives equation (10).

$$H_2 = c T_2 + d \quad (10)$$

Equation (10) shows that the total tritium evolved during the time interval from  $t^0$  to  $t$  should be a linear function of the total hydrogen liberated over the same time interval. Since the total activity of the hydrogen is directly proportional to the total tritium, equation (10) may be written in the form

$$V_T = c' A_T + d' \quad (11)$$

where  $V_T$  and  $A_T$  represent the total volume and total activity of the liberated hydrogen.

Using the data given in Table III for the reaction of potassium with the labeled solvent, a graph of  $V_T$  vs.  $A_T$  is shown in Figure 8. The resulting straight line has a slope of  $1.939 \times 10^{-3}$   $\mu\text{c./ml.}$ , this slope being the constant specific activity,  $\bar{A}$ , of the hydrogen liberated from the solvent. From column VIII, the average specific activity of the labeled ammonia,  $\bar{A}_{\text{NH}_3}$ , from  $t^0 + 0.5$  hours to  $t^0 + 28.0$  hours, was  $3.95 \times 10^{-2}$   $\mu\text{c./ml.}$  when the volume of the ammonia counted was 13.0 ml. Using equation (16) (page 54) to correct for the difference in the counting efficiencies of hydrogen and ammonia, the  $\bar{A}_{\text{NH}_3}$  value becomes  $3.72 \times 10^{-2}$   $\mu\text{c./ml.}$

Equation (12) defines the separation factor,  $S_{\text{NH}_3}$ , for the reaction of ammonia with the metal.

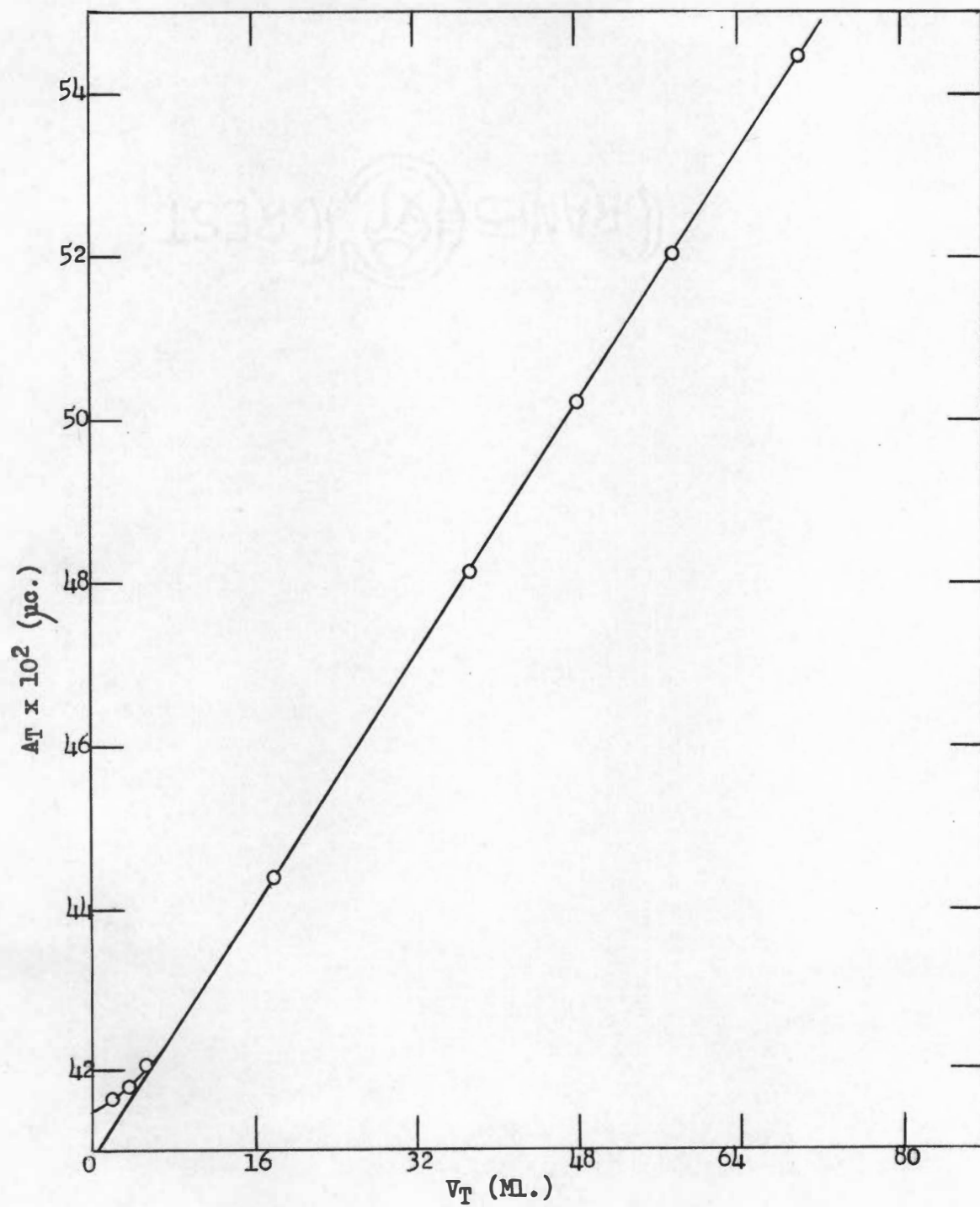


Figure 8. Potassium-Ammonia System:  $V_T$  versus  $A_T$ .

$$S_{\text{NH}_3} = \frac{\left( \frac{\bar{A}}{\bar{A}_{\text{NH}_3}} \right)_{\text{no isotope effect}}}{\left( \frac{\bar{A}}{\bar{A}_{\text{NH}_3}} \right)_{\text{experimental}}} \quad (12)$$

If there were no isotope effect on the liberation of hydrogen from the ammonia, the specific activity of the evolved hydrogen would be two-thirds that of the ammonia itself. Then

$$S_{\text{NH}_3} = \frac{2}{3} \left( \frac{\bar{A}_{\text{NH}_3}}{\bar{A}} \right)_{\text{experimental}} \quad (13)$$

and, for the experiment under discussion, the separation factor,  $S_{\text{NH}_3}$ , can be calculated.

$$S_{\text{NH}_3} = \frac{2}{3} \left( \frac{3.72 \times 10^{-2}}{1.939 \times 10^{-3}} \right) = 12.79$$

As a result of an isotope effect on the hydrogen liberation reaction, the ratio of the rates at which hydrogen and tritium were liberated was 12.79 times as great as would have been expected had no isotope effect been operative. The tritium was preferentially concentrated in the solvent.

In the metal-alcohol-ammonia systems, the metal was always employed in excess. Consequently, the reaction of the metal with the labeled solvent continued after the metal-alcohol reaction had gone to completion. If the separation factors for the two reactions differed, a plot of  $V_T$  vs.  $A_T$  should exhibit an initial slope corresponding to the specific activity of the hydrogen liberated from the alcohol, followed by a second linear section having a slope corresponding to the specific activity of the hydrogen liberated from the solvent.

In Figure 9, a plot of  $V_T$  vs.  $A_T$  is shown for a typical reaction of potassium with ethanol in liquid ammonia (see Table XIX, page 125). It is apparent that  $V_T$  is essentially a linear function of  $A_T$  from zero to 55 ml. The graph then exhibits a negative deviation from the initial slope until  $V_T$  reaches approximately 85 ml., at which point the graph breaks sharply and assumes a new linear section extending to 140 ml. Over this last section, the slope is  $2.113 \times 10^{-2} \mu\text{c./ml.}$  Since the specific activity of the solvent,  $\bar{A}_{\text{NH}_3}$ , was  $3.575 \times 10^{-1} \mu\text{c./ml.}$ , the separation factor calculated for this section by means of equation (13) is 11.28. It is apparent that the last section of the graph corresponds to the continuing reaction of the potassium with the labeled solvent.

The difference in the two separation factors, 12.79 and 11.28, might possibly be attributed to the effect of the alkoxide on the separation factor, or to an inaccuracy in the value of  $\bar{A}_{\text{NH}_3}$  used in calculating the separation factor of 12.79. The last section of the graph of  $V_T$  vs.  $A_T$  is shown in Figure 10 for another potassium-ethanol-ammonia reaction (see Table XXI, page 127) in which the solvent employed was the same as that used in the experiment that yielded a separation factor of 11.28. The slope of the straight line,  $\bar{A}$ , is  $2.138 \times 10^{-2} \mu\text{c./ml.}$  With equation (13), this gives a separation factor of 11.15, in agreement with the value of 11.28.

In the metal-alcohol-ammonia experiments, the total volume of hydrogen liberated,  $V_T$ , was equal to the sum of the hydrogen liberated from the alcohol,  $(V_T)_{\text{ROH}}$ , and the hydrogen liberated from the solvent,  $(V_T)_{\text{NH}_3}$ , i.e.,

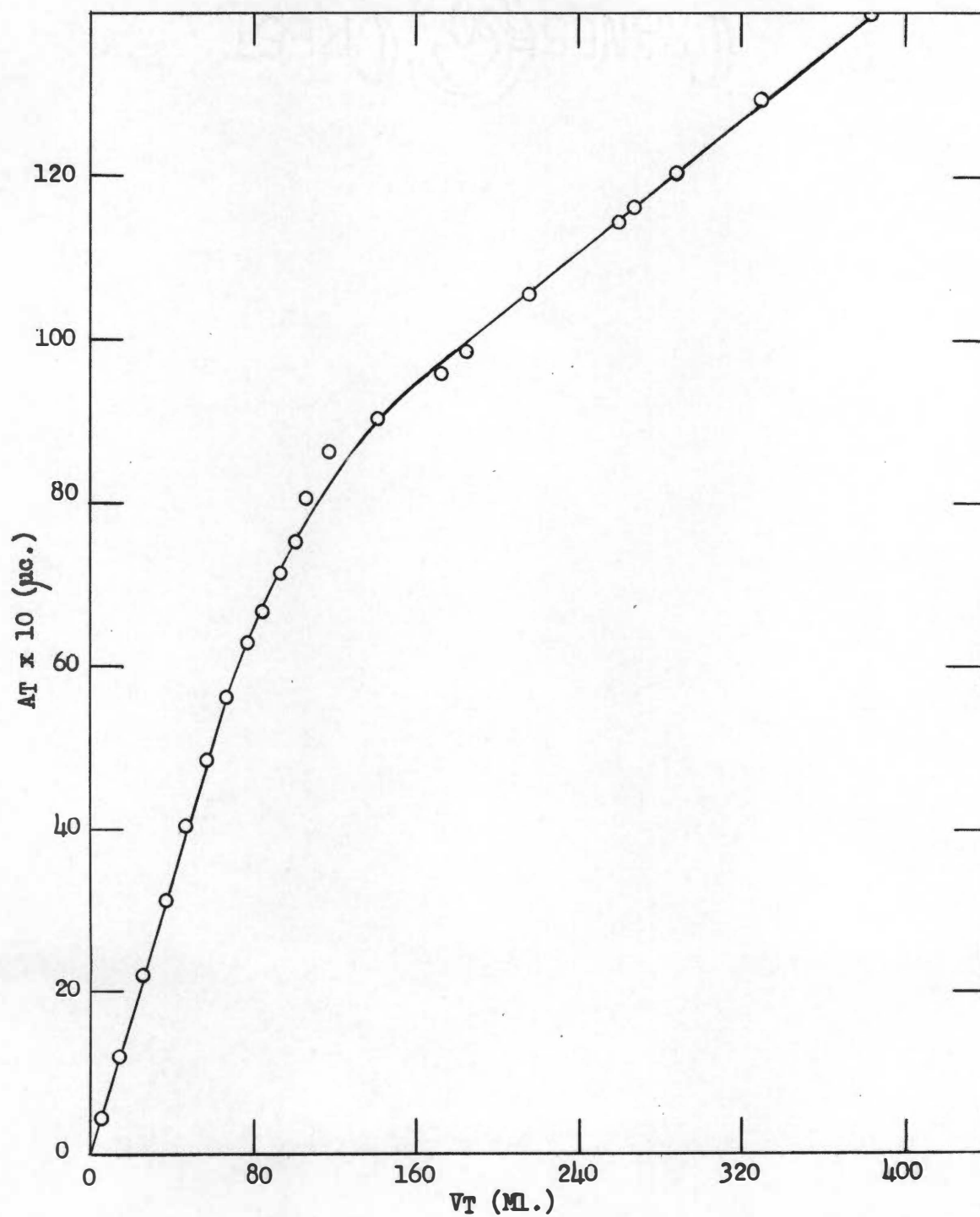


Figure 9. Potassium-Ethanol-Ammonia System, Run VIII:  $V_T$  versus  $AT$ .

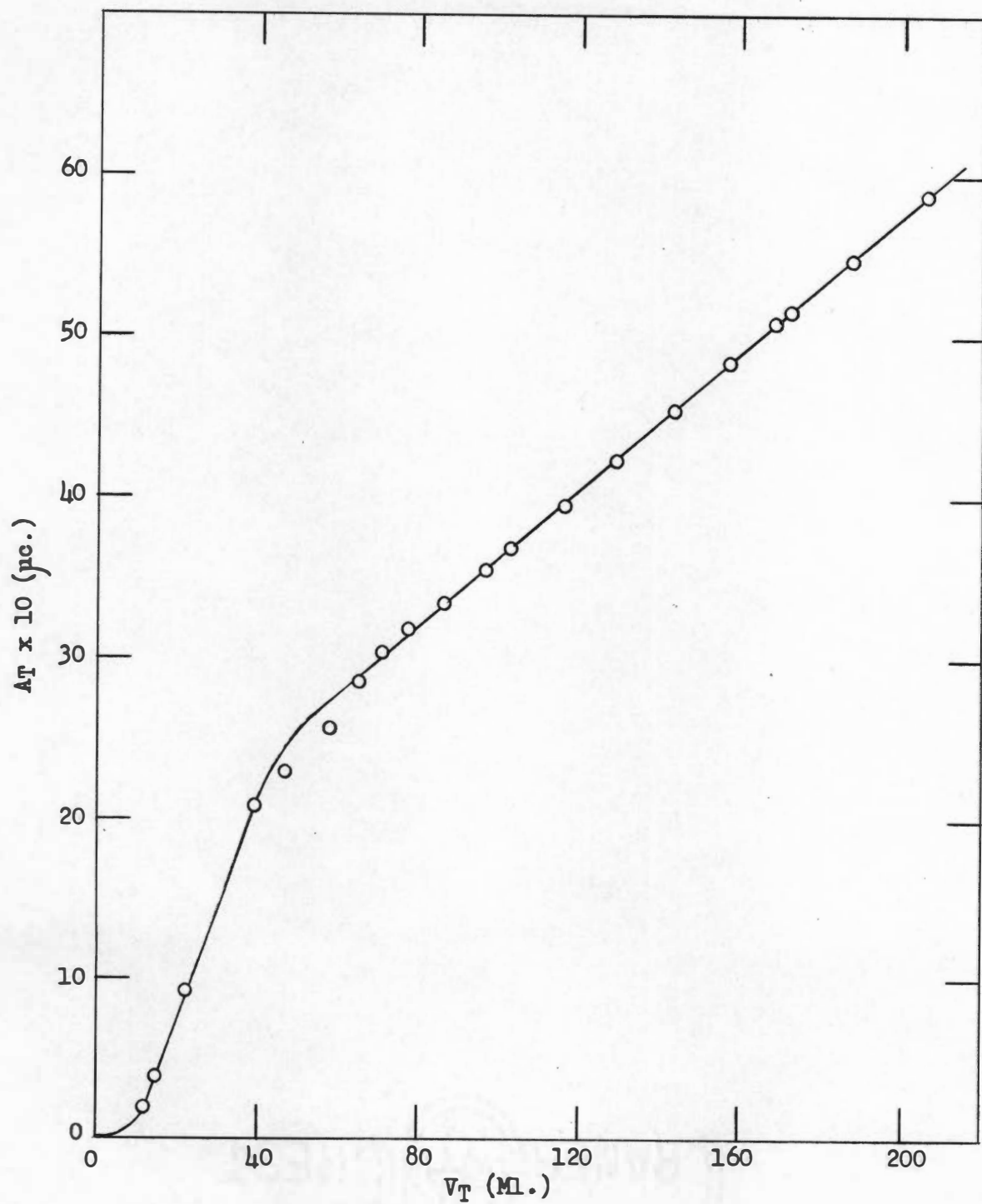


Figure 10. Potassium-Ethanol-Ammonia System, Run X:  $V_T$  versus  $A_T$ .



$$V_T = (V_T)_{ROH} + (V_T)_{NH_3} \quad (14)$$

and

$$\frac{dV_T}{dt} = \frac{d(V_T)_{ROH}}{dt} + \frac{d(V_T)_{NH_3}}{dt} \quad (15)$$

However, since in these experiments the reaction was followed beyond completion of the metal-alcohol reaction, the rate at which hydrogen was liberated by the metal-ammonia reaction eventually became equal to the experimentally measured rate at which  $V_T$  varied with time.

$$\left[ \frac{dV_T}{dt} \right]_{(V_T)_{ROH}} = \left[ \frac{d(V_T)_{NH_3}}{dt} \right]_{(V_T)_{ROH}} \quad (16)$$

By assuming that the rate of the metal-ammonia reaction was constant from  $t^0$  to  $t$ , equation (16) gives equation (17)

$$\left[ \frac{d(V_T)_{NH_3}}{dt} \right]_{(V_T)_{ROH}} = m \quad (17)$$

which, upon integration and evaluation becomes equation (18).

$$(V_T)_{NH_3} = mt \quad (18)$$

Substituting  $(V_T)_{NH_3}$  from equation (18) into equation (14), and rearranging, one obtains equation (19).

$$(V_T)_{ROH} = V_T - mt \quad (19)$$

After each experiment with the alcohol-metal-ammonia system, the value of  $m$  was determined and the volume of hydrogen liberated from the alcohol was calculated from equation (19). In other words, the experimental data was corrected to obviate the hydrogen from the metal-ammonia reaction. The sharp break in the graph of  $V_T$  vs.  $A_T$  from each experi-

ment served as a convenient indicator for the time of completion of the metal-alcohol reaction, after which time  $m$  was taken as equal to  $\Delta V_T / \Delta t$ .

In the metal-alcohol-ammonia experiments, the total activity,  $A_T$ , of the evolved hydrogen was equal to the sum of the activity resulting from the metal-alcohol reaction,  $(A_T)_{ROH}$ , and from the metal-ammonia reaction,  $(A_T)_{NH_3}$ , i.e.,

$$A_T = (A_T)_{ROH} + (A_T)_{NH_3} \quad (20)$$

The total activity of the hydrogen liberated from the solvent is given by equation (21), in which the specific activity of the hydrogen liberated

$$(A_T)_{NH_3} = (V_T)_{NH_3} (\bar{A})_{NH_3} \quad (21)$$

from the solvent,  $(\bar{A})_{NH_3}$ , could be evaluated in the manner described on page 67. Substituting the value of  $(V_T)_{NH_3}$  given by equation (18) into equation (21), one obtains equation (22).

$$(A_T)_{NH_3} = mt (\bar{A})_{NH_3} \quad (22)$$

By substituting this value of  $(A_T)_{NH_3}$  into equation (20) and rearranging, equation (23) is obtained.

$$(A_T)_{ROH} = A_T - mt (\bar{A})_{NH_3} \quad (23)$$

Alternately, since  $m (\bar{A})_{NH_3}$  is a constant,  $n$ , for any given experiment, equation (23) may be rewritten to give equation (24).

$$(A_T)_{ROH} = A_T - nt \quad (24)$$

Either equation (23) or equation (24) was used to correct the activity data for the contribution of the metal-ammonia reaction.

## B. Alcohol-Ammonia Exchange Reaction

In Chapter I (page 23), it was suggested that the isotopic exchange reaction, represented by equation (5), should be immeasurably fast. It will now be shown that this equilibrium was established and



maintained at a rate which was instantaneous relative to the rate at which hydrogen was liberated by the alkali metal-alcohol reaction. The equilibrium constant for the isotopic exchange reaction is given by equation (25) which, upon rearrangement, can be written as equation (26).

$$K_{\text{eq.}} = \frac{[\text{ROT}][\text{NH}_3]}{[\text{ROH}][\text{NH}_2\text{T}]} \quad (25)$$

$$\frac{[\text{ROH}]}{[\text{ROT}]} = \frac{1}{K_{\text{eq.}}} \frac{[\text{NH}_3]}{[\text{NH}_2\text{T}]} \quad (26)$$

Since in each experiment, the solvent was used in large excess, the ratio  $[\text{NH}_3]/[\text{NH}_2\text{T}]$  was essentially constant. Therefore, the isotopic exchange reaction served to maintain a constant ratio of unlabeled alcohol, ROH, to labeled alcohol, ROT, i.e., a constant H/T ratio in the species from which the hydrogen was liberated.

In the following discussion, extensive use will be made of  $V_T$  vs.  $A_T$  graphs such as those appearing in Figures 8, 9, and 10. In Figure 8, the plot of  $V_T$  vs.  $A_T$  was linear. In Figure 9, the entire graph of  $V_T$  vs.  $A_T$  was not linear, but it did exhibit distinct regions of linearity. One might well ask what conditions must be met in order that the graph of  $V_T$  vs.  $A_T$  be linear. Two conditions are necessary. First, it is necessary that the nature of the species from which the hydrogen is evolved

does not change. In Figure 9, the sharp break in the graph at 85 ml. resulted from the fact that up to that point, the hydrogen was being liberated primarily from the alcohol and, thereafter, exclusively from the ammonia. The difference in the isotope effect on the two reactions resulted in a change in the specific activity of the liberated hydrogen and, consequently, a change in the slope of the  $V_T$  vs.  $A_T$  curve. The second condition that must be met is that the hydrogen to tritium ratio, (H/T), in the species from which the hydrogen is liberated does not change. In Figure 8, the graph of  $V_T$  vs.  $A_T$  was linear because the fraction of the solvent that reacted was so small that both conditions were met. The same is true of Figure 10 and the last linear section of Figure 9.

In Figure 9,  $V_T$  was plotted against  $A_T$  for a typical reaction of potassium with ethanol in labeled liquid ammonia. Reactor System A was used for this experiment. Burette A contained the potassium dissolved in labeled ammonia, while burette B contained the ethanol dissolved in unlabeled ammonia. At time zero,  $t^0$ , the ethanol contained no tritium. In the region up to 85 ml., which corresponds to the metal-alcohol reaction, the graph is not linear but exhibits a negative deviation from the initial slope at about 55 ml. This deviation from linearity must be attributed either to a variation in the H/T ratio in the alcohol, or to a change in the form of the alcohol. If the deviation were a result of the slowness of the exchange reaction, then the specific activity should have increased as the reaction proceeded since the alcohol was initially unlabeled. Yet, as is shown in Figure 9, the specific activity of the hydrogen liberated from the alcohol, i.e., the slope of the graph, was

at a maximum at  $t^0$  and actually decreased as the reaction proceeded. Therefore, one might conclude that the isotopic exchange reaction had gone to completion within the time required for mixing the reactants (<1 sec.), and that the deviation of the graph of  $V_T$  vs.  $A_T$  from linearity resulted from a change in the reacting species of the metal-alcohol reaction as the reaction proceeded to completion.

More conclusive proof that the isotopic exchange reaction was instantaneous, relative to the rate of the hydrogen evolution reaction, was obtained by reversing the location of the tritium at  $t^0$  in two otherwise identical experiments. In one experiment, using Reactor System A, the ethanol was dissolved in unlabeled liquid ammonia in burette B, while sodium was dissolved in labeled liquid ammonia in burette A (Table IX). In this experiment, referred to as Run II, the approach at  $t^0$  toward equilibrium of the isotopic exchange reaction, as represented by equation (5), was from the left, as in the preceding potassium experiment. In Figure 11,  $V_T$  is shown as a function of  $A_T$ , the experimental data being represented by the circles. It is observed that the graph approaches a straight line, A, as  $V_T$  approaches zero. With increasing  $V_T$ , the curve exhibits a positive deviation from A and approaches a new straight line, B, as the reaction approaches completion. At 105 ml., a third linear section, C, begins. Section C of this graph corresponds to the continuing reaction of the sodium with the labeled solvent following completion of the sodium-ethanol reaction. Sections A and B relate to the latter reaction and will be discussed at length in the section of this chapter dealing with the sodium-ethanol-ammonia system.

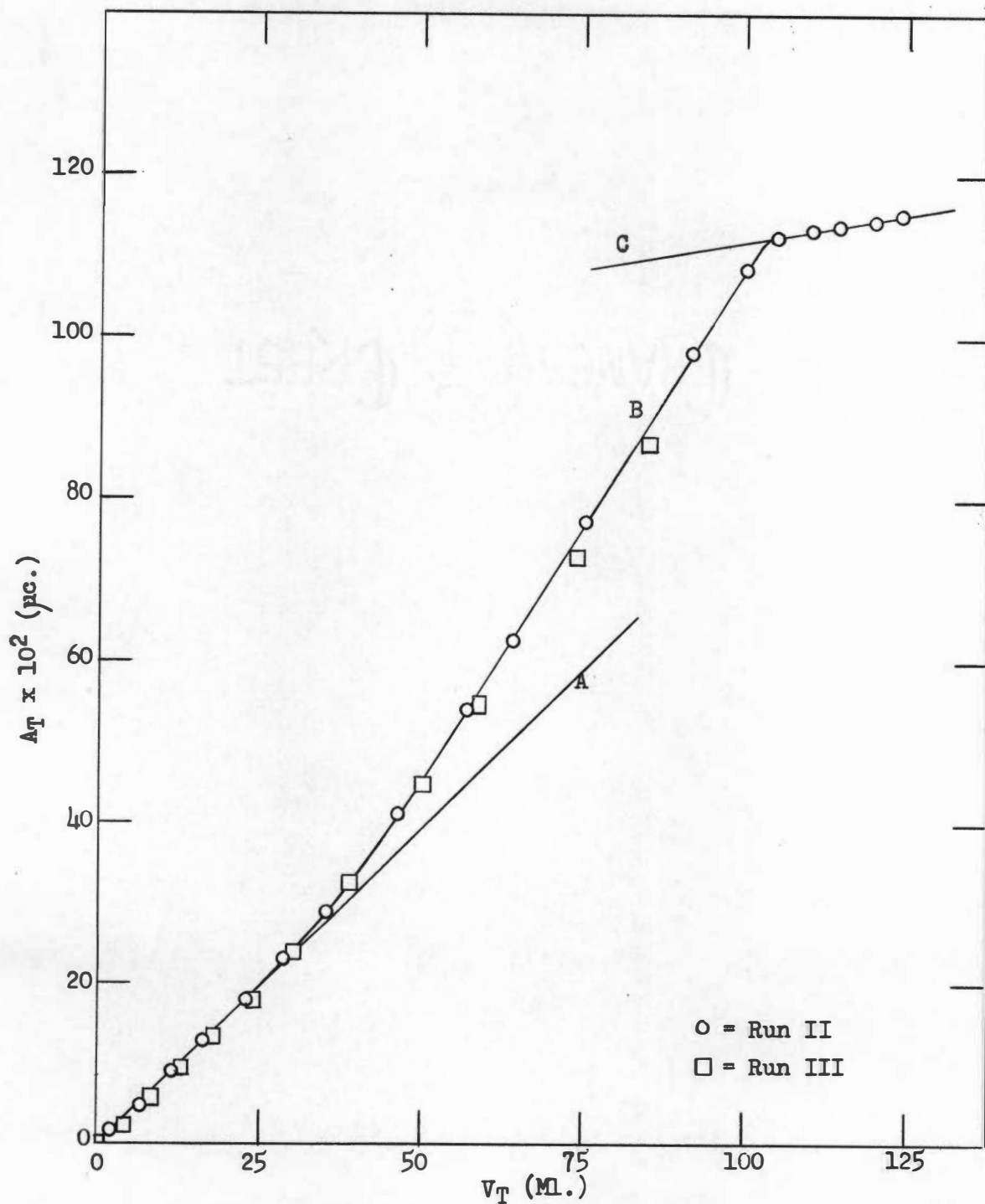


Figure 11. Sodium-Ethanol-Ammonia System, Runs II and III:  $V_T$  versus  $A_T$ .

It is of interest to note that the deviation of the graph of  $V_T$  vs.  $A_T$  (Figure 11) from the initial slope is positive rather than negative, as in the case of the potassium experiment (Figure 9). Yet, in both cases, the alcohol was initially unlabeled. This would again indicate that the deviation from linearity was not due to the isotopic exchange reaction which, obviously, was the same for both experiments. It will be shown in a later section of this chapter that the graph of  $V_T$  vs.  $A_T$  should be linear over the first 25 per cent of the reaction of the metal with the alcohol and that the slope of the initial linear section is equal to the specific activity of the hydrogen liberated from the alcohol. In Figure 11, this slope, i.e., the slope of the straight line, A, is equal to  $0.803 \times 10^{-2} \mu\text{c./ml.}$

In a second experiment, referred to as Run III, the ethanol was dissolved in labeled liquid ammonia in burette B, while the sodium was dissolved in unlabeled liquid ammonia in burette A. This experiment was a duplicate of Run II, except that at  $t^0$ , the approach to equilibrium of the isotopic exchange reaction was from the opposite direction, i.e., from the right instead of the left. Then, if the deviation of the plot of  $V_T$  vs.  $A_T$  from linearity resulted from the isotopic exchange reaction, the graph for Run III should have exhibited a negative deviation from the initial slope, i.e., the deviation should have been just the opposite of that found in Run II. In Figure 11, the experimental data for Run III (Table XI) are represented by the squares. It is seen that, despite reversing the location of the tritium at  $t^0$ , the plot of  $V_T$  vs.  $A_T$  traces that for Run II, the deviation from linearity again being positive. For

Run III, the initial slope is  $0.834 \times 10^{-2} \mu\text{c.}/\text{ml.}$  as compared to  $0.803 \times 10^{-2} \mu\text{c.}/\text{ml.}$  for Run II.

The above results show conclusively that the isotopic exchange reaction is instantaneous relative to the rate of the hydrogen evolution reaction. In subsequent sections of this chapter, it will be shown that the graph of  $V_T$  vs.  $A_T$  for a metal-alcohol reaction in liquid ammonia appears to be curved because, in reality, it is a composite curve, one which can be dissected into distinct linear sections. Each of the linear sections corresponds to the reaction of the metal with either the alcohol or an intermediate complex formed as the reaction proceeds to completion.

### C. Sodium-Ethanol-Ammonia System

Using Reactor System A (Figure 1), the data shown in Table V was obtained for the reaction of sodium with ethanol in liquid ammonia. In this particular experiment, Run I, the reactant solution in burette A consisted of 1.1574 gm. (0.050 gm. atoms) of sodium dissolved in liquid ammonia to 25.0 ml. of solution. Burette B contained 25.0 ml. of a solution consisting of approximately 0.020 moles of ethanol dissolved in liquid ammonia. The liquid ammonia used in the preparation of both of the reactant solutions was labeled with tritium in tracer quantities.

The data is presented in Table V in exactly the same manner as in Table III. Column II of Table V gives the time,  $t$ , measured from the start of the reaction,  $t^0$ , at which the hydrogen in the reactor was removed by the gas collection bulb whose number appears in column I. The volume ( $V$  ml., STP), specific activity ( $\bar{A}$ ,  $\mu\text{c.}/\text{ml.}$ ) and total activity



TABLE V

SODIUM-ETHANOL-AMMONIA SYSTEM  
Run I (Uncorrected Data)

Reactor System A						
Reactants: Burette A: 1.1574 gm. (0.0503 gm. atoms) of sodium plus NH <sub>2</sub> T to give 25.0 ml. of solution						
Burette B: 0.9101 gm. (0.0197 moles) of ethanol plus NH <sub>2</sub> T to give 25.0 ml. of solution						
I	II	III	IV	V	VI	VII
Sample Number	Time from t <sup>0</sup>	V (ml.)	$\bar{A} \times 10^2$ ( $\mu\text{c.}/\text{ml.}$ )	$A \times 10$ ( $\mu\text{c.}$ )	V <sub>T</sub> (ml.)	A <sub>T</sub> $\times 10$ ( $\mu\text{c.}$ )
1	<3 sec.	2.27	6.54	1.48	2.27	1.48
2	10 sec.	10.10	8.00	8.08	12.37	9.56
3	30 sec.	14.39	7.99	11.50	26.76	21.06
4	1 min.	10.84	8.35	9.06	37.61	30.12
5	2 min.	10.74	8.86	9.51	48.35	39.63
6	4 min.	11.48	9.61	11.03	59.82	50.66
7	8 min.	11.91	10.65	12.69	71.74	63.35
8	12 min.	9.15	12.24	11.20	80.89	74.54
9	20 min.	13.21	13.35	17.65	94.10	92.19
10	28 min.	11.52	13.71	15.80	105.63	107.99
11	40 min.	12.88	14.01	18.03	118.50	126.02
12	60 min.	12.38	14.35	17.76	130.88	143.78
13	80 min.	14.14	14.37	20.32	145.02	164.10
14	2 hrs.	15.52	14.85	23.04	160.54	187.14
15	3 hrs.	13.34	15.19	20.25	173.87	207.39
16	5 hrs.	13.02	15.39	20.04	186.89	227.43
17	8 hrs.	5.65	13.33	7.52	192.54	234.95
18	16 hrs.	2.28	3.44	0.79	194.82	235.74
19	24 hrs.	2.62	1.81	0.47	197.44	236.21
20	32.1 hrs.	2.40	1.80	0.43	199.84	236.64
21	42.5 hrs.	3.01	2.20	0.66	202.85	237.30

(A,  $\mu\text{c.}$ ) of the hydrogen contained in each gas collection bulb are listed in columns III, IV, and V, respectively. The total volume ( $V_T$ , ml., STP) and the total activity ( $A_T$ ,  $\mu\text{c.}$ ) of the hydrogen liberated from  $t^0$  through  $t$  are listed in columns VI and VII.

In Figure 12,  $V_T$  and  $A_T$  are shown plotted against the reaction time,  $t$ . It is apparent that after approximately ten hours, the rates at which hydrogen and tritium were evolved,  $\frac{dV_T}{dt}$  and  $\frac{dA_T}{dt}$ , respectively, became constant and remained so throughout the duration of the experiment. These linear sections of the two curves are a consequence of the continuing reactions of the sodium with the labeled solvent, equations (3) and (4), following completion of the sodium-ethanol reaction. The slopes of these linear sections,  $\left[\frac{dV_T}{dt}\right]_{(V_T)_{\text{ROH}}}$  and  $\left[\frac{dA_T}{dt}\right]_{(A_T)_{\text{ROH}}}$ , correspond to the constants  $m$  and  $n$  in equations (19) and (24), and have the values 0.3027 ml./hr. and 0.00591  $\mu\text{c.}/\text{hr.}$ , respectively. Using these correction factors, all of the data in Table V was corrected for the effect of the sodium-ammonia reaction by means of equations (19) and (24). The corrected data is presented in Table VI.

The total volume and the total activity of the hydrogen liberated from the ethanol at completion of the reaction, i.e.,  $V_T^\infty$  and  $A_T^\infty$  respectively, can be evaluated by extrapolating the linear sections of the  $V_T$  vs.  $t$  and  $A_T$  vs.  $t$  curves to  $t^0$ . The values found from Figure 12 are 190.07 ml. and 234.72  $\mu\text{c.}$  According to the weight of alcohol supposedly present at  $t^0$ , 0.9101 grams, the value of  $V_T^\infty$  should have been 221.40 ml. This discrepancy in  $V_T^\infty$  is due to two reasons. First, any reaction of sodium with the solvent forms amide ion which immediately reacts to

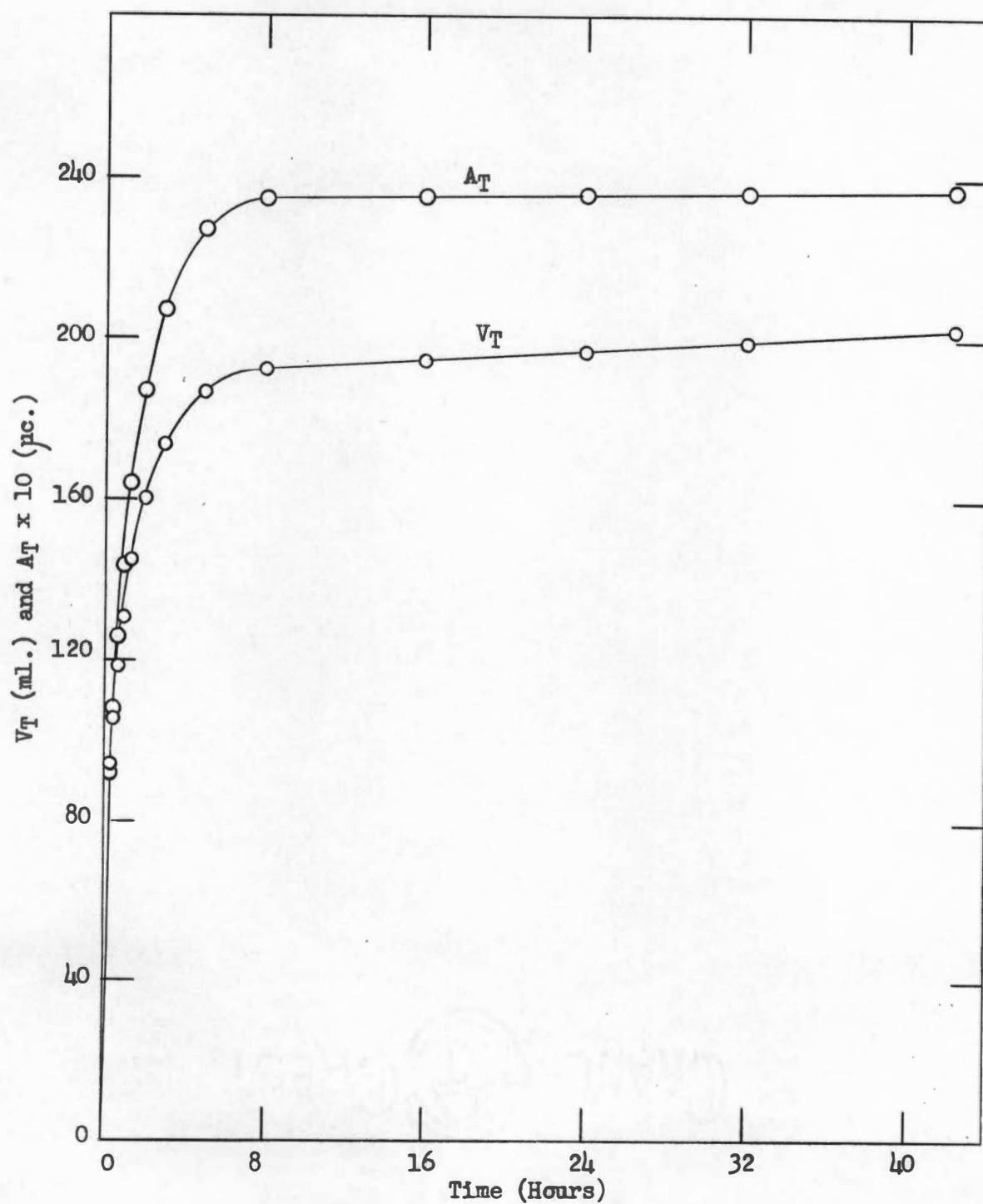


Figure 12. Sodium-Ethanol-Ammonia System, Run I:  $V_T$  and  $A_T$  versus time.

TABLE VI

SODIUM-ETHANOL-AMMONIA SYSTEM  
Run I (Corrected Data)

I	II	III	IV	V	VI	VII
Sample Number	Time from $t^0$	V (ML.)	$\bar{A} \times 10^2$ ( $\mu\text{c.}/\text{ML.}$ )	$A \times 10$ ( $\mu\text{c.}$ )	$V_T$ (ML.)	$A_T \times 10$ ( $\mu\text{c.}$ )
1	< 3 sec.	2.27	6.54	1.48	2.27	1.48
2	10 sec.	10.10	8.00	8.08	12.37	9.56
3	30 sec.	14.39	7.99	11.50	26.76	21.06
4	1 min.	10.84	8.35	9.06	37.60	30.12
5	2 min.	10.74	8.86	9.51	48.34	39.63
6	4 min.	11.47	9.61	11.02	59.80	50.65
7	8 min.	11.90	10.66	12.69	71.70	63.34
8	12 min.	9.13	12.26	11.19	80.83	74.53
9	20 min.	13.18	13.39	17.64	94.01	92.17
10	28 min.	11.48	13.75	15.79	105.49	107.96
11	40 min.	12.81	14.06	18.02	118.30	125.98
12	60 min.	12.28	14.45	17.74	130.58	143.72
13	80 min.	14.04	14.46	20.30	144.62	164.02
14	2 hrs.	15.31	15.02	23.00	159.93	187.02
15	3 hrs.	13.03	15.49	20.19	172.97	207.22
16	5 hrs.	12.41	16.04	19.92	185.38	227.13
17	8 hrs.	4.74	15.50	7.34	190.12	234.48
18	16 hrs.	0.00	- - -	- - -	190.12	234.48

$$V_T^\infty = 190.07 \text{ ML.}$$

$$m = 0.3027 \text{ ML./Hr.}$$

$$\bar{A}_{\text{NH}_3} = 0.3575 \mu\text{c.}/\text{ML.}$$

$$n = 0.0059 \mu\text{c.}/\text{Hr.}$$

remove ethanol by forming ammonia and alkoxide ion. Even prior to the



metal-alcohol reaction, some amide ion is undoubtedly formed in burette A while the metal-ammonia solution is stored previous to being mixed with the alcohol-ammonia solution. The second reason is that apparently all of the alcohol weighed out did not get into the metal-ammonia reaction solution. An examination of the fragments of the original alcohol bulbs from various runs showed that the capillary necks of these bulbs remained intact. It is therefore felt that a small amount of the original alcohol remained trapped in this neck and left in burette B. Because of these reasons, the  $V_T^\infty$  employed in the calculations is an experimentally derived value, not one based on the weight of the alcohol in the original bulbs.

In Figure 13,  $V_T$  is shown plotted against  $A_T$ , the data from Table VI being used. Since this data has been corrected for the reaction of the sodium with the solvent, Figure 13 does not have a section equivalent to section C of Figure 11. From Figure 13, it is evident that the reaction of sodium with the ethanol is complex. Since the isotopic exchange reaction has been shown to be instantaneous relative to the rate at which hydrogen is liberated from the alcohol, the deviation from linearity shown in Figure 13 can best be accounted for by assuming that the bonding of hydrogen in the species from which the hydrogen is being liberated changes as the reaction proceeds. The graph is essentially linear over the first 25 per cent reaction. The slope of this linear section,  $\bar{A}_1$ , is equal to 0.0804  $\mu\text{c.}/\text{ml.}$  The graph is also linear over almost the entire last half of the reaction. For this section, the slope,  $\bar{A}_3$ , is equal to 0.1511  $\mu\text{c.}/$

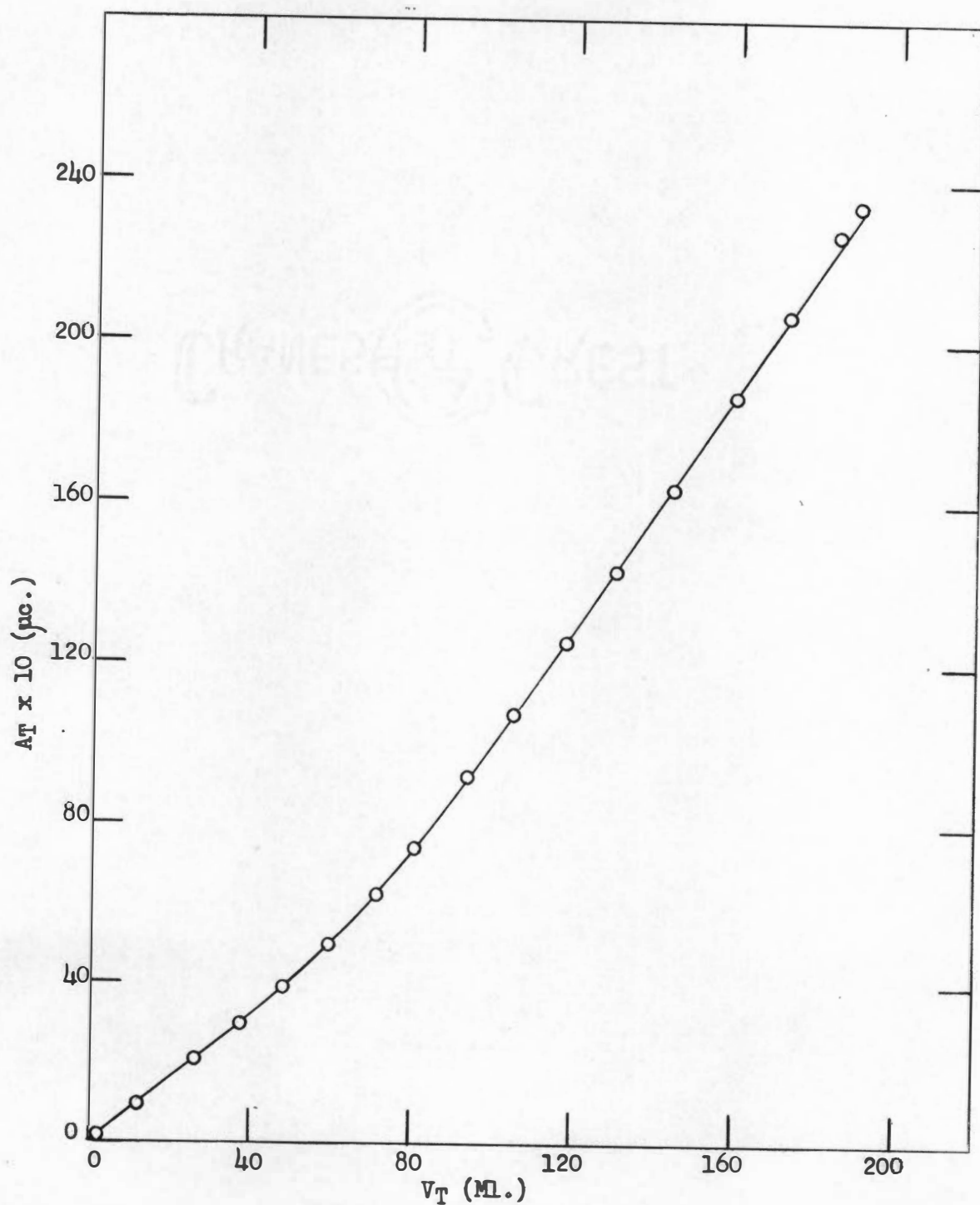


Figure 13. Sodium-Ethanol-Ammonia System, Run I:  $V_T$  versus  $A_T$ .

ml. From 25 to 50 per cent reaction, the graph exhibits a positive deviation from the original slope. Therefore, from this graph, one might conclude that the hydrogen is liberated from one species during the first fourth of the reaction, and from another species during the last half of the reaction. However, it is not evident from this graph how many intermediates are involved in passing from 25 to 50 per cent completion.

In Figure 14, the specific activity,  $\bar{A}$ , of the hydrogen is plotted against the per cent reaction, both for the data from Table VI (curve I) and for a run (Table X) in which the original amount of alcohol was halved (curve II). The graphs show that after 50 per cent reaction, the specific activity,  $\bar{A}_3$ , does change, increasing at a constant rate, but only slightly. Thus from curve I, although  $\bar{A}$  shows an increase of 88.0 per cent in going from 0 to 100 per cent reaction, it increases only 12.8 per cent during the entire last half of the reaction. Although a detailed explanation of this slow increase in activity of hydrogen apparently liberated from one species cannot be given, the phenomenon is probably a consequence of the increase in alkoxide ion,  $RO^\ominus$ , concentration as the reaction proceeds. Thus, in the reaction involving less alcohol (curve II, Figure 14) and hence less alkoxide ion,  $\bar{A}$  was less during the last half of the reaction.

Figure 14 also suggests that during the first fourth of the reaction the hydrogen is being liberated from one species and has a specific activity,  $\bar{A}$ , of approximately 0.080  $\mu\text{c./ml.}$  The first points are lower, 0.065  $\mu\text{c./ml.}$ , but this was probably due to the presence of some hydrogen

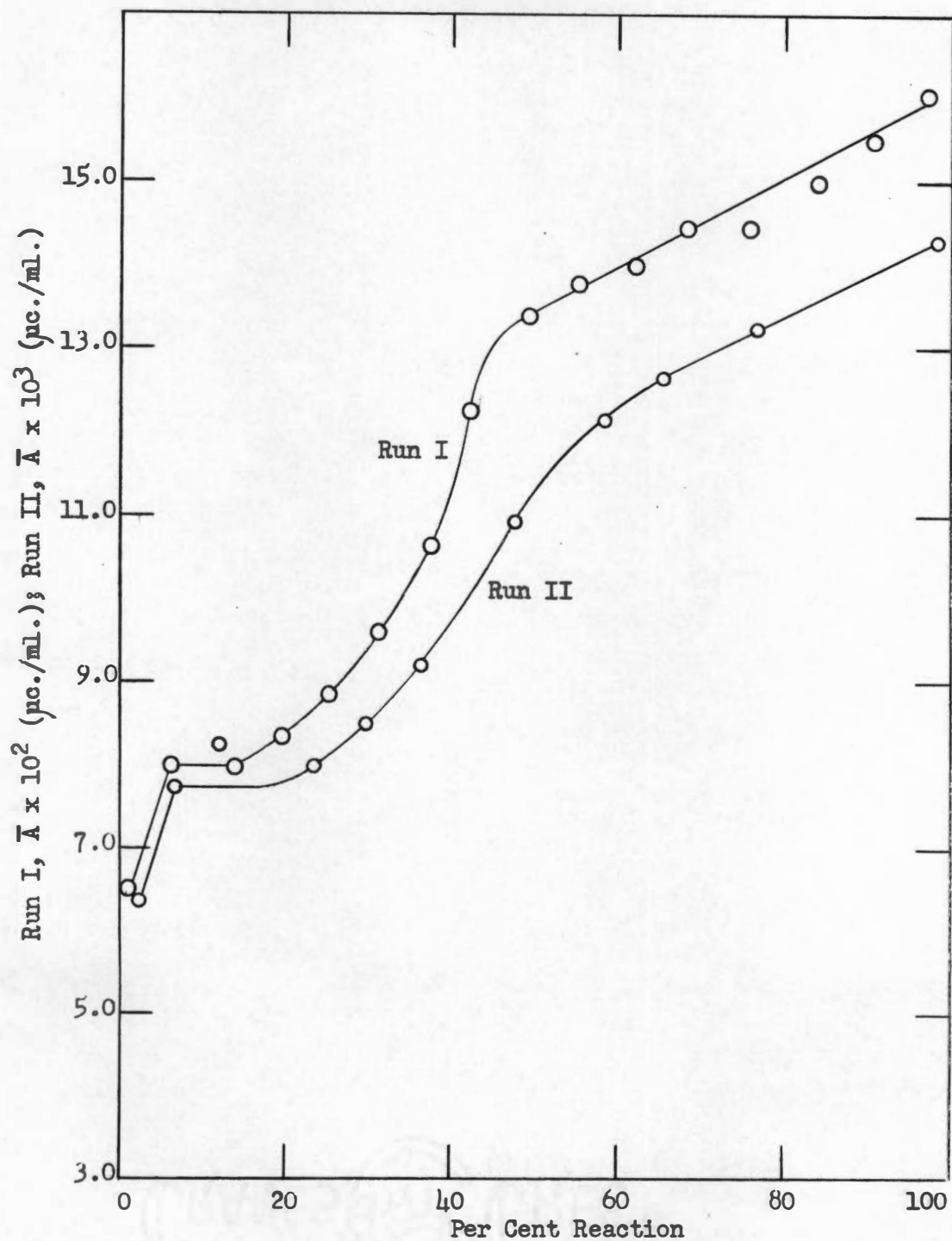


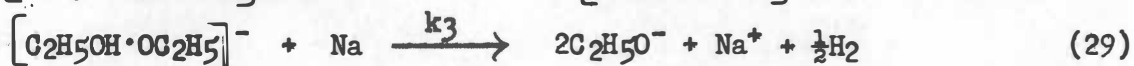
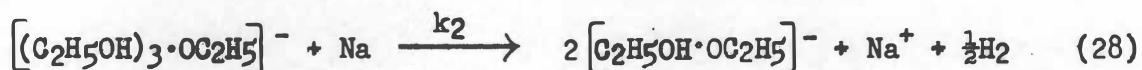
Figure 14. Sodium-Ethanol-Ammonia System, Runs I and II:  $\bar{A}$  versus per cent reaction.



resulting from the reaction of sodium with the solvent in burette A, the hydrogen having been forced into the reactor at  $t^0$ . From 25 to 50 per cent reaction, the hydrogen is apparently being evolved from a third species with an overlap at either end, particularly near 50 per cent, tending to obscure its presence.

Initial attempts at fitting a simple rate expression to the volume data failed. The preceding discussion indicates that the rate equation must be complex, containing at least a trinomial on the right hand side. However, experiments with different initial concentrations of ethanol showed that the rate of the hydrogen evolution reaction was first order in alcohol; these experiments will be discussed later in this section. Consequently, in any suitable rate expression, the term involving the alcohol concentration must factor out of the complex expression. Furthermore, as will be shown in the section on the potassium-ethanol-ammonia system, good evidence was found for the hydrogen liberation reaction being zero order in alkali metal.

A model for the reaction of ethanol with sodium, consistent with the aforementioned observations and the knowledge that the exchange reactions between the proton donors and the solvent ammonia are instantaneous, may be represented by equations (27), (28), and (29).



Similar equations may be written for the evolution of tritium from the corresponding labeled species. According to this model, hydrogen is

liberated from three distinct species during the course of the overall reaction. Consequently, there must be three values for the specific activity of the liberated hydrogen. If  $k_1 \gg k_2 \gg k_3$ , then one-fourth of the hydrogen would be liberated at a rate constant  $k_1$  and a specific activity of  $\bar{A}_1$ . The next one-fourth of the hydrogen would be liberated at a rate constant  $k_2$  and a specific activity of  $\bar{A}_2$ . Finally, the last half of the hydrogen would be liberated at a rate constant of  $k_3$  and a specific activity of  $\bar{A}_3$ .

The rate expression for the evolution of hydrogen from ethanol by sodium can be derived on the basis of the preceding model. It is assumed that the only rate-determining reactions are those represented by equations (27), (28), and (29). It is also assumed that  $k_1 \gg k_2$ . This assumption is supported by Figure 14 which is consistent with little overlap between reactions (27) and (28). Although this latter assumption is unnecessary, it does facilitate the derivation. It is also assumed that the overall reaction is first order in alcohol and zero order in the alkali metal, evidence for which will be discussed later.

The reaction represented by equation (27) may be treated independently of the other two reactions; in which case, the rate of consumption of  $C_2H_5OH$  may be expressed by equation (30).

$$\frac{-d[C_2H_5OH]}{dt} = k_1 [C_2H_5OH] \quad (30)$$

Letting  $a$  and  $x_1$  represent the moles of  $C_2H_5OH$  present at  $t^0$  and the moles of hydrogen liberated from  $C_2H_5OH$  at time  $t$ , respectively, equation (30) may be rewritten to give equation (31).

$$\frac{-d(a - 8x_1)}{dt} = k_1 (a - 8x_1) \quad (31)$$

Integration of equation (31) yields equation (32).

$$x_1 = \frac{a}{8} (1 - e^{-k_1 t}) \quad (32)$$

Let  $b$ ,  $B$ , and  $x_2$  represent the total moles of  $[(C_2H_5OH)_3 \cdot OC_2H_5]^-$  which react, the moles of  $[(C_2H_5OH)_3 \cdot OC_2H_5]$  which remain at time  $t$ , and the moles of hydrogen liberated from  $[(C_2H_5OH)_3 \cdot OC_2H_5]^-$  at time  $t$ , respectively. Similarly, let  $C$  and  $x_3$  represent the moles of  $[C_2H_5OH \cdot OC_2H_5]^-$  remaining at time  $t$ , and the moles of hydrogen liberated from  $[C_2H_5OH \cdot OC_2H_5]^-$  at time  $t$ . Then, equations (33) and (34) may be rewritten.

$$B = b - 2x_2 \quad (33)$$

$$C = 4x_2 - 2x_3 \quad (34)$$

The rate at which  $[(C_2H_5OH)_3 \cdot OC_2H_5]^-$  is consumed is given by equation (35)

$$\frac{-dB}{dt} = k_2 B \quad (35)$$

which, upon integration, becomes equation (36).

$$B = b e^{-k_2 t} \quad (36)$$

Inserting the value of  $B$  given by equation (33) into equation (36), and solving for  $x_2$ , one obtains equation (37).

$$x_2 = \frac{b}{2} (1 - e^{-k_2 t}) \quad (37)$$

The rate at which hydrogen is liberated from  $[C_2H_5OH \cdot OC_2H_5]^-$  is given by equation (38).

$$\frac{dx_3}{dt} = \frac{1}{2} k_3 C \quad (38)$$

Substituting the value of  $C$  given by equation (34) into equation (38), one obtains equation (39), which, upon inserting the value of  $x_2$  given

$$\frac{dx_3}{dt} = k_3 (2x_2 - x_3) \quad (39)$$

by equation (37), becomes equation (40). Equation (40) may be integrated

$$\frac{dx_3}{dt} = k_3 b (1 - e^{-k_3 t}) - k_3 x_3 \quad (40)$$

to give equation (41). By means of equations (32), (37), and (41), one

$$x_3 = b (1 - e^{-k_3 t}) + \frac{k_3 b}{k_3 - k_2} (e^{-k_3 t} - e^{-k_2 t}) \quad (41)$$

could calculate the moles of hydrogen liberated from  $C_2H_5OH$ ,  $[(C_2H_5OH)_3 \cdot OC_2H_5]^-$ , and  $[C_2H_5OH \cdot OC_2H_5]^-$  during the time interval from  $t^0$  to  $t$ . Since  $a$  and  $b$  are equal to  $2V_T^\infty/N$  and  $V_T^\infty/2N$ , respectively, equations (32), (37), and (41) may be rewritten in terms of the volume of hydrogen liberated rather than the moles of hydrogen liberated. The corresponding equations are (42), (43), and (44), respectively.

$$V_1 = \frac{V_T^\infty}{4} (1 - e^{-k_1 t}) \quad (42)$$

$$V_2 = \frac{V_T^\infty}{4} (1 - e^{-k_2 t}) \quad (43)$$

$$V_3 = \frac{V_T^\infty}{2} (1 - e^{-k_3 t}) + \frac{k_3 V_T^\infty}{2(k_3 - k_2)} (e^{-k_3 t} - e^{-k_2 t}) \quad (44)$$

The total volume of hydrogen liberated,  $V_T$ , is given by equation (45).

$$V_T = V_1 + V_2 + V_3 \quad (45)$$

By combining equations (42), (43), (44), and (45) one obtains equation (46).

$$V_T = V_T^\infty (1 - \frac{1}{4}e^{-k_1 t} - \frac{1}{4}e^{-k_2 t} - \frac{1}{2}e^{-k_3 t}) + \frac{k_3 V_T^\infty}{2(k_3 - k_2)} (e^{-k_3 t} - e^{-k_2 t}) \quad (46)$$

Equation (46) should enable one to calculate the total volume of hydrogen liberated at any reaction time from  $t^0$  to  $t^\infty$  after the rate constants  $k_1$ ,  $k_2$ , and  $k_3$  are evaluated for that reaction. The second term on the right side of equation (44) might be called an "overlap" term in that it takes into account any simultaneous liberation of hydrogen by reactions (28) and (29). When  $k_2$  is over five times greater than  $k_3$ , this overlap term becomes relatively insignificant. As a first approximation then, equation (44) becomes equation (47), and equation (46) may be rewritten to give equation (48).

$$V_3 = \frac{V_T^\infty}{2} (1 - e^{-k_3 t}) \quad (47)$$

$$V_T = V_T^\infty (1 - \frac{1}{4}e^{-k_1 t} - \frac{1}{4}e^{-k_2 t} - \frac{1}{2}e^{-k_3 t}) \quad (48)$$

From equations (42) and (43), it is apparent that near the end of the reaction, i.e., when  $t$  is very large, both  $V_1$  and  $V_2$  approach the value of  $V_T^\infty/4$ . Then, according to equation (45),  $V_3$  is given by equation (49). Substituting this value of  $V_3$  into equation (47), one obtains

$$V_3 \approx V_T - \frac{V_T^\infty}{2} \quad (49)$$

equation (50), or its equivalent, equation (51).

$$(V_T^\infty - V_T) = \frac{V_T^\infty}{2} e^{-k_3 t} \quad (50)$$

$$\ln (V_T^\infty - V_T) = -k_3 t + \ln \frac{V_T^\infty}{2} \quad (51)$$

According to equation (51), a plot of  $\ln (V_T^\infty - V_T)$  vs.  $t$  should approach a straight line, as  $t$  increases to  $t^\infty$ , having a slope of  $-k_3$ , and an intercept of  $\ln \frac{V_T^\infty}{2}$ . Using the data from Table VI, such a plot is shown in Figure 15. It is observed that a straight line is indeed attained, and

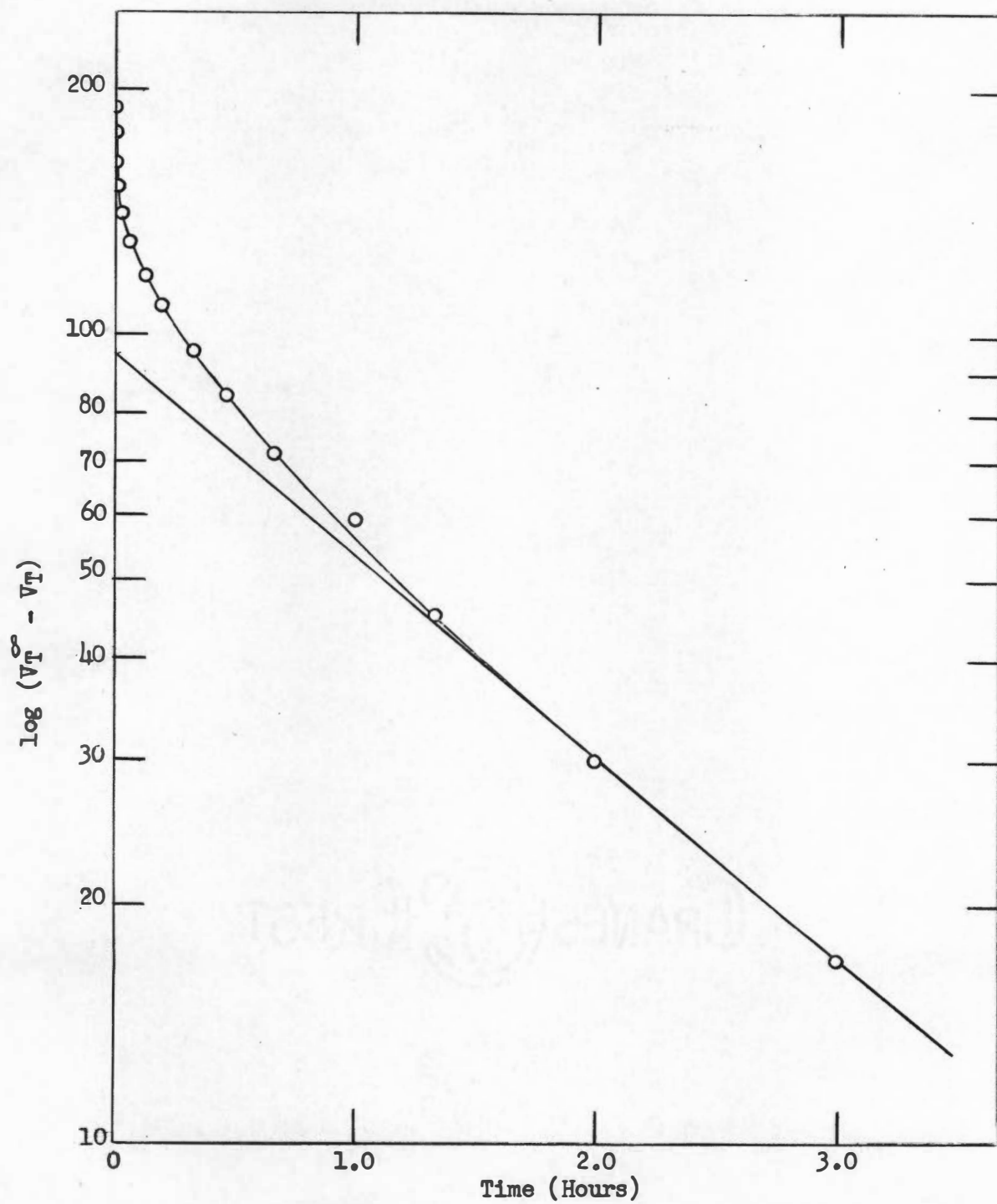


Figure 15. Sodium-Ethanol-Ammonia System, Run I:  $\log (V_T^\infty - V_T)$  versus time.

that the intercept is equal to  $\ln 95.0$  ml., or almost exactly  $\ln \frac{V_T^\infty}{2}$ , since  $V_T^\infty$  is equal to 190.07 ml. The value of  $k_3$ , calculated from the slope, is  $0.5718 \text{ hr.}^{-1}$ .

For any given reaction time  $t$ , the symbols  $P_1$  and  $P_2$  are defined by equations (52) and (53).

$$P_1 = V_T^\infty - V_T \quad (52)$$

$$P_2 = V_3^\infty - V_3 \quad (53)$$

Subtracting equation (53) from equation (52), one obtains equation (54).

$$P_1 - P_2 = \Delta P = (V_T^\infty - V_T) - (V_3^\infty - V_3) \quad (54)$$

The values of  $\Delta P$  may be obtained from Figure 15 by subtracting, at each time  $t$ , the linear extrapolation from the actual curve. But  $V_3^\infty$  is equal to  $\frac{V_T^\infty}{2}$  and, inserting this value along with the value of  $V_T$  given by equation (45), equation (54) may be rewritten to give equation (55).

$$\Delta P = \frac{V_T^\infty}{2} - (V_1 + V_2) \quad (55)$$

With  $V_1$  equal to  $\frac{V_T^\infty}{4}$ , equation (55) becomes equation (56).

$$\Delta P = \frac{V_T^\infty}{4} - V_2 \quad (56)$$

By rearranging equation (43), one obtains equation (57), which, upon

$$\frac{V_T^\infty}{4} - V_2 = \frac{V_T^\infty}{4} e^{-k_2 t} \quad (57)$$

taking the natural logarithm of both sides, becomes equation (58).

$$\ln \left( \frac{V_T^\infty}{4} - V_2 \right) = -k_2 t + \ln \frac{V_T^\infty}{4} \quad (58)$$

Comparing equations (56) and (58), it is seen that a plot of  $\ln \Delta P$  against  $t$  should approach a straight line having a slope of  $-k_2$  and an intercept

of  $\ln \frac{V_T^\infty}{4}$ . Such a plot is shown in Figure 16 (curve I). Once again, it is seen that a straight line is obtained, and the intercept,  $\ln V_2^\infty$ , does equal  $\ln \frac{V_T^\infty}{4}$ , the intercept being 47.5 ml. The value of  $k_2$  calculated from the straight line is  $2.918 \text{ hr.}^{-1}$ .

For any given reaction time  $t$ , the symbols  $P_1'$  and  $P_2'$  are defined by equations (59) and (60).

$$P_1' = (V_T^\infty - V_T) - (V_3^\infty - V_3) \quad (59)$$

$$P_2' = (V_2^\infty - V_2) \quad (60)$$

Subtracting equation (60) from equation (59), one obtains equation (61). As in the case of  $\Delta P$ , the value of  $\Delta P'$  may be obtained graphically,

$$P_1' - P_2' = \Delta P' = (V_T^\infty - V_T) - (V_3^\infty - V_3) - (V_2^\infty - V_2) \quad (61)$$

this time by subtracting the linear extrapolation of curve I (Figure 16) from the actual curve. By following the same procedure used for obtaining equation (55), it can be shown the  $\Delta P'$  is given by equation (62).

$$\Delta P' = \frac{V_T^\infty}{4} - V_1 \quad (62)$$

However, equation (42) can be rewritten as equation (63), and it is there-

$$\ln \left( \frac{V_T^\infty}{4} - V_1 \right) = -k_1 t + \ln \frac{V_T^\infty}{4} \quad (63)$$

fore apparent that a plot of  $\ln \Delta P'$  against  $t$  should give a straight line of slope  $-k_1$  and an intercept of  $\ln \frac{V_T^\infty}{4}$ . This plot is shown in Figure 16, curve II. The intercept is equal to  $\ln \frac{V_T^\infty}{4}$ , i.e.,  $V_1^\infty$  equals 47.5 ml. or  $V_T^\infty/4$ , and the slope gives a calculated value of  $k_1$  of  $80.8 \text{ hr.}^{-1}$ .

Equation (63) may be rewritten to give equation (64). Since the

$$\ln (V_T^\infty - 4V_1) = -k_1 t + \ln V_T^\infty \quad (64)$$



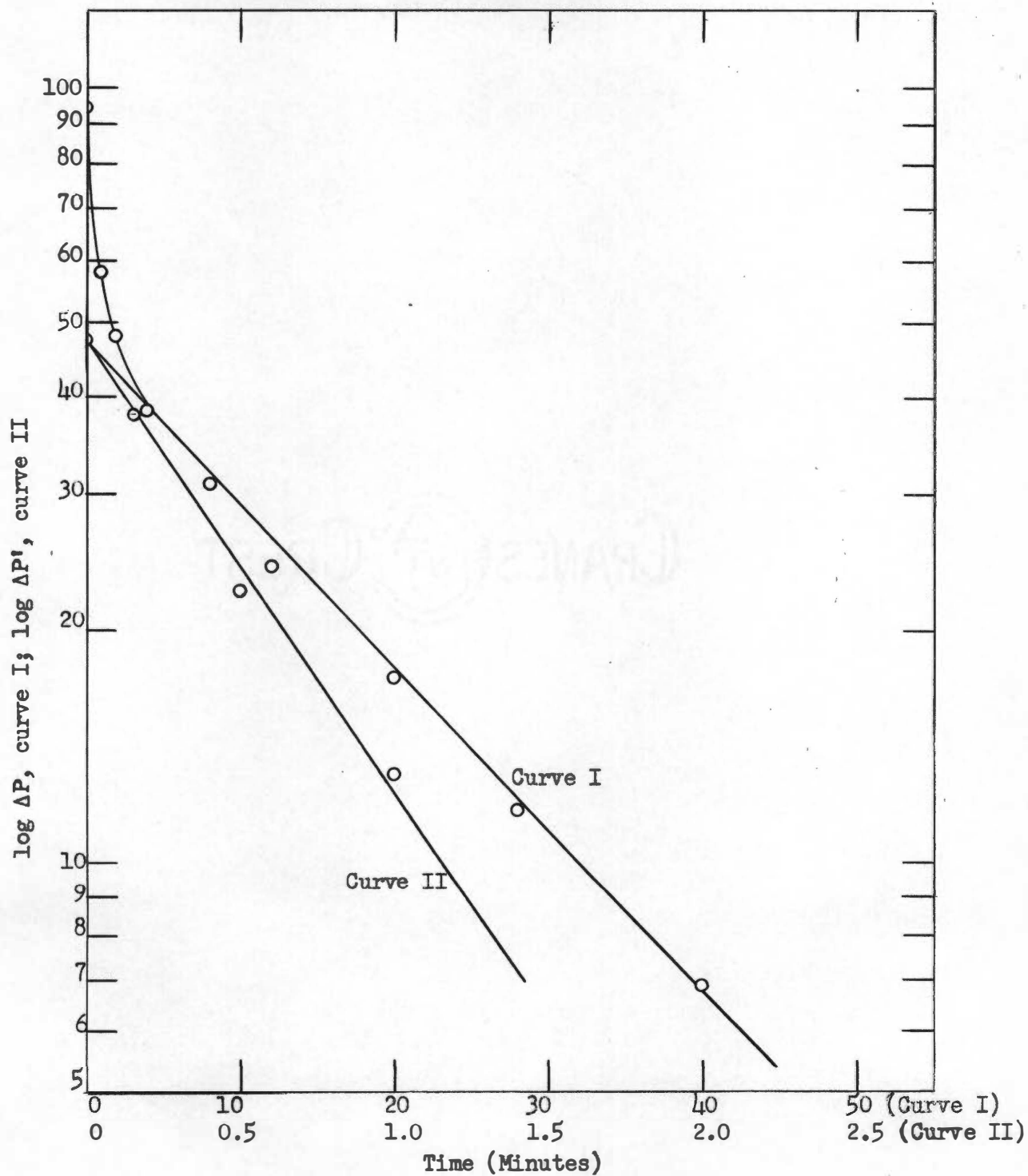


Figure 16. Sodium-Ethanol-Ammonia System, Run I:  $\log \Delta P$  versus time (curve I) and  $\log \Delta P'$  versus time (curve II).

reaction represented by equation (27) is independent of the other reactions, and goes to completion before they commence, a plot of  $\ln (V_T^\infty - 4V_T)$  against  $t$  should give a straight line over the first 25 per cent of reaction, the slope of the line being equal to  $-k_1$ , and the intercept being  $\ln V_T^\infty$ . This plot is shown in Figure 17. The value of  $k_1$  obtained from the resulting straight line is  $94.24 \text{ hr.}^{-1}$ . This value of  $k_1$  is considered to be more accurate than the value obtained by plotting  $\ln \Delta P'$  against  $t$ ,  $80.8 \text{ hr.}^{-1}$ , since the process of obtaining  $\Delta P'$ , a consecutive subtraction of curves, introduces an appreciable uncertainty.

Knowing the values of  $k_1$ ,  $k_2$ , and  $k_3$ , equation (48) may be rewritten to give equation (65), wherein  $t$  must be expressed in hours. It might be

$$V_T = V_T^\infty (1 - \frac{1}{4}e^{-94.24t} - \frac{1}{4}e^{-2.918t} - \frac{1}{2}e^{-0.5718t}) \quad (65)$$

pointed out that although the expression is complex, it does show that the per cent of reaction at any time  $t$  should be independent of the initial alcohol concentration, i.e., first order in alcohol.

In Table VII, the values of  $V_T$  calculated by means of equation (65) are compared with the observed values of  $V_T$  listed in column VI of Table VI. The calculated and observed values of  $V_T$  are in good agreement, the disparity being greatest near  $t^0$  where experiment error was also the greatest.

The hydrogen produced by the reaction represented by equation (27), i.e.,  $V_1$ , has a fixed specific activity,  $\bar{A}_1$ . Therefore,

$$A_1 = \bar{A}_1 V_1$$

or

$$V_1 = \frac{A_1}{\bar{A}_1}$$

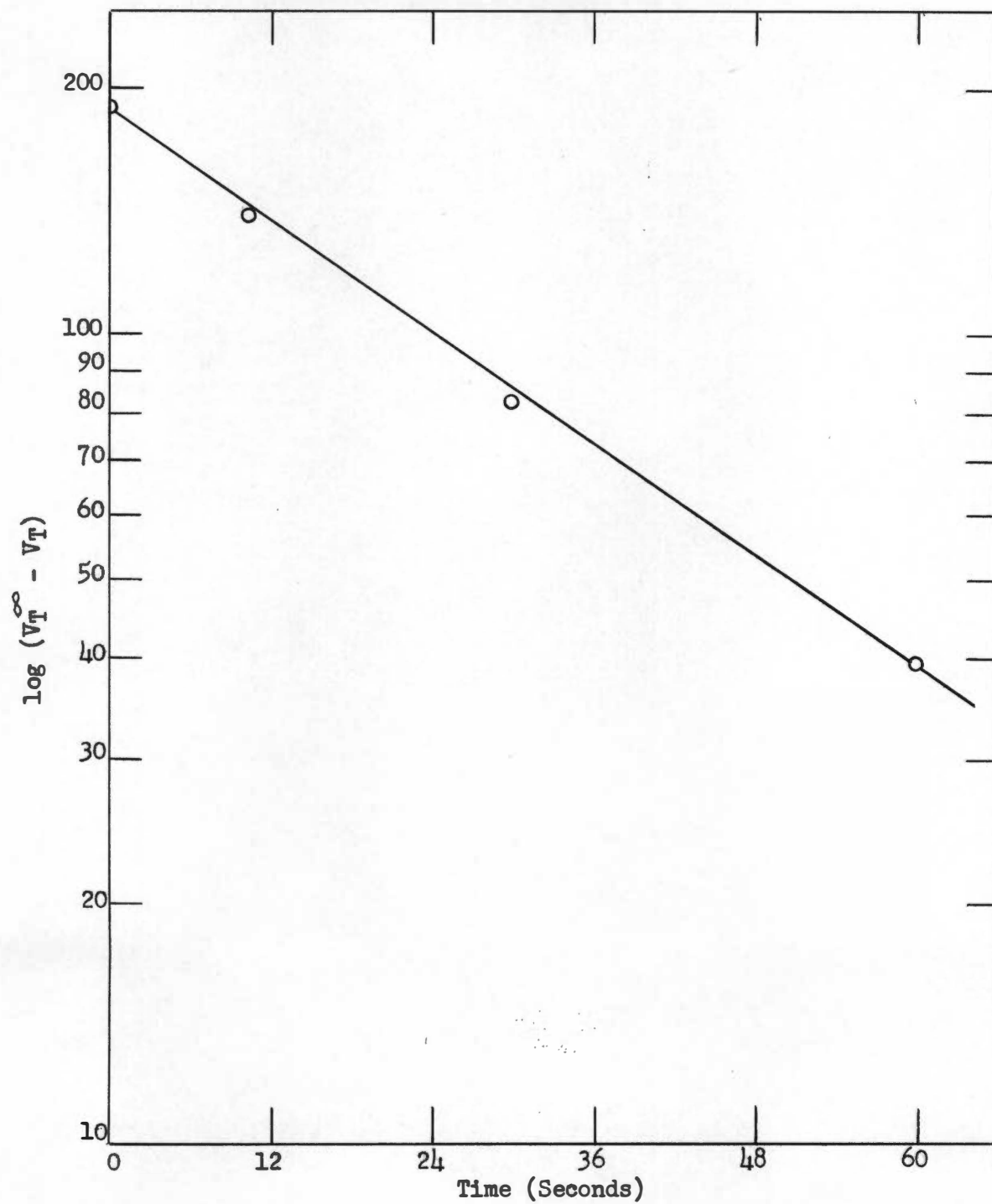


Figure 17. Sodium-Ethanol-Ammonia System, Run I:  $\log (V_T^\infty - V_T)$  versus time.

TABLE VII

SODIUM-ETHANOL-AMMONIA SYSTEM  
Run I  
 $V_T$  (Calculated) and  $V_T$  (Observed)

Time from $t^0$	$V_T$ (Ml.) (Calc. by Eq. 65)	$V_T$ (Ml.) (Obs.)
0	0	0
10 sec.	11.33	12.37
30 sec.	27.45	26.76
1 min.	40.14	37.60
2 min.	51.66	48.39
4 min.	59.40	59.80
8 min.	69.81	71.70
12 min.	78.82	80.83
20 min.	93.63	94.01
28 min.	105.11	105.49
40 min.	118.36	118.30
60 min.	133.85	130.58
80 min.	144.79	144.62
2 hrs.	159.73	159.93
3 hrs.	172.96	172.97
5 hrs.	184.63	185.38
8 hrs.	189.08	190.12
$\infty$	190.07	190.07

and

$$V_1^\infty = \frac{A_1^\infty}{\bar{A}_1} = \frac{V_T^\infty}{4} .$$

Substituting these values of  $V_T^\infty/4$  and  $V_1$  into equation (42), one obtains equation (66).

$$A_1 = A_1^\infty (1 - e^{-k_1 t}) \quad (66)$$

Similarly, equations (43) and (47) become equations (67) and (68).

$$A_2 = A_2^\infty (1 - e^{-k_2 t}) \quad (67)$$

$$A_3 = A_3^\infty (1 - e^{-k_3 t}) \quad (68)$$

In these equations

$$\bar{A}_1^\infty = \frac{V_T^\infty \bar{A}_1}{4}$$

$$\bar{A}_2^\infty = \frac{V_T^\infty \bar{A}_2}{4}$$

and

$$\bar{A}_3^\infty = \frac{V_T^\infty \bar{A}_3}{2} .$$

The total activity of the evolved hydrogen,  $A_T$ , is given by equation (69)

$$A_T = A_1 + A_2 + A_3 \quad (69)$$

which upon inserting the expressions for  $A_1$ ,  $A_2$ ,  $A_3$ ,  $\bar{A}_1^\infty$ ,  $\bar{A}_2^\infty$ , and  $\bar{A}_3^\infty$ , becomes equation (70).

$$A_T = V_T^\infty \left( \frac{\bar{A}_1}{4} + \frac{\bar{A}_2}{4} + \frac{\bar{A}_3}{2} \right) - V_T^\infty \left( \frac{\bar{A}_1}{4} e^{-k_1 t} + \frac{\bar{A}_2}{4} e^{-k_2 t} + \frac{\bar{A}_3}{2} e^{-k_3 t} \right) \quad (70)$$

Equation (70) should enable one to calculate the total activity,  $A_T$ , of the hydrogen liberated from  $t^0$  to  $t$ . In order to use this equation, it is necessary to know, in addition to the rate constants  $k_1$ ,  $k_2$ , and  $k_3$ , the specific activities  $\bar{A}_1$ ,  $\bar{A}_2$ , and  $\bar{A}_3$ . These specific activities may be determined by any of several methods.

Equation (68) may be written in the form of equation (71). From

$$\ln (\bar{A}_3^\infty - A_3) = -k_3 t + \ln \bar{A}_3^\infty \quad (71)$$

equation (69), it is obvious that  $\bar{A}_3^\infty$  is equal to  $(A_T^\infty - A_1^\infty - A_2^\infty)$ , and that for a large value of  $t$ , i.e., near the end of the reaction,  $A_3$  is given by equation (72).

$$A_3 \approx A_T - A_1^\infty - A_2^\infty \quad (72)$$

Inserting these values of  $\bar{A}_3^\infty$  and  $A_3$  into equation (71), one obtains equation (73).

$$\ln (A_T^\infty - A_T) = -k_3 t + \ln \bar{A}_3^\infty \quad (73)$$

According to this equation, a plot of  $\ln (A_T^\infty - A_T)$  against time  $t$ , should approach a straight line having a slope of  $-k_3$  and an intercept of  $\ln \bar{A}_3^\infty$ . This graph is shown in Figure 18. The value of  $k_3$  calculated from the slope is  $0.5508 \text{ hr.}^{-1}$  as compared to the value of  $0.5718 \text{ hr.}^{-1}$  obtained from Figure 15. From the intercept,  $\bar{A}_3^\infty$  is found to be  $143.5 \times 10^{-1} \mu\text{c.}$  The value of  $V_3^\infty$  is  $95.03 \text{ ml.}$  Therefore, since  $\bar{A}_3$  is equal to  $\bar{A}_3^\infty / V_3^\infty$ , the value of  $\bar{A}_3$  is  $0.1510 \mu\text{c./ml.}$

The specific activity,  $\bar{A}_3$ , may also be obtained directly from Figure 13, in which  $A_T$  was plotted against  $V_T$ . The resulting graph exhibits only a slight curvature over the last half of the reaction, approaching a straight line near the end of the reaction. The slope of this linear section,  $\bar{A}_3$ , is equal to  $0.1511 \mu\text{c./ml.}$

It should be noted that the two preceding methods for evaluating  $\bar{A}_3$  give the value of  $\bar{A}_3$  near 100 per cent reaction. However, in Figure 14, it was shown that  $\bar{A}_3$  is not constant from 50 to 100 per cent reaction, but actually increases by 12.8 per cent in this region. Referring to

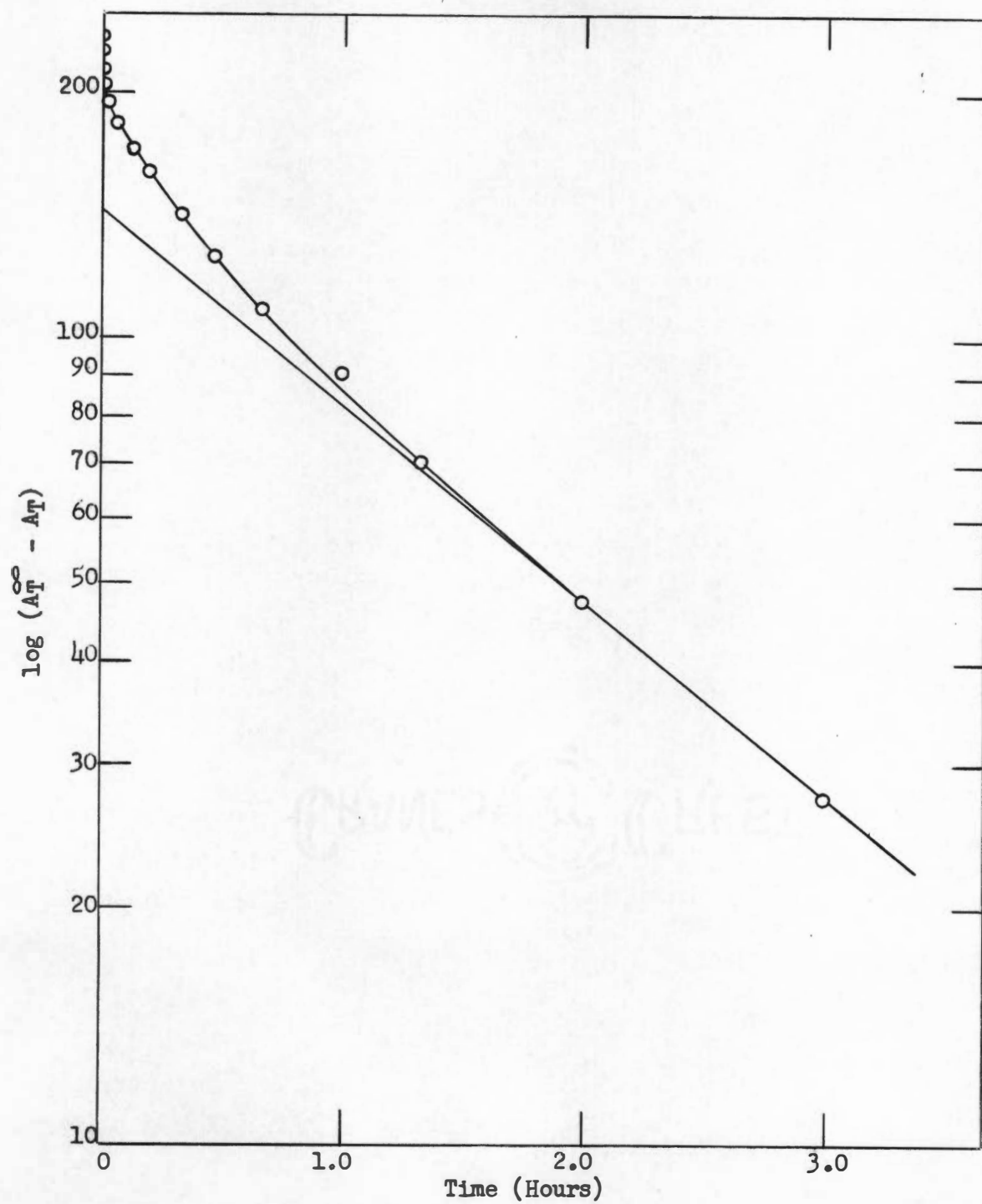


Figure 18. Sodium-Ethanol-Ammonia System, Run I:  $\log (A_T^\infty - A_T)$  versus time.

Figure 14 (curve I) it is apparent that  $\bar{A}_3$  has a minimum value of approximately 0.133  $\mu\text{c./ml.}$  and a maximum value of about 0.158  $\mu\text{c./ml.}$  Therefore, in equation (70), it might be best to use the average value of  $\bar{A}_3$ , i.e., 0.145  $\mu\text{c./ml.}$

The value of  $\bar{A}_1$  can best be obtained from Figure 13. In this figure, the slope of the linear section over the first fourth of the reaction is equal to  $\bar{A}_1$  and has the value, 0.0804  $\mu\text{c./ml.}$  The same value is obtained from Figure 15 if the first point is neglected.

An accurate value of  $\bar{A}_2$  cannot be obtained from Figures 13 or 14. However,  $\bar{A}_2$  can be obtained graphically in the manner by which  $k_2$  was obtained. Let  $Q_1$  and  $Q_2$ , at any given reaction time  $t$ , be defined by equations (74) and (75). Then,  $\Delta Q$  is given by equation (76).

$$Q_1 = A_T^\infty - A_T \quad (74)$$

$$Q_2 = A_3^\infty - A_3 \quad (75)$$

$$\Delta Q = Q_1 - Q_2 = (A_T^\infty - A_T) - (A_3^\infty - A_3) \quad (76)$$

The values of  $\Delta Q$  can be obtained from Figure 18 by subtracting the linear extrapolation from the actual curve. Using equation (69), equation (76) becomes equation (77). However, since reaction (27) is over before reaction (28) commences,  $A_1$  may be set equal to  $A_1^\infty$  and  $\Delta Q$  is given by equation (78).

$$\Delta Q = (A_2^\infty - A_2) - (A_1^\infty - A_1) \quad (77)$$

tion (28) commences,  $A_1$  may be set equal to  $A_1^\infty$  and  $\Delta Q$  is given by equation (78).

$$\Delta Q = (A_2^\infty - A_2) \quad (78)$$

But, equation (67) can be written in the form shown by equation (79).

$$\ln (A_2^\infty - A_2) = -k_2 t + \ln A_2^\infty \quad (79)$$

Comparing equations (78) and (79), it is obvious that a plot of  $\ln \Delta Q$



against time should give a straight line having a slope of  $-k_2$  and an intercept of  $\ln \bar{A}_3^\infty$ . This plot is shown in Figure 19. The value of  $k_2$  calculated from the slope is  $2.635 \text{ hr.}^{-1}$  as compared to  $2.918 \text{ hr.}^{-1}$  obtained from Figure 16 (curve I). The intercept gives a value of  $\bar{A}_2^\infty$  of  $56.7 \times 10^{-1} \mu\text{c.}$  Since  $V_2^\infty$  is  $47.52 \text{ ml.}$ ,  $\bar{A}_2$ , i.e.,  $\bar{A}_2^\infty/V_2^\infty$ , has a value of  $0.1193 \mu\text{c./ml.}$

Using the values of  $0.0804 \mu\text{c./ml.}$ ,  $0.1193 \mu\text{c./ml.}$ , and  $0.1510 \mu\text{c./ml.}$  for  $\bar{A}_1$ ,  $\bar{A}_2$ , and  $\bar{A}_3$ , respectively, and the values of  $94.24 \text{ hr.}^{-1}$ ,  $2.918 \text{ hr.}^{-1}$ , and  $0.5718 \text{ hr.}^{-1}$  for  $k_1$ ,  $k_2$ , and  $k_3$ , respectively, equation (70) becomes equation (80).

$$A_T = V_T^\infty (0.1254 - 0.0201 e^{-94.24t} - 0.0298 e^{-2.918t} - 0.0755 e^{-0.5718t}) \quad (80)$$

In Table VIII, the values of  $A_T$  calculated by means of equation (80) are compared with the actual values listed in column VII of Table VI. It is observed that the calculated values are always slightly greater than the actual values. It has already been shown that the value of  $\bar{A}_3$  varies from about  $0.133 \mu\text{c./ml.}$  to  $0.158 \mu\text{c./ml.}$  in going from 50 to 100 per cent reaction. In equation (80), the relatively high value,  $0.1510 \mu\text{c./ml.}$ , was used. Similarly, the values of  $\bar{A}_1$  and  $\bar{A}_2$  might be expected to be less than those values used in equation (80) since the methods by which they were determined also gave the maximum value possible.

Let the separation factor,  $S_1$ , for the liberation of hydrogen from alcohol be defined by equation (81), where  $\bar{A}_1$  represents the specific

$$S_1 = \frac{\left( \frac{\bar{A}_1}{\bar{A}_{\text{NH}_3}} \right)_{\text{no isotope effect}}}{\left( \frac{\bar{A}_1}{\bar{A}_{\text{NH}_3}} \right)_{\text{experimental}}} \quad (81)$$

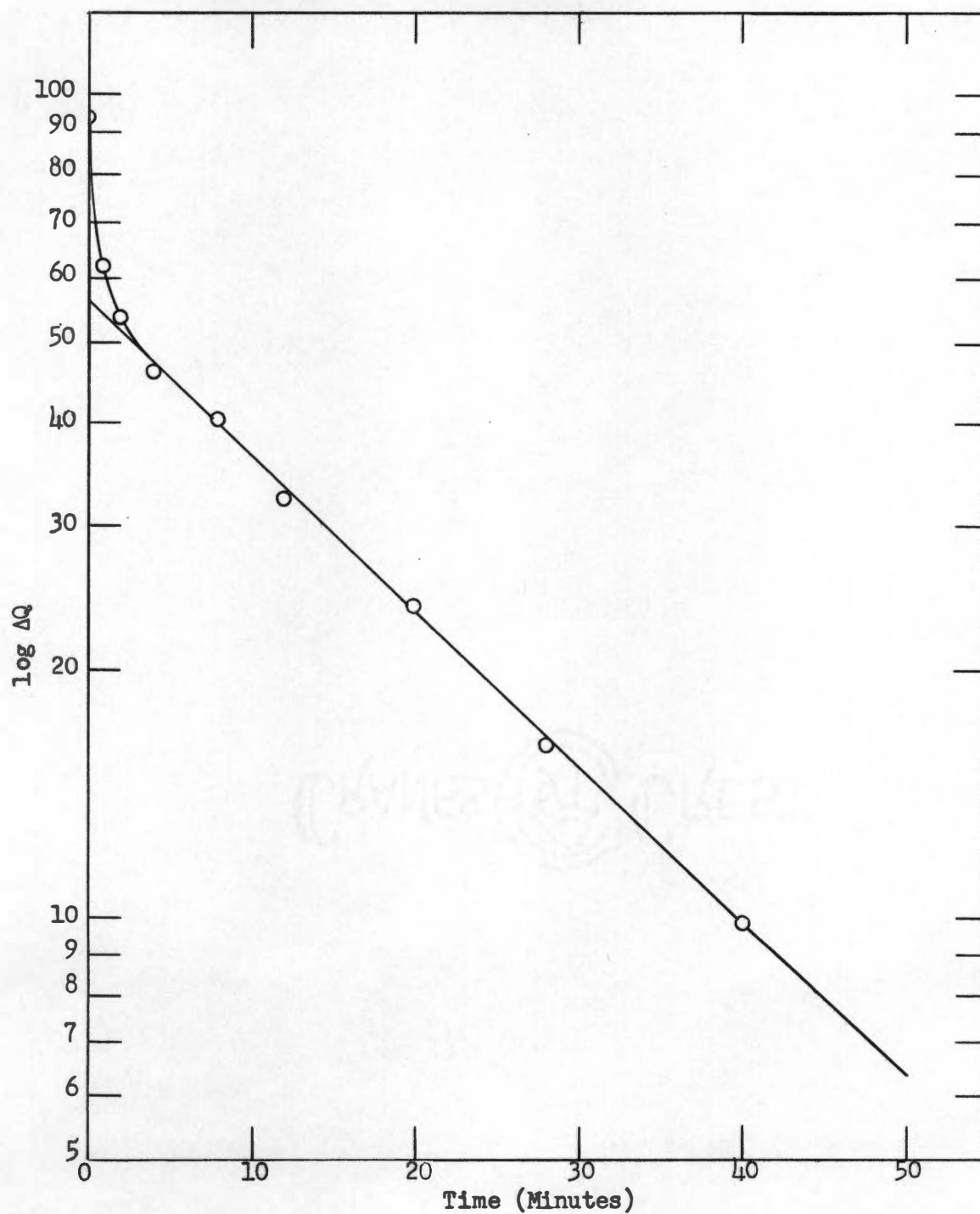


Figure 19. Sodium-Ethanol-Ammonia System, Run I:  $\log \Delta Q$  versus time.

TABLE VIII

SODIUM-ETHANOL-AMMONIA SYSTEM  
 Run I  
 $A_T$  (Calculated) and  $A_T$  (Observed)

Time from $t^0$	$A_T$ ( $\mu\text{c.}$ ) (Calc. by Eq. 80)	$A_T$ ( $\mu\text{c.}$ ) (Obs.)
0	0	0
10 sec.	1.01	0.96
30 sec.	2.28	2.11
1 min.	3.36	3.01
2 min.	4.45	3.96
4 min.	5.36	5.06
8 min.	6.71	6.33
12 min.	7.87	7.45
20 min.	9.85	9.22
28 min.	11.40	10.80
40 min.	13.23	12.60
60 min.	15.44	14.37
80 min.	17.04	16.40
2 hrs.	19.28	18.70
3 hrs.	21.28	20.72
5 hrs.	23.04	22.71
8 hrs.	23.70	23.45
	23.86	23.47

activity of the hydrogen liberated from the  $i^{\text{th}}$  species, and  $\bar{A}_{\text{NH}_3}$  represents the specific activity of the solvent. If there were no isotope effect on the liberation reaction, then  $\bar{A}_1$  would be equal to  $2/3 \bar{A}_{\text{NH}_3}$ . Consequently, equation (81) may be rewritten to give equation (82).

$$S_1 = \frac{2}{3} \left( \frac{\bar{A}_{\text{NH}_3}}{\bar{A}_1} \right)_{\text{experimental}} \quad (82)$$

The specific activity of the ammonia,  $\bar{A}_{\text{NH}_3}$  was equal to 0.3575  $\mu\text{c./ml.}$  Therefore, the separation factors,  $S_1$ ,  $S_2$ , and  $S_3$  corresponding to the specific activities  $\bar{A}_1$ ,  $\bar{A}_2$ , and  $\bar{A}_3$  calculated by equation (82), are 2.96, 2.00, and 1.58 respectively. The specific activity of the hydrogen liberated from the ammonia,  $(\bar{A})_{\text{NH}_3}$ , is equal to the ratio of the correction factors,  $\frac{n}{m}$  (Table VI) or 0.0195  $\mu\text{c./ml.}$  The corresponding separation factor,  $S_{\text{NH}_3}$ , calculated by means of equation (13), is 12.22.

Up to this point, results of one sodium-ethanol-ammonia experiment, Run I, have been discussed in detail. The results of the other experiments on this system are presented in Tables IX through XIII. In Table IX, the data for Run II is given without correction for the reaction of sodium with the solvent. The uncorrected data was used in Figure 11. The corrected data for this experiment, shown in Table X, was used in Figure 14. The data in Table XI is for Run III. This uncorrected data was also used in Figure 11. The duration of this particular experiment was only five hours. Consequently, it was not possible to accurately determine  $m$  and  $n$ . However, it was possible to estimate  $m$  and, using the value of 1.16 ml./hr. for this correction factor, all of the total volume data was corrected and is tabulated in column VIII. The corrected data

TABLE IX

SODIUM-ETHANOL-AMMONIA SYSTEM  
Run II (Uncorrected Data)

Reactor System A						
Reactants: Burette A: 0.9551 gm. (0.0415 gm. atoms) of sodium plus NH <sub>2</sub> T to give 25.0 ml. of solution						
Burette B: 0.4585 gm. (0.0099 moles) ethanol plus NH <sub>3</sub> to give 25.0 ml. of solution						
I	II	III	IV	V	VI	VII
Sample Number	Time from t <sup>o</sup>	V (ML.)	$\bar{A} \times 10^3$ (μc./ML.)	$A \times 10^2$ (μc.)	V <sub>T</sub> (ML.)	A <sub>T</sub> × 10 <sup>2</sup> (μc.)
1	<3 sec.	2.34	6.39	1.50	2.34	1.50
2	10 sec.	4.27	7.75	3.31	6.62	4.81
3	30 sec.	5.10	8.24	4.20	11.72	9.01
4	1 min.	4.86	8.05	3.91	16.57	12.92
5	2 min.	6.45	8.02	5.17	23.02	18.10
6	4 min.	6.00	8.51	5.10	29.02	23.20
7	8 min.	6.57	9.17	6.02	35.59	29.22
8	20 min.	11.04	10.83	11.96	46.63	41.18
9	40 min.	10.74	11.96	12.85	57.37	54.03
10	1 hr.	7.01	12.37	8.67	64.38	62.70
11	2 hrs.	11.53	12.72	14.67	75.91	77.37
12	5 hrs.	15.95	13.00	20.74	91.86	98.12
13	8 hrs.	8.21	12.69	10.41	100.07	108.53
14	16 hrs.	4.81	8.27	3.98	104.88	112.51
15	24.1 hrs.	5.34	1.38	0.74	110.23	113.25
16	32 hrs.	4.25	1.46	0.62	114.48	113.87
17	42 hrs.	5.39	1.44	0.78	119.87	114.64
18	52 hrs.	4.17	1.62	0.68	124.04	115.32

TABLE X

SODIUM-ETHANOL-AMMONIA SYSTEM  
Run II (Corrected Data)

I	II	III	IV	V	VI	VII
Sample Number	Time from $t^0$	V (ML.)	$\bar{A} \times 10^3$ ( $\mu\text{c.}/\text{ML.}$ )	$A \times 10^2$ ( $\mu\text{c.}$ )	$V_T$ (ML.)	$A_T \times 10^2$ ( $\mu\text{c.}$ )
1	<3 sec.	2.34	6.39	1.50	2.34	1.50
2	10 sec.	4.27	7.76	3.31	6.61	4.81
3	30 sec.	5.10	8.25	4.20	11.71	9.01
4	1 min.	4.85	8.05	3.91	16.57	12.92
5	2 min.	6.44	8.03	5.17	23.00	18.09
6	4 min.	5.98	8.53	5.10	28.98	23.20
7	8 min.	6.54	9.21	6.02	35.52	29.21
8	20 min.	10.94	10.92	11.94	46.45	41.16
9	40 min.	10.56	12.14	12.82	57.02	53.98
10	1 hr.	6.83	12.65	8.64	63.85	62.63
11	2 hrs.	11.00	13.26	14.59	74.85	77.22
12	5 hrs.	14.35	14.29	20.51	89.20	97.73
13	8 hrs.	6.61	15.40	10.18	95.82	107.90
14	16 hrs.	0.56	60.34	3.36	96.37	111.26

$$V_T^\infty = 97.18 \text{ ML.}$$

$$m = 0.5322 \text{ ML./Hr.}$$

$$\bar{A}_{\text{NH}_3} = 0.0380 \mu\text{c.}/\text{ML.}$$

$$n = 0.00078 \mu\text{c.}/\text{Hr.}$$

TABLE XI

SODIUM-ETHANOL-AMMONIA SYSTEM  
Run III (Uncorrected Data)

Reactor System A							
Reactants: Burette A: 0.9151 gm. (0.0398 gm. atoms) of sodium plus NH <sub>3</sub> to give 25.0 ml. of solution							
Burette B: 0.4563 gm. (0.0099 moles) of sodium plus NH <sub>2</sub> T to give 25.0 ml. of solution							
I	II	III	IV	V	VI	VII	VIII
Sample Number	Time from t <sup>o</sup>	V (Ml.)	$\bar{A} \times 10^3$ (μc./Ml.)	$A \times 10^2$ (μc.)	V <sub>T</sub> (Ml.)	$A_T \times 10^2$ (μc.)	V <sub>T</sub> (Corr.) (Ml.)
1	<3 sec.	0.18	6.05	0.11	0.18	0.11	0.18
2	10 sec.	4.11	5.01	2.06	4.29	2.17	4.29
3	30 sec.	4.28	8.28	3.55	8.57	5.72	8.56
4	1 min.	4.37	8.35	3.65	12.95	9.37	12.93
5	2 min.	5.03	8.28	4.16	17.97	13.53	17.94
6	4 min.	5.87	8.47	4.97	23.84	18.50	23.76
7	8 min.	6.32	8.98	5.68	30.16	24.17	30.01
8	20 min.	8.89	9.64	8.58	39.05	32.75	38.67
9	40 min.	11.09	10.90	12.09	50.14	44.84	49.37
10	1 hr.	8.86	11.15	9.87	59.00	54.71	57.84
11	2.5 hrs.	15.01	12.08	18.13	74.01	72.84	71.12
12	5 hrs.	11.07	12.35	13.67	85.09	86.52	79.30

$$V_T^{\infty} = 79.30 \text{ ML.}$$

$$\bar{A}_{\text{NH}_3} = 0.0430 \text{ μc./ML.}$$

$$m = 1.16 \text{ ML./Hr.}$$

TABLE XII

SODIUM-ETHANOL-AMMONIA SYSTEM  
Run IV (Corrected Data)

Reactor System A

Reactants: Burette A: 0.8674 gm. (0.0377 gm. atoms) of sodium plus  $\text{NH}_2\text{T}$  to give 25.0 ml. of solution

Burette B: 0.4641 gm. (0.0101 moles) ethanol plus  $\text{NH}_3$  to give 25.0 ml. of solution

I	II	III	IV	V	VI	VII
Sample Number	Time from $t^0$	V (ML.)	$\bar{A} \times 10^3$ ( $\mu\text{c.}/\text{ML.}$ )	$A \times 10^2$ ( $\mu\text{c.}$ )	$V_T$ (ML.)	$A_T \times 10^2$ ( $\mu\text{c.}$ )
1	<3 sec.	4.36	9.86	4.30	4.36	4.30
2	10 sec.	3.02	9.65	2.91	7.38	7.22
3	30 sec.	4.25	9.49	4.04	11.64	11.26
4	1 min.	5.50	9.07	4.99	17.14	16.25
5	2 min.	7.16	9.36	6.70	24.30	22.95
6	4 min.	7.74	9.45	7.31	32.04	30.26
7	8 min.	8.79	9.18	8.07	40.83	38.33
8	20 min.	9.91	10.60	10.51	50.74	48.84
9	40 min.	10.48	11.80	12.38	61.22	61.21
10	1 hr.	7.32	12.26	8.97	68.54	70.19
11	2 hrs.	11.67	12.55	14.64	80.21	84.83
12	5 hrs.	13.09	12.88	16.86	93.30	101.69
13	8 hrs.	5.01	12.80	6.41	98.31	108.10
14	16 hrs.	0.71	14.49	1.03	99.02	109.13

$$V_T^\infty = 99.02 \text{ ML.}$$

$$m = 0.0482 \text{ ML./Hr.}$$

$$\bar{A}_{\text{NH}_3} = 0.0379 \mu\text{c.}/\text{ML.}$$

$$n = 0.000082 \mu\text{c.}/\text{Hr.}$$





for Run IV is given in Table XII, and the corrected data for Run V is shown in Table XIII.

According to equation (65), the per cent reaction at any given time  $t$  should be independent of the initial alcohol concentration, i.e., independent of  $V_T^\infty$ . This is a consequence of assuming, as was done in the derivation of equation (65), that the overall reaction of sodium with ethanol is first order in ethanol. Table XIV, the per cents reaction at various reaction times  $t$ , are listed for all of the experiments on the sodium-ethanol-ammonia system. The reaction time  $t$ , as measured from  $t^0$ , is listed in column I. In column II, the per cent reaction, calculated by means of equation (65), is listed. The per cents reaction for Runs I, II, III, IV, and V are then listed in columns III, IV, V, VI, and VII, respectively. The value of  $V_T^\infty$  is also tabulated for each experiment.

It has already been shown that equation (65) correlates well the experimental results for Run I (see Table VII). This fact, re-emphasized in columns II and III of Table XIV, might well be accepted as sufficient proof that the reaction is first order in ethanol. In Runs II, III, IV, and V, the initial ethanol concentration was reduced to approximately one-half that used in Run I. This may be seen by comparing the  $V_T^\infty$  values listed for the various experiments. The fact that the per cents reaction at any given times  $t$  for Runs II, III, and IV are in good agreement with the values for Run I establishes that the reaction is first order in ethanol. The results for Run V are not in harmony with the results for the other experiments, the per cent reaction at any given time being greater than expected. However, it is of interest to note that Run V was the only

TABLE XIV

SODIUM-ETHANOL-AMMONIA SYSTEM  
(Per Cent Reaction vs. Time)

Time from $t^0$	P E R C E N T R E A C T I O N					
	I	II	III	IV	V	VI
	Eq. 65	Run I	Run II	Run III	Run IV	Run V
0	0	0	0	0	0	0
10 sec.	5.96	6.51	6.81	5.41	7.46	5.36
30 sec.	14.44	14.08	12.05	10.80	11.75	12.35
1 min.	21.12	19.78	17.05	16.30	17.31	20.46
2 min.	27.18	25.43	23.67	22.62	24.54	- - -
2.5 min.	28.55	- - -	- - -	- - -	- - -	31.13
4 min.	31.25	31.46	29.82	29.96	32.35	37.24
8 min.	36.73	37.72	36.55	37.84	41.23	45.81
12 min.	41.47	42.53	- - -	- - -	- - -	- - -
20 min.	49.26	49.46	47.80	48.76	51.24	57.15
28 min.	55.30	55.50	- - -	- - -	- - -	- - -
40 min.	62.28	62.24	58.67	62.26	61.83	- - -
60 min.	70.42	68.70	65.70	72.94	69.22	76.76
80 min.	76.18	76.09	- - -	- - -	- - -	- - -
2 hrs.	84.04	84.14	77.02	- - -	81.00	- - -
2.5 hrs.	88.01	- - -	- - -	89.68	- - -	90.07
3 hrs.	91.00	91.00	- - -	- - -	- - -	- - -
5 hrs.	97.14	97.53	98.59	- - -	94.22	95.64
$\infty$	100.00	100.00	100.00	100.00	100.00	100.00
$V_T^\infty$	190.07	190.07	97.18	79.30	99.02	87.47

experiment on this system in which a single tube reactor (Figure 2) was employed. In all of the other experiments, Reactor System A (Figure 1) was used. The inadequacies of the single tube reactor have already been discussed (page 41) and could well account for the results obtained in Run V.

#### D. Potassium-Ethanol-Ammonia System

Using Reactor System A (Figure 1), the data shown in Table XV was obtained for a reaction between potassium and ethanol in liquid ammonia. Burette A contained 3.1667 grams (0.081 gm. atoms) of potassium dissolved in liquid ammonia to give 25.0 ml. of solution. Approximately 0.020 moles of ethanol were dissolved in sufficient liquid ammonia to give 25.0 ml. of solution in burette B. The liquid ammonia used in the preparation of the two reactant solutions was labeled with tritium. This experiment will be referred to as Run VI.

The constants  $m$  and  $n$ , i.e., the rates at which the total hydrogen,  $V_T$ , and the total activity,  $A_T$ , varied with time as a consequence of the reaction of the potassium with the labeled solvent, are equal to 1.880 ml./hr. and 0.4843  $\mu$ c./hr., respectively. These correction factors were applied with equations (19) and (24) to obtain the corrected data listed in Table XVI. It should be pointed out that by the time the first sample of hydrogen was collected, the reaction had already gone to 36.74 per cent completion.

TABLE XV

POTASSIUM-ETHANOL-AMMONIA SYSTEM  
Run VI (Uncorrected Data)

Reactor System A

Reactants: Burette A: 3.1667 gm. (0.0810 gm. atoms) of potassium  
plus  $\text{NH}_2\text{T}$  to give 25.0 ml. of solution

Burette B: 0.9173 gm. (0.0198 moles) of ethanol plus  
 $\text{NH}_2\text{T}$  to give 25.0 ml. of solution

I	II	III	IV	V	VI	VII
Sample Number	Time from $t^0$	V (Ml.)	$\bar{A} \times 10^2$ ( $\mu\text{c.}/\text{Ml.}$ )	$A \times 10$ ( $\mu\text{c.}$ )	$V_T$ (Ml.)	$A_T \times 10$ ( $\mu\text{c.}$ )
1	1.2 min.	67.26	10.30	69.30	67.26	69.30
2	3 min.	18.11	9.14	16.56	85.36	85.86
3	6 min.	12.03	10.27	12.35	97.40	98.21
4	10 min.	8.66	8.32	7.20	106.06	105.41
5	20 min.	11.54	7.37	8.50	117.59	113.92
6	31 min.	10.06	7.44	7.49	127.66	121.41
7	45 min.	11.33	7.80	8.83	138.99	130.24
8	60 min.	9.82	7.88	7.73	148.80	137.97
9	80 min.	9.20	8.24	7.58	158.00	145.56
10	121 min.	14.88	9.06	13.47	172.88	159.03
11	4 hrs.	15.79	7.38	11.66	188.68	170.69
12	6 hrs.	5.60	3.63	2.03	194.28	172.72
13	12 hrs.	9.04	2.52	2.27	203.31	174.99
14	18 hrs.	13.52	2.62	3.54	216.83	178.53

TABLE XVI

POTASSIUM-ETHANOL-AMMONIA SYSTEM  
Run VI (Corrected Data)

I	II	III	IV	V	VI	VII
Sample Number	Time from $t^0$	V (ML.)	$\bar{A} \times 10^2$ ( $\mu\text{c.}/\text{ML.}$ )	$A \times 10$ ( $\mu\text{c.}$ )	$V_T$ (ML.)	$A_T \times 10$ ( $\mu\text{c.}$ )
1	1.2 min.	67.22	10.31	69.29	67.22	69.29
2	3 min.	18.05	9.17	16.55	85.27	85.84
3	6 min.	11.94	10.33	12.33	97.21	98.17
4	10 min.	8.53	8.40	7.17	105.74	105.34
5	20 min.	11.22	7.50	8.42	116.97	113.76
6	31 min.	9.72	7.62	7.40	126.69	121.16
7	45 min.	10.89	8.00	8.72	137.58	129.88
8	60 min.	9.35	8.14	7.61	146.92	137.49
9	80 min.	8.57	8.66	7.42	155.50	144.91
10	121 min.	13.59	9.67	13.14	169.09	158.05
11	4 hrs.	12.03	8.88	10.69	181.12	168.74
12	6 hrs.	1.84	5.76	1.06	182.96	169.80

$$V_T^\infty = 182.96 \text{ ML.}$$

$$m = 1.880 \text{ ML./Hr.}$$

$$\bar{A}_{\text{NH}_3} = 0.3575 \mu\text{c.}/\text{ML.}$$

$$n = 0.0484 \mu\text{c.}/\text{Hr.}$$

The kinetic nature of the potassium-ethanol reaction was interpretable on the same basis as that of the sodium-ethanol reaction, as represented by equations (27), (28), and (29). According to equation (51), a plot of  $\ln (V_T^\infty - V_T)$  against time  $t$ , should yield a straight line having a slope of  $-k_3$  and an intercept of  $\ln \frac{V_T^\infty}{2}$ . This graph is shown in Figure 20 (curve I). The resulting straight line has an intercept of  $\ln 91.5$  which is equivalent to  $\ln \frac{V_T^\infty}{2}$  since  $V_T^\infty$  is equal to 182.96. The specific rate constant,  $k_3$ , calculated from the slope of the straight line, is  $0.9271 \text{ hr.}^{-1}$ .

According to equations (56) and (58), a graph of  $\ln \Delta P$  against time  $t$ , should result in a straight line having a slope corresponding to  $-k_2$  and an intercept of  $\ln \frac{V_T^\infty}{4}$ . This plot is shown in Figure 20 (curve II). Again a straight line is observed. The intercept is equal to  $\ln 45.7$  or  $\ln \frac{V_T^\infty}{4}$ . The rate constant,  $k_2$ , calculated from the slope, is equal to  $29.27 \text{ hr.}^{-1}$ .

Knowing the values of  $k_2$  and  $k_3$ , equation (48) may be rewritten to give equation (83). In this equation the time,  $t$ , must be expressed in

$$V_T = V_T^\infty (1 - \frac{1}{4}e^{-k_1 t} - \frac{1}{4}e^{-29.27t} - \frac{1}{2}e^{-0.9271t}) \quad (83)$$

hours. The specific rate constant,  $k_1$ , corresponding to the first one-fourth of the reaction obviously cannot be evaluated from Run VI since the reaction was already 36.75 per cent complete when the first sample of gas was collected. Consequently,  $k_1$  was evaluated by inserting into equation (83) the data shown in Table XIX for another potassium-ethanol experiment. The value of  $k_1$  is  $160 \text{ hr.}^{-1}$ . Equation (83) becomes equation (84).

$$V_T = V_T^\infty (1 - \frac{1}{4}e^{-160t} - \frac{1}{4}e^{-29.27t} - \frac{1}{2}e^{-0.9271t}) \quad (84)$$

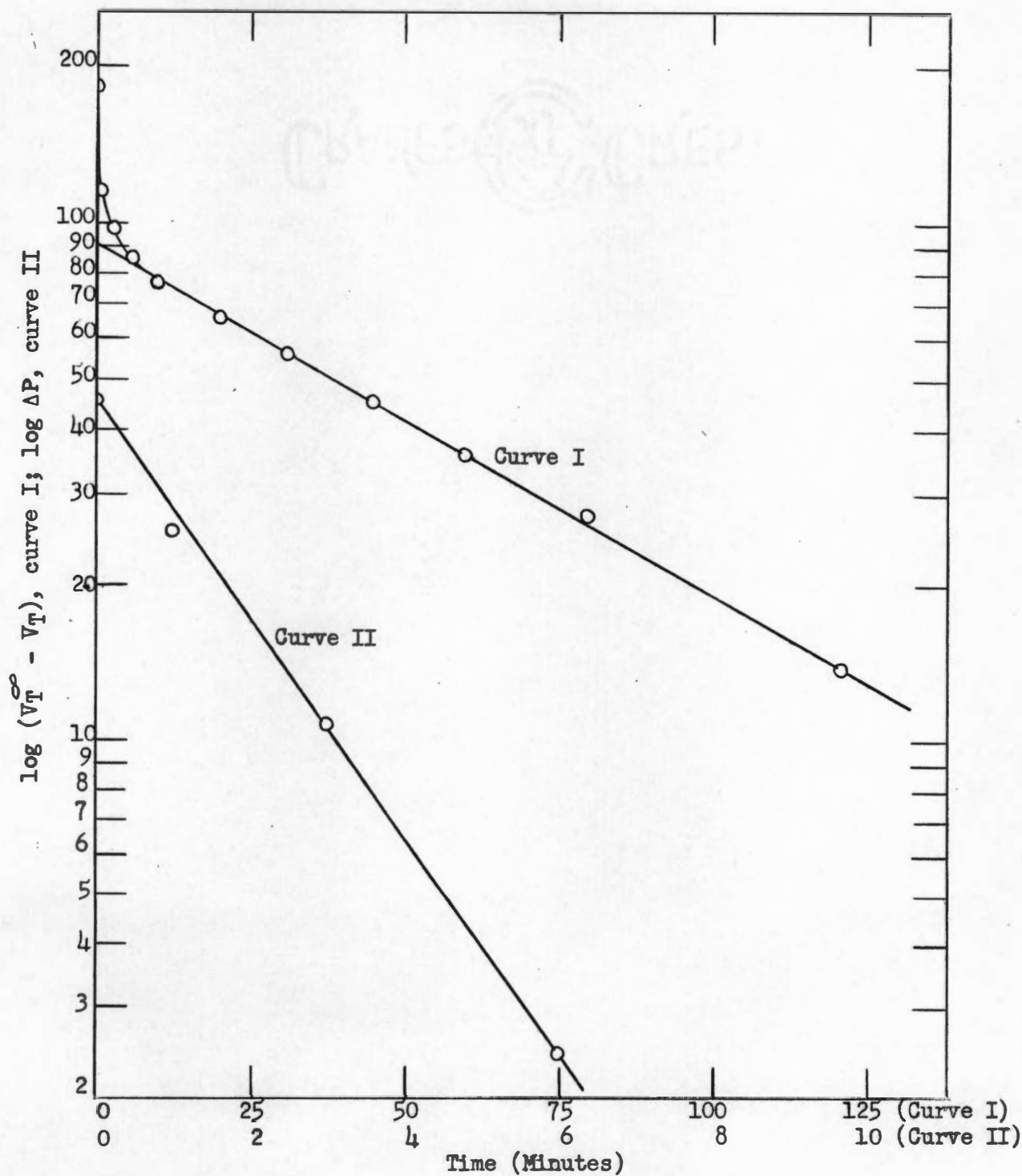


Figure 20. Potassium-Ethanol-Ammonia System, Run VI:  $\log (V_T^\infty - V_T)$  versus time (curve I) and  $\log \Delta P$  versus time (curve II).



In Table XVII, the values of  $V_T$  calculated by means of equation (84) are compared to the observed values listed in column VI of Table XVI. The calculated and observed values of  $V_T$  are in very close agreement, the difference generally amounting to a fraction of one per cent.

The specific activities  $\bar{A}_1$ ,  $\bar{A}_2$ , and  $\bar{A}_3$ , can be obtained in exactly the same manner in which those of the sodium-ethanol system were evaluated. Thus, according to equation (73), a plot of  $\ln (A_T^\infty - A_T)$  against time should give a straight line having an intercept of  $\ln A_3^\infty$ , and a slope equal to  $-k_3$ . This graph is shown in Figure 21. From the intercept,  $A_3^\infty$  is equal to 73.8  $\mu\text{c.}$  Then, since  $\bar{A}_3$  is equal to  $A_3^\infty / V_3$ , and  $V_3$  is equal to 91.5 ml., the value of  $\bar{A}_3$  is 0.0806  $\mu\text{c./ml.}$  Substituting the values of 0.0806  $\mu\text{c./ml.}$  and 0.3575  $\mu\text{c./ml.}$  for  $\bar{A}_3$  and  $\bar{A}_{\text{NH}_3}$ , respectively, into equation (82), one obtains the separation factor,  $S_3$ , of 3.06. The specific activity,  $\bar{A}_2$ , obtained either by plotting  $V_T$  vs.  $A_T$  or by plotting  $\ln \Delta Q$  vs.  $t$  (equations (78) and (79)), is equal to 0.1029  $\mu\text{c./ml.}$  The corresponding separation factor,  $S_2$ , is 2.31. The specific activity,  $\bar{A}_1$ , cannot be evaluated for Run VI. However, from other potassium-ethanol experiments, the separation factor,  $S_1$ , may be estimated to be equal to 1.75.

The results of other potassium-ethanol experiments are tabulated in Tables XVIII, XIX, XX, and XXI, the corresponding experiments being referred to as Runs VII, VIII, IX, and X, respectively. In Run VII and Run IX, the labeled liquid ammonia was not preswept with tank hydrogen to remove traces of  $T_2$ . Consequently, the specific activity of the first gas sample in each of these experiments is seen to be abnormally high. The

TABLE XVII

POTASSIUM-ETHANOL-AMMONIA SYSTEM  
Run VI  
 $V_T$  (Calculated) and  $V_T$  (Observed)

Time from $t^0$	$V_T$ (ML.) (Calc. by Eq. 84)	$V_T$ (ML.) (Obs.)
0	0	0
1.2 min.	65.52	67.22
3 min.	85.06	85.27
6 min.	97.18	97.21
10 min.	104.27	105.74
20 min.	115.86	116.97
31 min.	126.29	126.69
45 min.	137.38	137.58
60 min.	146.78	146.92
80 min.	156.38	155.50
121 min.	168.87	169.09
4 hrs.	180.67	181.12
6 hrs.	182.61	182.96
$\infty$	182.96	182.96

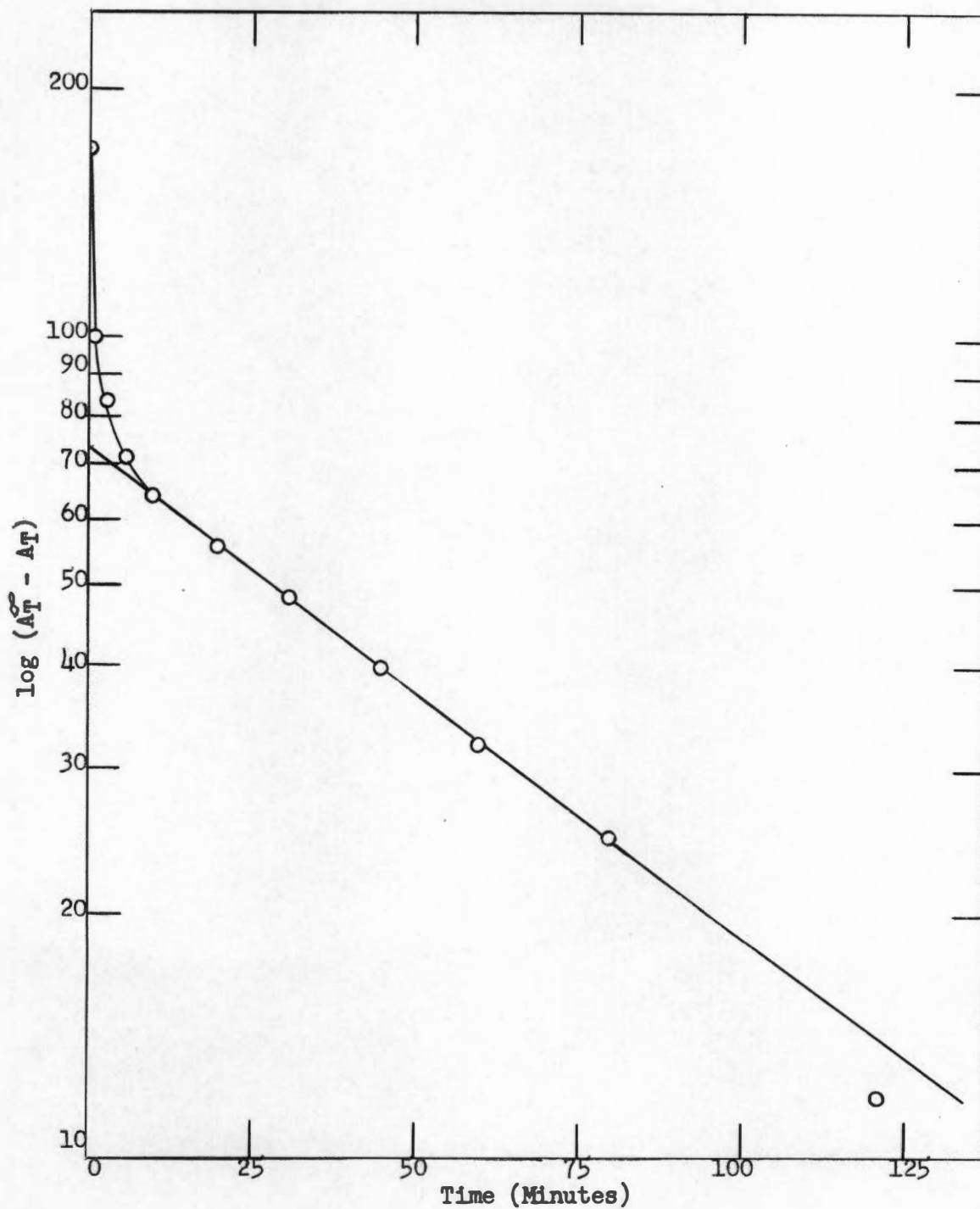


Figure 21. Potassium-Ethanol-Ammonia System, Run VI:  $\log (A_T^\infty - A_T)$  versus time.

$$n = 0.00051 \text{ } \mu\text{c.}/\text{Hr.}$$

TABLE XIX

POTASSIUM-ETHANOL-AMMONIA SYSTEM  
Run VIII (Uncorrected Data)

## Reactor System A

Reactants: Burette A: 3.2197 gm. (0.0821 gm. atoms) of potassium plus  $\text{NH}_2\text{T}$  to give 25.0 ml. of solution

Burette B: 0.4623 gm. (0.0100 moles) of ethanol plus  $\text{NH}_2\text{T}$  to give 25.0 ml. of solution

I	II	III	IV	V	VI	VII	VIII
Sample Number	Time from $t^0$	V (ml.)	$\bar{A} \times 10^2$ ( $\mu\text{c.}/\text{ml.}$ )	$A \times 10$ ( $\mu\text{c.}$ )	$V_T$ (ml.)	$A_T \times 10$ ( $\mu\text{c.}$ )	$V_T$ (Corr.) (ml.)
1	<3 sec.	5.77	6.67	3.85	5.77	3.85	5.76
2	10 sec.	7.99	9.66	7.72	13.76	11.57	13.74
3	30 sec.	11.52	8.73	10.06	25.28	21.63	25.24
4	1 min.	11.01	8.56	9.43	36.28	31.06	36.19
5	2 min.	10.99	8.31	9.13	47.27	40.19	47.09
6	4 min.	9.76	8.10	7.91	57.03	48.10	56.68
7	8 min.	9.99	7.88	7.83	67.02	55.92	66.31
8	16 min.	9.86	6.70	6.61	76.87	62.53	75.46
9	26 min.	7.04	5.57	3.92	83.92	66.45	81.63
10	45 min.	9.24	5.04	4.66	93.16	71.11	89.19
11	75 min.	7.31	5.52	4.03	100.46	75.14	93.85
12	2 hrs.	5.94	8.74	5.19	106.40	80.33	95.82
13	3 hrs.	11.23	5.04	5.67	117.63	86.00	101.77
14	5 hrs.	23.09	1.84	4.24	140.72	90.24	114.27
15	9 hrs.	31.56	1.72	5.44	172.28	95.68	- - -
16	17 hrs.	12.65	2.01	2.54	184.94	98.23	- - -
17	25 hrs.	30.94	2.35	7.28	215.87	105.50	- - -
18	31 hrs.	44.25	1.98	8.79	260.12	114.29	- - -
19	31 hrs.	7.58	2.35	1.78	267.70	116.07	- - -
20	33 hrs.	20.75	2.11	4.38	288.44	120.45	- - -
21	41 hrs.	41.89	2.13	8.93	330.33	129.38	- - -
22	49 hrs.	53.60	2.16	11.60	383.94	140.98	- - -

$$V_T^\infty = 114.27$$

$$m = 5.29 \text{ ml./Hr.}$$

$$\bar{A}_{\text{NH}_3} = 0.3575 \mu\text{c.}/\text{ml.}$$

$$n = 0.112 \mu\text{c.}/\text{Hr.}$$

TABLE XX

POTASSIUM-ETHANOL-AMMONIA SYSTEM  
Run IX (Corrected Data)

Reactor System A

Reactants: Burette A: 1.5296 gm. (0.0391 gm. atoms) of potassium plus  $\text{NH}_2\text{T}$  to give 25.0 ml. of solution

Burette B: 0.4607 gm. (0.0100 moles) of ethanol plus  $\text{NH}_3$  to give 25.0 ml. of solution

I	II	III	IV	V	VI	VII
Sample Number	Time from $t^0$	V (ML.)	$\bar{A} \times 10^3$ ( $\mu\text{c.}/\text{ML.}$ )	$A \times 10^2$ ( $\mu\text{c.}$ )	$V_T$ (ML.)	$A_T$ ( $\mu\text{c.}$ )
1	20 sec. (?)	30.78	94.89	292.01	30.78	292.01
2	3 min.	15.13	8.70	13.16	45.91	305.17
3	10 min.	17.42	7.58	13.20	63.33	318.37
4	30 min.	12.02	5.96	7.16	73.35	325.53
5	3 hrs.	24.05	6.75	16.22	99.40	341.75
6	5 hrs.	2.15	- - -	4.52	101.55	346.37
7	8 hrs.	0	- - -	0	101.55	346.37
$V_T^\infty = 101.55$				$m = 3.144 \text{ ML.}/\text{Hr.}$		
$\bar{A}_{\text{NH}_3} = 0.03772 \mu\text{c.}/\text{ML.}$				$n = 0.00686 \mu\text{c.}/\text{Hr.}$		

TABLE XXI

POTASSIUM-ETHANOL-AMMONIA SYSTEM  
Run X (Uncorrected Data)

Reactor System B

Reactants: 3.2000 gm. (0.0819 gm. atoms) of potassium;  $\text{NH}_2\text{T}$  to give 300 ml. of solution; an unknown amount of alcohol\*

I	II	III	IV	V	VI	VII
Sample Number	Time from $t^0$	V (ml.)	$\bar{A} \times 10^{-2}$ ( $\mu\text{c.}/\text{ml.}$ )	$A \times 10$ ( $\mu\text{c.}$ )	$V_T$ (ml.)	$A_T \times 10$ ( $\mu\text{c.}$ )
1	20 sec.	11.51	1.69	1.94	11.51	1.94
2	1 min.	3.22	5.70	1.83	14.73	3.77
3	5 min.	7.19	7.59	5.46	21.92	9.23
4	25 min.	16.87	6.90	11.64	38.79	20.87
5	55 min.	7.86	2.73	2.14	46.65	23.01
6	100 min.	11.04	2.39	2.64	57.69	25.65
7	160 min.	7.61	3.80	2.90	65.30	28.55
8	250 min.	5.58	3.25	1.81	70.88	30.36
9	7 hrs.	6.91	2.14	1.47	77.79	31.83
10	11 hrs.	8.35	1.91	1.60	86.14	33.43
11	16 hrs.	10.91	1.97	2.14	97.05	35.57
12	26 hrs.	6.08	2.06	1.25	103.13	36.82
13	26 hrs.	~0.48	- - -	- - -	- - -	- - -
14	33 hrs.	13.05	2.11	2.75	116.18	39.57
15	40 hrs.	13.18	2.09	2.76	129.36	42.33
16	48 hrs.	14.44	2.13	3.08	143.80	45.41
17	56 hrs.	13.60	2.16	2.94	157.40	48.35
18	63 hrs.	11.51	2.14	2.46	168.91	50.81
19	73 hrs.	3.46	2.12	0.74	172.37	51.55
20	84 hrs.	15.34	2.14	3.28	187.71	54.83
21	98 hrs.	18.42	2.15	3.96	206.13	58.79

\*In this experiment the alcohol bulb was fractured in such a manner that at  $t^0$  the ethanol was not discharged into the ammonia solution but was allowed to diffuse slowly into the solution. This diffusion, which continued over a period of a few hours, apparently stopped after only a fraction of the alcohol had left the bulb. Examination of the bulb recovered after this experiment corroborated this interpretation.

data for Run VIII is shown in uncorrected form since it was in this form that the data was shown in Figure 9. The corrected total volume data is shown in column VIII. The magnitude of the correction factors,  $m$  and  $n$ , are such that beyond about 75 minutes or 80 per cent completion of reaction, a considerable uncertainty exists in the corrected data for this experiment. The data for Run X is also given in uncorrected form. It should be noted that this experiment was a failure as far as giving any information on the reaction of potassium with ethanol because, as the data indicates, a homogeneous solution was not obtained at  $t^0$ . In this experiment, a single-tube reactor was used, and at  $t^0$ , only the tip of the bulb containing the alcohol was broken. The alcohol then slowly diffused into the ammonia and reacted. However, this experiment was of considerable value in that the reaction of the potassium with the solvent was observed over a very long period of time (98 hours). The data corresponding to this reaction has been shown in Figure 10 in which  $V_T$  was plotted against  $At$ .

In the study of the sodium-ethanol-ammonia system, experiments were performed in which the initial ethanol concentration was varied while the initial sodium concentration was held constant. It was shown that the per cent reaction at any reaction time was indeed independent of the initial ethanol concentration, thus establishing that the overall reaction is first order in ethanol. In the study of the potassium-ethanol-ammonia system, again the initial ethanol concentration was varied while the initial potassium concentration was held constant. In addition, the initial potassium concentration was varied while the initial ethanol concentration was held essentially constant.



In Table XXII, the per cent reaction at various reaction times,  $t$ , are tabulated for each of the potassium-ethanol-ammonia Runs VI through IX. The reaction time,  $t$ , as measured from  $t^0$ , is listed in column I. In column II, the per cents reaction as calculated by means of equation (84) are shown. In columns III, IV, V, and VI, the observed per cents reaction for Runs VI, VIII, VII, and IX, respectively, are shown. For each run there are listed the values of  $V_T^\infty$ , as an indication of the initial ethanol concentration, and the initial potassium concentrations,  $[K]^0$ .

The results listed in columns II and III re-emphasize the accuracy with which the theoretical equation, equation (48), represents the kinetics

$$V_T = V_T^\infty (1 - \frac{1}{4}e^{-k_1t} - \frac{1}{4}e^{-k_2t} - \frac{1}{2}e^{-k_3t}) \quad (48)$$

of the metal-alcohol reaction measured in Run VI. In comparing Run VI with Run VIII, it is seen that while the initial potassium concentration was held constant, the initial ethanol concentration in Run VI was double that in Run VIII. Yet, the data in columns III and IV show that, up to approximately 80 per cent reaction, the per cent reaction at any specified reaction time is in good agreement for the two experiments. This again shows that the reaction is first order in ethanol. Beyond 80 per cent reaction, the data for Run VIII is not reliable, as mentioned previously.

In comparing Runs VI and VIII with Runs VII and IX, it is observed that, although the initial potassium concentrations were halved for the latter runs, the per cent reaction at any given time was not greatly changed. If anything, the reactions at the lower concentration of metal went slightly faster. If the reaction of potassium with ethanol were

TABLE XXII

POTASSIUM-ETHANOL-AMMONIA SYSTEM  
(Per Cent Reaction vs. Time)

Time from $t^0$	PER CENT REACTION					
I	II	III	IV	V	VI	VII
	Eq. 84	Run VI	Run VIII	Run VII	Run IX	Eq. 84'
0	0	0	0	0	0	0
<3 sec.	2.57	- - -	5.04	5.85	- - -	2.14
10 sec.	11.07	- - -	12.03	12.78	- - -	8.56
20 sec.	18.24	- - -	- - -	- - -	30.30(?)	11.04
30 sec.	24.22	- - -	22.10	23.30	- - -	15.25
1 min.	33.70	- - -	31.68	34.05	- - -	24.23
1.2 min.	35.81	36.74	- - -	- - -	- - -	26.36
2 min.	42.00	- - -	41.21	- - -	- - -	33.69
2.25 min.	43.46	- - -	- - -	45.79	- - -	36.43
3 min.	46.49	46.60	- - -	- - -	45.21	39.14
4 min.	49.45	- - -	49.60	52.94	- - -	42.09
5 min.	51.58	- - -	- - -	- - -	- - -	44.56
6 min.	53.11	53.13	- - -	- - -	- - -	46.50
8 min.	55.32	- - -	58.03	60.75	- - -	49.44
10 min.	56.99	57.79	- - -	- - -	62.25	51.54
16 min.	60.90	- - -	66.06	- - -	- - -	53.22
20 min.	63.30	63.93	- - -	71.76	- - -	57.18
26 min.	66.58	- - -	71.48	- - -	- - -	59.10
30 min.	68.56	- - -	- - -	- - -	72.20	60.36
31 min.	69.05	69.24	- - -	- - -	- - -	60.68
40 min.	73.07	- - -	- - -	79.93	- - -	63.00
45 min.	77.08	75.19	78.09	- - -	- - -	66.15
60 min.	80.22	80.30	- - -	- - -	- - -	68.57
75 min.	84.32	- - -	82.20	85.63	- - -	72.00
80 min.	85.50	84.89	- - -	- - -	- - -	73.08
120 min.	92.19	- - -	83.84	89.46	- - -	80.24
121 min.	92.48	92.42	- - -	- - -	- - -	80.60
3 hrs.	96.90	- - -	89.10	- - -	97.85	87.56
3.5 hrs.	98.60	- - -	- - -	99.60	- - -	90.15
4 hrs.	98.78	98.99	- - -	- - -	- - -	92.18
5 hrs.	99.52	- - -	100.00	- - -	- - -	95.08
6 hrs.	99.81	100.00	- - -	100.00	100.00	96.91
$\infty$	100.00	100.00	100.00	100.00	100.00	100.00
$V_T^0$ (ML.)	- - -	182.96	114.27	92.35	101.55	- - -
$[K]^0$ (gm. atoms/liter)	- - -	1.620	1.642	0.800	0.782	- - -

first order in potassium rather than the zero order assumed in deriving equation (48), the effect on equation (84) of halving the initial potassium concentration would be to cut each rate constant in half. This follows since the reaction solutions (Runs VI through IX) were always "flooded" in potassium. With its rate constants cut in half, equation (84) would predict the values listed in column VII for the per cent reaction at any time  $t$ . These values, predicted if the reaction were first order in metal, are uniformly and significantly lower than observed values for Runs VII and IX. The results of these experiments therefore establish that the reaction is zero order in metal.

#### E. Lithium-Ethanol-Ammonia System

The data shown in Table XXIII was obtained, using Reactor System A, for the reaction of lithium with ethanol in liquid ammonia. This experiment will be referred to as Run XI. Burette A contained 0.2794 grams (0.0406 gm. atoms) of lithium dissolved in liquid ammonia to give 25.0 ml. of solution. Approximately 0.010 moles of ethanol were dissolved in liquid ammonia to give 25.0 ml. of solution in burette B. The liquid ammonia used in the preparation of the two reactant solutions was labeled with tritium.

From Table XXIII, it is apparent that the reaction of lithium with ethanol is a much faster reaction than the corresponding sodium or potassium reactions. It is also apparent that the reaction of lithium with the solvent is extremely slow, the values of the correction factors,  $m$  and  $n$ , being only 0.0705 ml./hr. and 0.00034  $\mu$ c./hr. Using these correc-

TABLE XXIII

LITHIUM-ETHANOL-AMMONIA SYSTEM  
Run XI (Uncorrected Data)

Reactor System A						
Reactants: Burette A: 0.2895 gm. (0.0417 gm. atoms) of lithium plus NH <sub>2</sub> T to give 25.0 ml. of solution						
Burette B: 0.4568 gm. (0.0099 moles) of ethanol plus NH <sub>2</sub> T to give 25.0 ml. of solution						
I	II	III	IV	V	VI	VII
Sample Number	Time from t <sup>o</sup>	V (ml.)	$\bar{A} \times 10^2$ (mc./ml.)	A x 10 (mc.)	V <sub>T</sub> (ml.)	A <sub>T</sub> x 10 (mc.)
1	<1 sec.	0.84	8.50	0.72	0.84	0.72
2	10 sec.	10.26	9.34	9.58	11.10	10.30
3	18 sec.	4.65	11.25	5.23	15.75	15.52
4	30 sec.	9.34	11.63	10.86	25.08	26.38
5	1 min.	12.46	11.94	14.87	37.54	41.26
6	1.75 min.	12.68	11.95	15.16	50.23	56.41
7	2.75 min.	12.04	11.91	14.34	62.27	70.75
8	4 min.	11.73	11.67	13.70	74.00	84.44
9	6.5 min.	14.86	11.58	17.21	88.86	101.66
10	10 min.	13.26	10.69	14.17	102.13	115.83
11	16 min.	12.93	8.83	11.42	115.06	127.25
12	24 min.	3.73	7.06	2.64	118.79	129.89
13	40 min.	0.04	- - -	- - -	118.83	- - -
14	75 min.	0.07	- - -	- - -	118.90	- - -
15	2 hrs.	~ 0	- - -	- - -	- - -	- - -
16	48 hrs.	3.24	0.51	0.16	122.14	130.05

tion factors, the data in Table XXIII has been corrected, and retabulated in Table XXIV. The data in Table XXIV is essentially the same as that in Table XXIII, showing that the correction for the reaction of lithium with the solvent is not necessary.

The data presented in Table XXV was obtained for a second experiment on the lithium-ethanol-ammonia system. The initial conditions of this experiment referred to as Run XII, were a duplicate of those in Run XI. The magnitudes of the correction factors,  $m$  and  $n$ , for Run XII are such that, as in the case of Run XI, the corrections for the reaction of lithium with the solvent are unnecessary.

It should be mentioned that Run XII was the first experiment performed on the lithium-ethanol-ammonia system. The fast rate of this reaction came as something of a surprise and, consequently, the time intervals between the consecutive gas samples were too large. In Run XI, a train of eight gas collection bulbs was employed for the first eight samples, thus enabling the fast sampling necessary for collection of samples at optimum time intervals.

In seeking an explanation for the unexpectedly fast rate of the lithium-ethanol reaction, graphs of  $V_T$  vs.  $A_T$  were made for the two experiments. These curves are shown in Figure 22. For Run XI, the plot of  $V_T$  vs.  $A_T$  is essentially linear from 10 ml. to about 95.0 ml. The slope of this linear section,  $\bar{A}_2$ , is equal to  $0.1173 \mu\text{c./ml.}$  Similarly, the plot of  $V_T$  vs.  $A_T$  for Run XII exhibits a linear section extending from 45 ml. to the end of the reaction, i.e., to about 120 ml. The slope of this linear section,  $\bar{A}_2$ , is  $0.1156 \mu\text{c./ml.}$ , in excellent agreement with Run XI.

TABLE XXIV

LITHIUM-ETHANOL-AMMONIA SYSTEM  
Run XI (Corrected Data)

I	II	III	IV	V	VI	VII
Sample Number	Time from $t^0$	V (ML.)	$\bar{A} \times 10^2$ ( $\mu\text{c.}/\text{ML.}$ )	$A \times 10$ ( $\mu\text{c.}$ )	$V_T$ (ML.)	$A_T \times 10$ ( $\mu\text{c.}$ )
1	<1 sec.	0.84	8.49	0.72	0.84	0.72
2	10 sec.	10.26	9.34	9.58	11.10	10.30
3	18 sec.	4.65	11.24	5.23	15.75	15.53
4	30 sec.	9.34	11.63	10.86	25.08	26.38
5	1 min.	12.46	11.94	14.87	37.54	41.26
6	1.75 min.	12.68	11.95	15.16	50.22	56.41
7	2.75 min.	12.04	11.91	14.34	62.26	70.75
8	4 min.	11.73	11.67	13.70	74.00	84.44
9	6.5 min.	14.86	11.58	17.21	88.86	101.66
10	10 min.	13.26	10.69	14.17	102.12	115.83
11	16 min.	12.93	8.84	11.42	115.04	127.25
12	24 min.	3.72	7.08	2.64	118.76	129.89

$$V_T^\infty = 118.81 \text{ ML.}$$

$$m = 0.0705 \text{ ML./Hr.}$$

$$\bar{A}_{\text{NH}_3} = 0.3575 \text{ } \mu\text{c.}/\text{ML.}$$

$$n = 0.00034 \text{ } \mu\text{c.}/\text{Hr.}$$

TABLE XXV

LITHIUM-ETHANOL-AMMONIA SYSTEM  
Run XII (Uncorrected Data)

Reactor System A						
Reactants: Burette A: 0.2794 gm. (0.0406 gm. atoms) of lithium plus NH <sub>2</sub> T to give 25.0 ml. of solution						
Burette B: 0.4563 gm. (0.0099 moles) of ethanol plus NH <sub>2</sub> T to give 25.0 ml. of solution						
I	II	III	IV	V	VI	VII
Sample Number	Time from t <sup>o</sup>	V (ML.)	$\bar{A} \times 10^2$ ( $\mu\text{c.}/\text{ML.}$ )	$A \times 10$ ( $\mu\text{c.}$ )	V <sub>T</sub> (ML.)	A <sub>T</sub> $\times 10$ ( $\mu\text{c.}$ )
1	<3 sec.	9.65	8.32	8.03	9.65	8.03
2	10 sec.	9.32	7.32	6.82	18.97	14.85
3	30 sec.	22.85	8.31	19.00	41.82	33.85
4	1 min.	10.74	10.70	11.49	52.56	45.34
5	2 min.	13.00	11.47	14.91	65.56	60.25
6	4 min.	15.49	11.69	18.11	81.05	78.36
7	8 min.	16.74	11.49	19.24	97.80	97.60
8	20 min.	17.54	10.97	19.23	115.33	116.83
9	40 min.	4.78	9.42	4.50	120.11	121.32
10	75 min.	0.32	4.14	0.13	120.42	121.46
11	2 hrs.	0.04	- - -	- - -	120.46	- - -
12	3 hrs.	0.06	- - -	- - -	120.52	- - -
13	4.5 hrs.	0.12	- - -	- - -	120.65	- - -
14	6.5 hrs.	0.16	- - -	- - -	120.81	- - -
15	9 hrs.	0.54	0.30	0.01	121.36	121.47
16	17.5 hrs.	0.84	0.57	0.05	122.20	121.51
17	45.5 hrs.	3.86	0.63	0.24	126.05	121.76
18	72.5 hrs.	5.32	0.93	0.49	131.37	122.25

$$V_T^\infty = 120.30 \text{ ML.}$$

$$m = 0.17 \text{ ML./Hr.}$$

$$\bar{A}_{\text{NH}_3} = 0.3575 \mu\text{c.}/\text{ML.}$$

$$n = 0.0003 \mu\text{c.}/\text{Hr.}$$

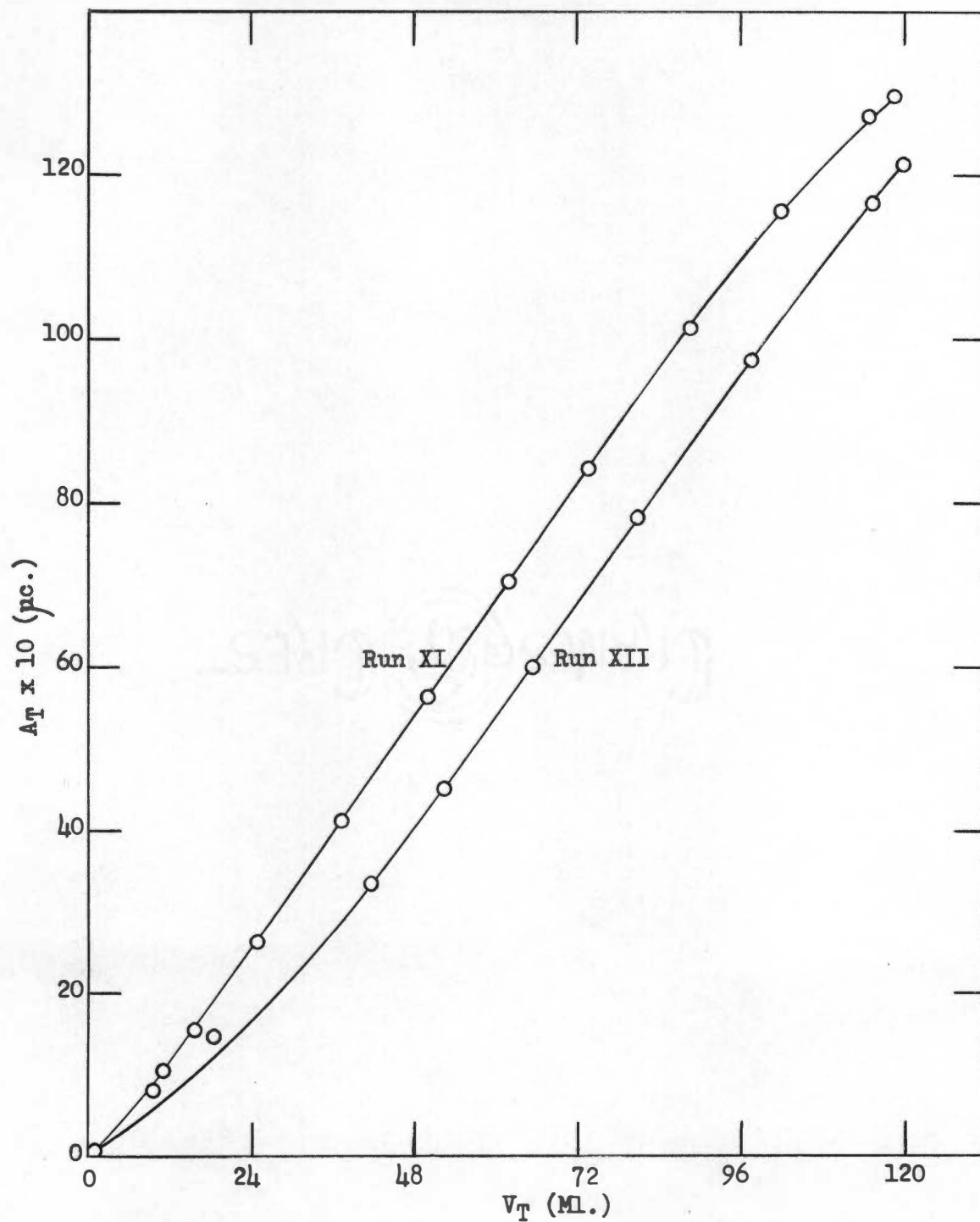


Figure 22. Lithium-Ethanol-Ammonia System, Runs XI and XII:  $V_T$  versus  $A_T$ .



In both experiments, the specific activity,  $\bar{A}_1$ , approaches the value of 0.083  $\mu\text{c./ml.}$  at  $t^0$ .

The shapes of the two curves (Figure 22) disagree at their extremities, which is probably a consequence of the experimental difficulties inherent in handling such a fast reaction. In Run XII, both the volume and the activity data for bulbs 2 and 3, particularly the latter, suggest that a small quantity of air may have been measured along with the hydrogen, thus giving rise to the relatively large curvature near  $t^0$ . With reference to Run XI, it is significant that the deviation from linearity near  $t^\infty$  accompanied the change from the train of eight bulbs to single gas collection bulbs. The time ( $\Delta t$  from column II) available for changing bulbs, pumping down the new bulb and the intervening glass tubing, and taking the next sample was, perhaps, insufficient to guarantee the exclusion of air, particularly in the case of bulbs 9 and 10. This difficulty did not arise in Run XII and, consequently, the curvature near  $t^0$  is insignificant.

Allowing for such experimental errors, the two curves combine to suggest that the specific activity changes in the early stages of the reaction and then remains at a constant level throughout the remainder of the reaction, i.e., over approximately the last 75 per cent of reaction. The most important conclusion, derived from either curve, is that, in contrast to the reactions of sodium and potassium with ethanol, there is definitely no change in the specific activity at 50 per cent completion of reaction. It therefore appears that reaction of lithium with a one-to-one complex,  $[\text{C}_2\text{H}_5\text{OH} \cdot \text{OC}_2\text{H}_5]^-$ , a step (equation (29)) postulated for the sodium and potassium reactions with ethanol does not occur.

Because the data for Run XI (Table XXV) was collected at more appropriate time intervals and is considered to be more accurate than that for Run XII, it will be used in the following treatment. In Figure 23,  $\log (V_T^\infty - V_T)$  is plotted against time. It is observed that, as  $t$  increases, a straight line is approached. The intercept of this straight line on the  $y$  axis is equal to  $\log 89.0$  ml. Since  $V_T^\infty$  is equal to 118.81 ml., this intercept is equal to almost exactly  $\log \frac{3V_T^\infty}{4}$ , which would be  $\log 89.11$ . In Figure 24,  $\log \Delta P$  is plotted against time, the values of  $\Delta P$  being obtained in the usual manner described in the discussion of the sodium-ethanol system. Again, a straight line is obtained. The intercept of this line on the  $y$  axis is equal to  $\log \frac{V_T^\infty}{4}$ . From these two graphs (Figures 23 and 24) one can conclude that one-fourth of the initial ethanol reacts at a rate constant,  $k_1$ , and that the remaining three-fourths of the ethanol reacts at a rate constant,  $k_2$ . The values of the rate constants,  $k_1$  and  $k_2$ , calculated from the slopes of the straight lines in Figures 24 and 23 are  $97.69 \text{ hr.}^{-1}$  and  $10.10 \text{ hr.}^{-1}$ , respectively. The corresponding specific activities,  $\bar{A}_1$  and  $\bar{A}_2$ , are  $0.083 \mu\text{c./ml.}$  and  $0.1173 \mu\text{c./ml.}$  The separation factors calculated for the two reactions by means of equation (82) are 2.87 and 2.03 for  $S_1$  and  $S_2$ , respectively.

The preceding observations show that the model proposed for the reaction of sodium and potassium with ethanol, i.e., the reactions represented by equations (27), (28), and (29), must be modified in the case of the lithium-ethanol reaction. The only necessary modification is the elimination of the reaction represented by equation (29), i.e., the reaction involving the complex,  $[\text{C}_2\text{H}_5\text{OH} \cdot \text{OC}_2\text{H}_5]^-$ . The model for the lithium-ethanol

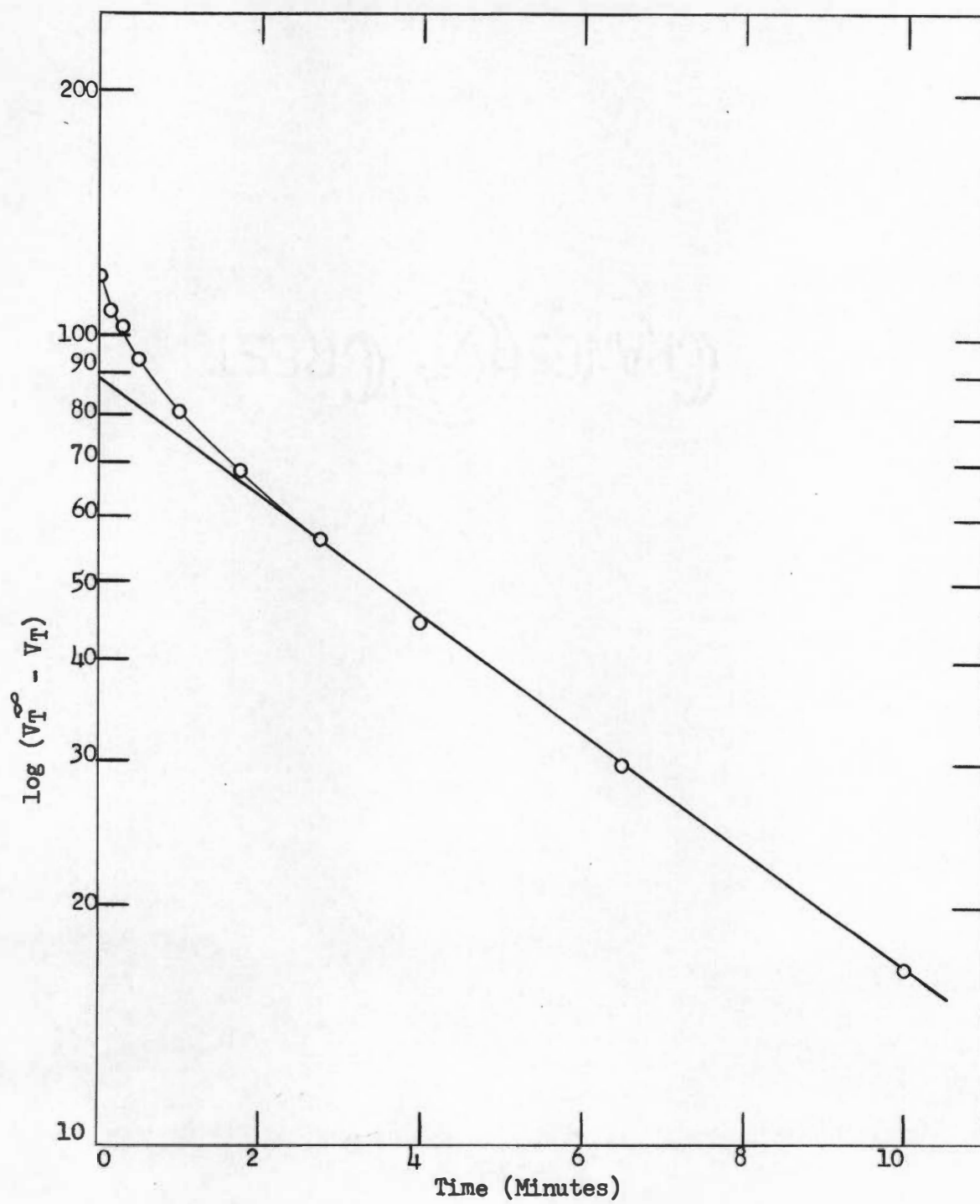


Figure 23. Lithium-Ethanol-Ammonia System, Run XI:  $\log(V_T^\infty - V_T)$  versus time.

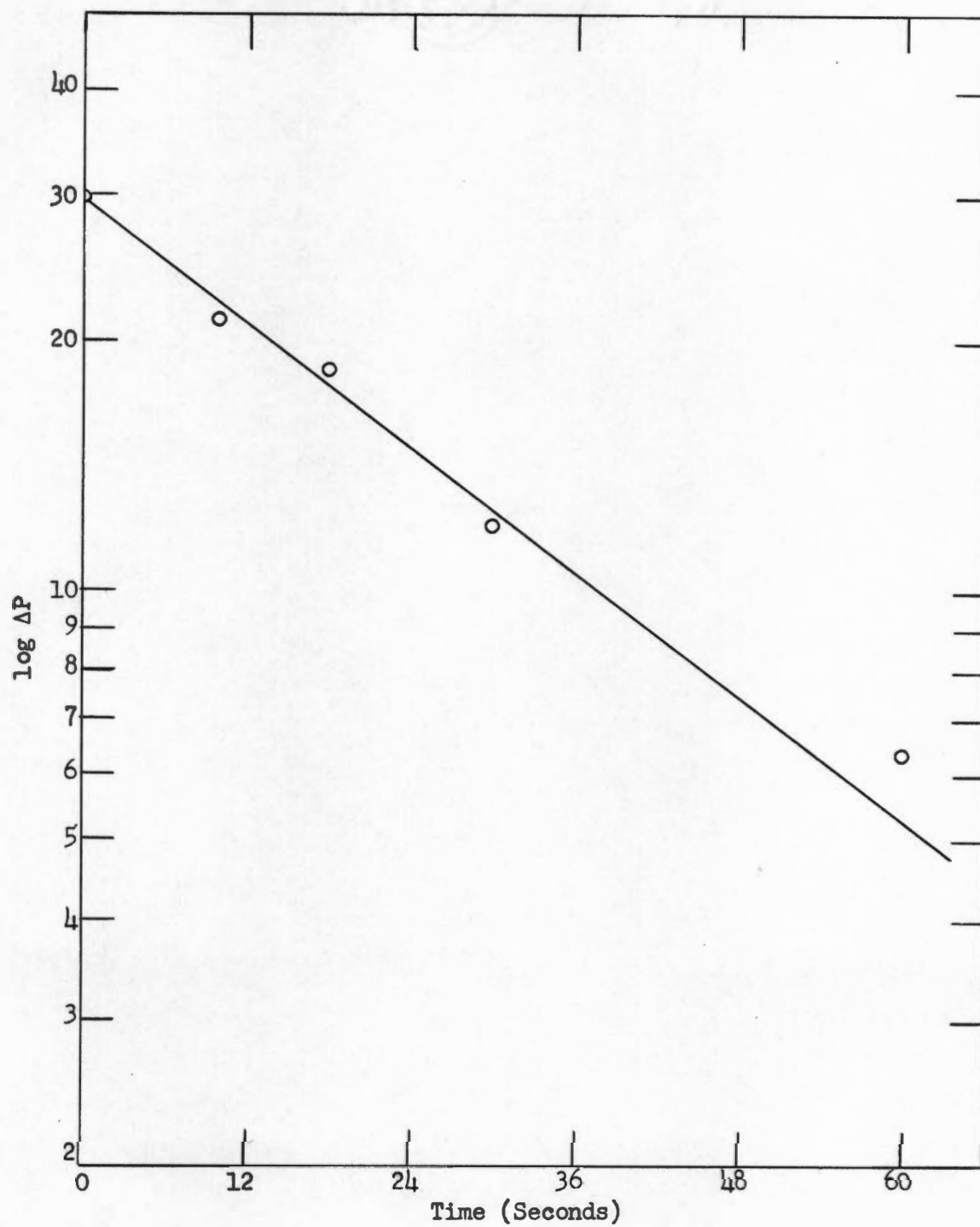
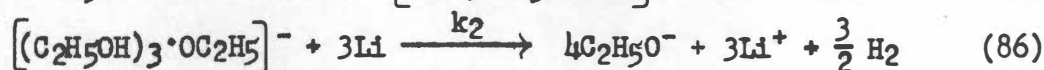
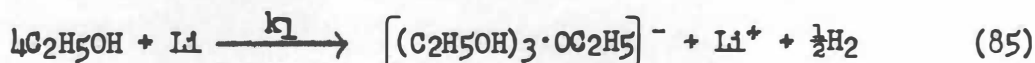


Figure 24. Lithium-Ethanol-Ammonia System, Run XII:  $\log \Delta P$  versus time.

reaction is then represented by equations (85) and (86).



The volumes of hydrogen liberated in the reactions represented by equations (85) and (86), i.e.,  $V_1$  and  $V_2$ , respectively, are given by equations (87) and (88).

$$V_1 = \frac{V_T^\infty}{4} (1 - e^{-k_1 t}) \quad (87)$$

$$V_2 = \frac{3V_T^\infty}{4} (1 - e^{-k_2 t}) \quad (88)$$

These equations predict that the intercepts on the y axis of linear sections of Figures 23 and 24 should be  $\log \frac{3V_T^\infty}{4}$  and  $\log \frac{V_T^\infty}{4}$ , as observed. The total volume of hydrogen,  $V_T$ , is equal to  $V_1$  plus  $V_2$  and is, therefore, given by equation (89).

$$V_T = V_T^\infty \left(1 - \frac{1}{4}e^{-k_1 t} - \frac{3}{4}e^{-k_2 t}\right) \quad (89)$$

It is seen that equation (89) is the same as equation (48) if one sets  $k_2$  and  $k_3$  equal in the latter expression. Substituting the values of  $k_1$  and  $k_2$  obtained from Figures 24 and 23 into equation (89), one obtains equation (90) in which the reaction time,  $t$ , is expressed in hours. In

$$V_T = V_T^\infty \left(1 - \frac{1}{4}e^{-97.69t} - \frac{3}{4}e^{-10.10t}\right) \quad (90)$$

Table XXVI, the values of  $V_T$  at various reaction times, calculated by means of equation (90), are compared with the observed values for Runs XI and XII. The observed and calculated values agree very well for Run XI. For Run XII the agreement is not good, the error decreasing rapidly after the first few samples, i.e., beyond 30 seconds. An error in the

TABLE XXVI

LITHIUM-ETHANOL-AMMONIA SYSTEM  
 $V_T$  (Calculated) and  $V_T$  (Observed)

Time from $t^0$	Run XI		Run XII	
	$V_T$ (Ml.) (Calc.)	$V_T$ (Ml.) (Obs.)	$V_T$ (Ml.) (Calc.)	$V_T$ (Ml.) (Obs.)
0	0	0	0	0
10 sec.	9.53	11.10	9.65	18.97
18 sec.	15.88	15.75	- - -	- - -
30 sec.	23.77	25.08	24.07	41.82
1 min.	37.71	37.54	38.18	52.56
1.75 min.	50.76	50.22	- - -	- - -
2 min.	- - -	- - -	54.74	65.56
2.75 min.	62.42	62.26	- - -	- - -
4 min.	73.32	74.00	74.24	81.05
6.5 min.	89.06	88.86	- - -	- - -
8 min.	- - -	- - -	96.84	97.80
10 min.	102.32	102.12	- - -	- - -
16 min.	112.79	115.04	- - -	- - -
20 min.	- - -	- - -	117.20	115.33
24 min.	117.25	118.76	- - -	- - -
40 min.	118.70	118.81	120.19	120.11
$\infty$	118.81	118.81	120.30	120.30

second and third gas samples is suggested, i.e., air was probably included in the measured volumes, as was suggested by the activity data plotted in Figure 22.

#### F. Potassium-Isopropyl Alcohol-Ammonia System

During the early development stages of this research program, i.e., when various reactor systems and techniques were being devised and tested, a few experiments were performed on the potassium-isopropyl alcohol-ammonia system. The results of one such experiment are presented in Table XXVII. The isopropyl alcohol was labeled with tritium in the hydroxyl hydrogen position and sealed in the usual bulb in a one-tube reactor. The liquid ammonia was not labeled. Consequently, this experiment differs from the experiments discussed in previous sections of this chapter in that at  $t^0$  no activity was located in the solvent.

Referring to Table XXVII, it is apparent that the reaction was not observed over a sufficiently long period of time to permit a correction of the activity data. However, such a correction should not affect the activity data for the first four samples and would probably affect the fifth sample only to a slight degree. From the weight of alcohol used,  $V_T^0$  should have equaled 109.75 ml. After six hours,  $V_T$  equaled 130.66 ml. and, therefore, the correction factor for the volume data,  $m$ , is estimated to be 3.49 ml./hr. Using this correction factor, the  $V_T$  data in column VI has been corrected for the potassium-ammonia reaction, the corrected values being listed in column VIII. For comparison, the per cent reaction has been tabulated in column IX.

TABLE XXVII

## POTASSIUM-ISOPROPYL ALCOHOL-AMMONIA SYSTEM

Reactor System B								
Reactants: 0.0612 gm. atoms of potassium plus 0.00979 moles of tritium-labeled isopropyl alcohol in NH <sub>3</sub> to give 50.0 ml. of solution								
I	II	III	IV	V	VI	VII	VIII	IX
Sample Number	Time from t <sup>0</sup>	V (ML.)	$\bar{A} \times 10^3$ (μc./ML.)	$A \times 10^2$ (μc.)	V <sub>T</sub> (ML.)	$A_T \times 10^2$ (μc.)	V <sub>T</sub> (Corr.) (ML.)	Per Cent Reaction
1	30 sec.	15.50	8.14	12.62	15.50	12.61	15.47	14.10
2	1 min.	5.71	6.50	3.71	21.21	16.33	21.15	19.26
3	4 min.	13.46	5.30	7.14	34.67	23.46	34.44	31.38
4	20 min.	19.62	4.21	8.27	54.29	31.73	52.12	47.50
5	1 hr.	26.59	3.15	8.38	80.88	40.11	77.39	70.52
6	6 hrs.	49.78	1.09	5.43	130.66	45.54	109.75	100.00

$$V_T^\infty = 109.75 \text{ ML.}$$

$$\bar{A}_{\text{NH}_3} = 2.13 \times 10^{-2} \text{ uc./ML.}$$

$$m = 3.49 \text{ ML./Hr.}$$



The original isopropyl alcohol had a specific activity of  $0.996 \times 10^5 \mu\text{c./mole}$ . Using this activity, the known quantities of alcohol and ammonia employed in the experiment, the following equation, and

$$K = \frac{[\text{NH}_2\text{T}][\text{ROH}]}{[\text{NH}_3][\text{ROT}]}$$

the equilibrium constant value of three, i.e., the value uncorrected for any small isotope effect, one can show that, as a result of the isotopic exchange reaction between the alcohol and the ammonia, the specific activity of the alcohol should have been reduced to  $1.617 \times 10^2 \mu\text{c./mole}$ . The specific activity of the ammonia should be three times greater than the specific activity of the alcohol, i.e., equal to  $4.851 \times 10^2 \mu\text{c./mole}$ . The measured specific activity of the ammonia was found to be  $4.774 \times 10^2 \mu\text{c./mole}$ , in good agreement with the value calculated assuming no isotope effect.

It is particularly interesting to note that, whereas the specific activity of the initial alcohol was equal to  $0.996 \times 10^5 \mu\text{c./mole}$ , the specific activity of the first sample of hydrogen liberated from the alcohol was only  $8.137 \times 10^{-3} \mu\text{c./ml}$ . or  $1.824 \times 10^2 \mu\text{c./mole}$ . Since without an isotope effect the activity of the hydrogen should be twice that of the alcohol, assuming a normal isotope effect of approximately two, one can estimate that the activity of the alcohol giving rise to the hydrogen was about  $1.8 \times 10^2$ . In other words, in the time used to take the first sample, thirty seconds, the specific activity of the alcohol had already been reduced to roughly 1/500 of its initial specific activity. Throughout the remainder of the reaction, the specific activity

is further decreased, but by a factor of only one-third. These observations are further evidence for the great rate with which the isotopic equilibrium is established (equation (5)).

In Table XXII, the per cent reaction at various time intervals from  $t^0$  was listed for the reaction of potassium with ethanol in liquid ammonia. A comparison of this data to that shown in column IX of Table XXVII shows that the reaction of potassium with isopropyl alcohol is much slower than the reaction with ethanol. The time required to complete half of the reaction,  $t_{\frac{1}{2}}$ , is about 23.4 minutes for the potassium-isopropyl alcohol reaction and only 4.25 minutes for the potassium-ethanol reaction. Assuming that equation (48) is applicable to the potassium-isopropyl alcohol reaction, the values of the rate constants,  $k_1$ ,  $k_2$ , and  $k_3$ , may be approximated by inserting the  $V_T$  and  $V_T^\infty$  values given in Table XXVII. Using the data given at thirty seconds,  $k_1$  is found to equal  $100 \text{ hr.}^{-1}$ . Similarly using the data given at four minutes and one hour,  $k_2$  and  $k_3$  are found to be  $4.3 \text{ hr.}^{-1}$  and  $0.54 \text{ hr.}^{-1}$ , respectively. Using these values, the per cent of reaction at one minute and at twenty minutes may be calculated. The calculated values are 22.4 and 52.4 per cent, respectively, as compared to the corresponding observed values of 19.3 and 47.5 per cent. Allowing for experimental errors and the approximations made, this agreement suggests that equation (48) is applicable to isopropyl as well as to ethyl alcohol.

As in the case of the potassium-ethanol reaction, but in contrast to the reactions of sodium and lithium with ethanol, the specific activity of the liberated hydrogen continually decreases from  $t^0$  to the end of the

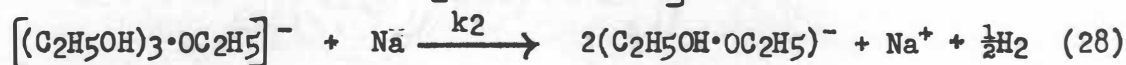
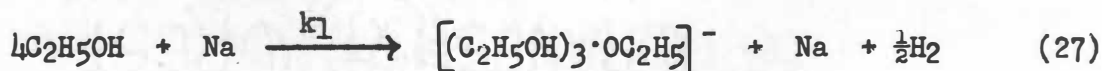
potassium-isopropyl alcohol reaction. The separation factor, therefore, increases correspondingly from the initial separation factor of 1.75 to approximately 3.5.

### G. Discussion of Results

Any model which might be postulated for the reaction of excess alkali metal with alcohol in liquid ammonia must be consistent with the following experimental observations:

1. The overall reaction is first order in ethanol, but zero order in sodium.
2. When the reaction is carried out in tritium-labeled ammonia, the specific activity of the evolved hydrogen changes as the reaction proceeds to completion, the change being marked by inflections at 25 and 50 per cent completion.
3. The proton exchange reaction between the proton donor and the solvent is instantaneous relative to the rate at which hydrogen is liberated from the proton donor.

The preceding observations, coupled with the fact that with tritium-labeled ammonia the H/T ratio in this solvent remains constant throughout the reaction, require that the H/T ratio in a particular proton donor also remains constant. These observations led to the model represented by equations (27), (28), and (29). Corresponding equations

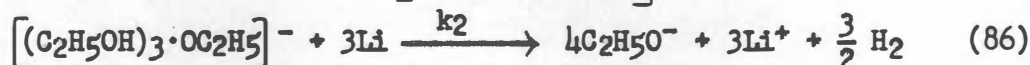
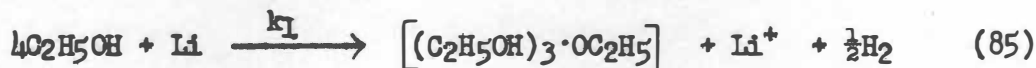


may be written for tritium-labeled species. Using this model and the experimental observations, equations were derived which express the total volume and the total activity of the liberated hydrogen as a function of the reaction time and the values of these quantities at infinite reaction time. These are equations (48) and (70), respectively.

$$V_T^\infty = V_T (1 - \frac{1}{4}e^{-k_1t} - \frac{1}{4}e^{-k_2t} - \frac{1}{2}e^{-k_3t}) \quad (48)$$

$$A_T = V_T^\infty \left( \frac{\bar{A}_1}{4} + \frac{\bar{A}_2}{4} + \frac{\bar{A}_3}{2} \right) - V_T^\infty \left( \frac{\bar{A}_1}{4} e^{-k_1t} + \frac{\bar{A}_2}{4} e^{-k_2t} + \frac{\bar{A}_3}{2} e^{-k_3t} \right) \quad (70)$$

Equations (48) and (70) apply equally well to the reaction of potassium and of sodium with ethanol. Lithium reacted with ethanol at a much faster overall rate than did either sodium or potassium (see Table XXVIII). The model postulated for this reaction is given by equations (85) and (86).



This model is the same as that postulated for the reactions of sodium and potassium with ethanol with one exception; the reaction of lithium with a one-to-one ethanol-ethoxide ion complex,  $(C_2H_5OH \cdot OC_2H_5)^-$ , does not occur. The expression relating the total volume of the liberated hydrogen to the reaction time is given by equation (89). It is seen that this equation

$$V_T = V_T^\infty (1 - \frac{1}{4}e^{-k_1t} - \frac{3}{4}e^{-k_2t}) \quad (89)$$

is identical to equation (48) if  $k_2$  and  $k_3$  are equal to one another in equation (48).

In the derivation of equations (48) and (70), it was necessary to assume only that the reactions represented by equations (27), (28), and (29) were the sole rate-determining reactions for the evolution of hydro-

TABLE XXVIII

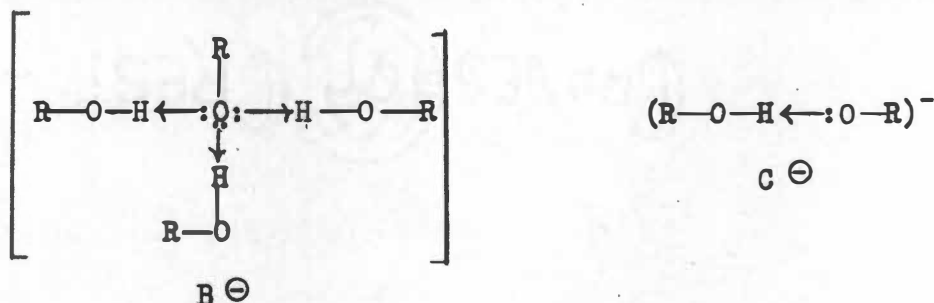
SUMMARY OF RESULTS FOR THE ALKALI METAL-ETHANOL REACTION  
IN TRITIUM-LABELED LIQUID AMMONIA\*

	A L K A L I   M E T A L		
	Na	K	Li
Specific Rate Constants			
$k_1$ (Hr. <sup>-1</sup> )	$9.4 \times 10$	$1.6 \times 10^2$	$9.8 \times 10$
$k_2$ (Hr. <sup>-1</sup> )	2.9	$2.9 \times 10$	$1.0 \times 10$
$k_3$ (Hr. <sup>-1</sup> )	$5.7 \times 10^{-1}$	$9.2 \times 10^{-1}$	- - -
Separation Factors			
$S_1$	3.0	1.7	2.8
$S_2$	2.0	2.3	2.0
$S_3$	1.6	3.1	- - -
$S_{NH_3}$	12	10	12

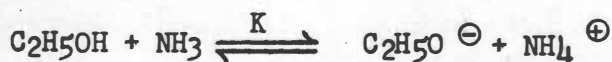
\*Prior to this table, the specific rate constants and the separation factors have been recorded with more than a justifiable number of significant figures. In this table, the correct number of significant figures is used.

gen from alcohol. This same assumption was necessary in the derivation of equation (89) from equations (85) and (86). It is appropriate, therefore, to consider these reactions in greater detail, particularly in regard to the nature of the three proton donors and to the mechanism by which hydrogen is liberated from them.

Using the symbol R to represent the ethyl group, the two ethanol-ethoxide ion complexes,  $[(C_2H_5OH)_3 \cdot OC_2H_5]^-$  and  $(C_2H_5OH \cdot OC_2H_5)^-$ , may be represented by the structural formulas  $B^\ominus$  and  $C^\ominus$ , respectively. That a

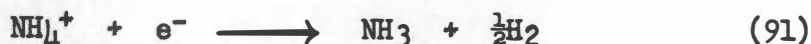


one-to-one ethanol-ethoxide ion complex  $C^\ominus$  may exist in liquid ammonia has been suggested by other investigators.<sup>36</sup> The same cannot be said of the three-to-one complex,  $B^\ominus$ . However, the structural formula for the latter complex would not seem to preclude its existence, particularly in a solvent of low dielectric constant.

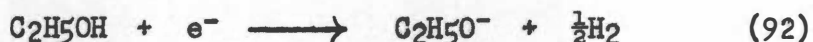


Although the ionization constant (K) for ethanol in ammonia (dielectric constant 22) has not been determined, one may estimate that it is quite small. (In water (dielectric constant 81) the pK value for the ionization of ethanol is 14.0, but in ethanol (dielectric constant 24) the pK value is 19.5.)<sup>56</sup> Consequently, an insignificant fraction of the alcohol is ionized in an equilibrated alcohol-ammonia solution. The addition of an alkali metal to the solution will result in the rapid

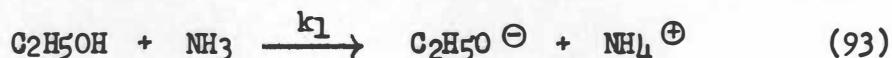
liberation of hydrogen via the reaction of any ammonium ions, i.e., solvated protons, with the solvated electrons, equation (91). In order



that more hydrogen be liberated, either the electrons must then attack the remaining undissociated ethanol, equation (92), or more ethanol must



dissociate to produce more ammonium ions, equation (93). If either the

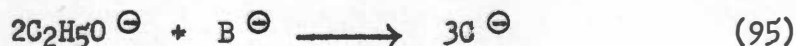


reaction between the solvated protons and the solvated electrons or the reaction of the undissociated ethanol with the electrons were rate-determining, then the overall reaction would have to show an order with respect to metal. Therefore the experimental observation that the hydrogen evolution reaction is zero order in alkali metal rules out each of these reactions as the rate-determining step. Consequently, it is postulated that the rate-determining step controlling the first quarter of the reaction is that given in equation (93), the dissociation of ethanol to produce solvated protons, and that this step is followed by the very fast reaction given in equation (91).

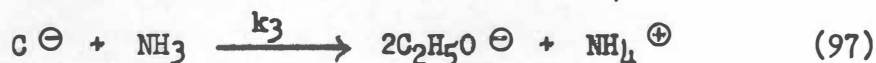
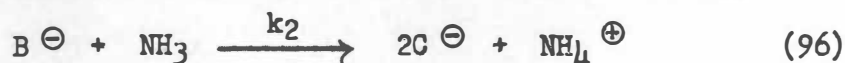
As the hydrogen evolution reaction proceeds, the ethoxide ion produced complexes with the remaining undissociated ethanol, equation (94),



to form immediately the three-to-one complex,  $\text{B}^-$ , and as more ethoxide ion is produced, the one-to-one complex,  $\text{C}^-$ , equation (95). Each complex



can be ionized to produce solvated protons, equations (96) and (97), which again react rapidly through equation (91). In other words, the



rate determining steps for the second quarter and the last half of the reactions are given in equations (96) and (97) respectively. The overall rate of hydrogen evolution reaction will, consequently, be dependent on three separate rate constants,  $k_1$ ,  $k_2$ , and  $k_3$ .

Since the proton is bonded differently in the three proton donors,  $C_2H_5OH$ ,  $B^{\ominus}$  and  $C^{\ominus}$ , the isotope effect on the hydrogen evolution reaction from each species will differ, i.e., three distinct separation factors should be observed as the reaction proceeds to completion (see Table XXVIII). It might be pointed out that if the rate-determining reaction were the reaction of solvated protons with solvated electrons, equation (91), this variation in the isotope effect would not be expected. That this variation was observed is further evidence against this reaction (91) as the rate-determining step.

Although the hydrogen evolution reaction is zero order in alkali metal, the overall rate of the reaction depends on which alkali metal is employed. When lithium is used, the rate of the reaction is unusually fast. Lithium is commonly characterized as being less reactive than the other alkali metals, even in liquid ammonia.<sup>57</sup> This surprisingly fast rate found for lithium, compared with the sodium and potassium reactions with alcohol, has been attributed to the fact that the one-to-one ethanol-ethoxide ion complex,  $C^{\ominus}$ , does not form in the lithium-



ethanol-liquid ammonia system. The lithium ion has a very large charge to radius ratio. As a result, it may compete with the proton bond from ethanol for the ethoxide ion and thereby prevent the formation of the one-to-one complex. In the case of the sodium and potassium reactions, the interaction of the metallic ions with the ethoxide ions is apparently not sufficient to prevent the formation of the one-to-one complex.

However, any of the alkali metal ions will interact with the proton donors to a certain extent and thereby affect the overall rate of the hydrogen evolution reaction. The difference in the rate of the hydrogen evolution from a particular proton donor accompanying a change from one alkali metal to another may then be attributed to a difference in this interaction of the metallic ions with the proton donors. Two possibilities are conceivable for the nature of this interaction. One is a direct interaction as a consequence of the metal cations pairing with the proton sources to yield ion pairs such as  $\text{Li}^{\oplus}$ ,  $\text{B}^{\ominus}$  and  $\text{Na}^{\oplus}$ ,  $\text{B}^{\ominus}$ ; the rates at which such ion pairs yield solvated protons should differ. Another possibility is a general medium effect as a consequence of the dielectric characteristics of ammonia solutions of the three different metal ions being quite different; the rates of reaction of many species are profoundly affected by their medium. Since neither the phenomenon of ion pairing in ammonia nor the dielectric characteristics of various ammonia solutions has been studied, a further elaboration of the nature of this interaction between metal ions with the proton donors is not possible.

Referring to Table XXVIII, it is seen that as the reaction proceeds the separation factors for the sodium-ethanol-liquid ammonia system de-

crease from 3.0 to 2.0 and finally to 1.6. Similarly, the separation factors for the lithium-ethanol-liquid ammonia system decrease from 2.8 to 2.0. However, the separation factors for the potassium-ethanol-liquid ammonia system increase from 1.7 to 2.3 and finally to 3.1, the values being almost reversed from those of the sodium and lithium systems. No explanation is offered for this difference. In any event, the separation factors for the metal-ethanol-liquid ammonia systems are relatively small. The separation factor for the metal-ammonia reactions are, as anticipated (see page 25), several times larger.

Finally, it should be stressed that all of the statements in this last section are restricted to a rationalization of the reaction of alcohol with excess alkali metal, and that many of the statements are speculative. One consequence of the proposed mechanism is that the rate at which ammonium ions will react with electrons, equation (91), must be greater than the rate at which the ammonium ions exchange hydrogen with the solvent. A second consequence of the proposed mechanism is the existence of the three-to-one complex,  $B^{\ominus}$ . There is little independent evidence to support either of these consequences.

## CHAPTER IV

### SUMMARY

The kinetics of the reaction of an alkali metal with an alcohol in tritium-labeled liquid ammonia were investigated. New apparatus and techniques were developed for this purpose. The experimental procedure involved quantitatively collecting the liberated hydrogen in consecutive, discrete increments throughout the course of the reaction. The volume and the specific activity of the hydrogen contained in each increment were then measured. These measurements were corrected for the effect of the reaction occurring between the alkali metal and the solvent. In addition, the initial concentrations of the reactants were known, and the specific activity of the solvent was measured.

It was observed that as the reaction between sodium or potassium with ethanol proceeded to completion, the specific activity of the liberated hydrogen varied continuously. These changes were particularly pronounced at 25 and 50 per cent completion of reaction. It was shown that the isotopic exchange reaction between the proton donor and the solvent was instantaneous relative to the rate at which hydrogen was liberated from the proton donor. Consequently, since the H/T ratio in the solvent remained constant throughout the reaction, the variation in the specific activity of the liberated hydrogen was attributed to a change in the nature of the proton donor.

On the basis of the preceding observations, a model for the reaction of sodium or potassium with ethanol in tritium-labeled liquid

ammonia was proposed. This model assumes that one-fourth of the hydrogen initially present in the ethanol is liberated from  $\text{C}_2\text{H}_5\text{OH}$ . The next one-fourth of the hydrogen is liberated from an ethanol-ethoxide ion complex,  $[(\text{C}_2\text{H}_5\text{OH})_3\cdot\text{OC}_2\text{H}_5]^-$ , while the remaining half of the hydrogen is liberated from a second complex,  $(\text{C}_2\text{H}_5\text{OH}\cdot\text{OC}_2\text{H}_5)^-$ . The overall hydrogen evolution reaction was found to be first order in ethanol, but zero order in alkali metal. It was therefore concluded that the rate at which hydrogen was liberated was determined by the rates of dissociation of the proton donors to produce solvated protons. The solvated protons then react with the solvated electrons of the metal-ammonia solution to produce molecular hydrogen in a non-rate-determining reaction.

The overall rate of the hydrogen evolution reaction, although zero order in alkali metal, varied from one alkali metal to another. This variation was attributed to the differences in the interactions of the alkali metal ions with the proton donors. The reaction of lithium with ethanol was found to be abnormally fast compared to the corresponding sodium and potassium reactions, and to exhibit no change in the specific activity of the liberated hydrogen at 50 per cent completion of reaction. As a result, it was postulated that lithium did not react with a one-to-one ethanol-ethoxide ion complex,  $(\text{C}_2\text{H}_5\text{OH}\cdot\text{OC}_2\text{H}_5)^-$ . The absence of this reaction was attributed to the fact that lithium, with a high charge to radius ratio, might compete with the proton donor for the ethoxide ion and prevent the formation of this complex.

On the basis of the models proposed for the reactions of sodium or potassium and lithium with ethanol in tritium-labeled liquid ammonia,

equations were derived which relate the total volume and the total activity of the liberated hydrogen to the reaction time and the values of the quantities at infinite reaction time. The experimental results were found to agree well with those predicted by the equations.

The reaction of potassium with isopropyl alcohol was also studied briefly and found to have a half-time approximately six times greater than the corresponding ethanol reaction.

The separation factor for the evolution of hydrogen from ethanol was found to vary from 1.5 to 3.1, depending on the alkali metal employed, and on the per cent completion of reaction. The separation factor for the reaction of the alkali metals with the solvent was approximately 12.

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## VITA

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