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**KINETICS OF THE REACTION BETWEEN
LITHIUM AND WATER VAPOR**

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KINETICS OF THE REACTION BETWEEN
LITHIUM AND WATER VAPOR*

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Bruce E. Deal and H. J. Svec

I. ABSTRACT

A critical examination of the reaction between lithium and water vapor has been made at 35.0°, 45.0°, 55.0°, 65.0°, and 75.0°C. Analyses of the products have indicated that LiOH and H₂ are the species formed corresponding to the equation

Three rate variables have been examined for this reaction: time, pressure, and temperature. The reaction data have been found to obey the logarithmic rate law $w = k \log(1 + 0.45t)$, where w = weight of water reacted per unit area of lithium surface, t = time, and k is the rate constant. It has been shown that the reaction rate decreases as a function of pressure at any particular temperature, becoming independent of the water vapor pressure when the pressure is reduced below a certain limit. This limiting pressure was found to be approximately 50 mm. of Hg at 45.0°C. and 60 mm. of Hg at 55.0°C. No investigation was made to determine the minimum limiting pressure below which the reaction rate would again decrease. The Arrhenius equation $\ln k = -E/RT + c$, where k = reaction rate constant, E = activation energy, T = absolute temperature, and R and c are constants, was used to determine the activation energy. Values for the activation energy of the lithium-water vapor reaction were estimated to be 6.2 kcal./mole when the water vapor pressure was about 50 mm. Hg and 5.5 kcal./mole when the water vapor pressure was approximately 100 mm. Hg.

II. INTRODUCTION

During the first 100 years following its discovery in 1817, the alkali element lithium remained a laboratory curiosity and was essentially neglected by the chemical industry. Elemental lithium is very reactive and difficult to prepare in pure form. A freshly exposed

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metal surface tarnishes in moist air at ordinary room temperatures with the formation of a dark metallic-appearing film. This film turns white after the reaction proceeds enough for the film to have considerable thickness. It adheres to the metal surface acting as a protective layer.

This process of film formation is similar to that which occurs when many metals react with oxygen gas or corrode in various liquid medium. Considerable interest is attached to a better understanding of these processes, since they have such vast economic influences on our lives. For this reason a program has been initiated to study the reaction of an active metal, lithium, with water vapor. This program includes a close examination of the rate at which the reaction occurs, the identification of the reaction products, and an attempt to correlate the results of the study with those found for other gas-metal reactions. From the conclusions of such a study should come the guideposts for studies with less active metals.

III. HISTORICAL AND REVIEW OF LITERATURE

A. Lithium

In 1817, August Arfvedson (1), a Swedish scientist, discovered lithium. This came as a result of analyzing the mineral petalite, an aluminum-lithium silicate, now known to have the formula $\text{LiAl}(\text{Si}_2\text{O}_5)_2$, found in the iron mines of Sweden. During his analysis, Arfvedson observed a 4 per cent loss in weight in the mineral which he was unable to account for. A sulfate was prepared which, although similar in some properties to the other alkali sulfates, did not show reactions typical of sodium or potassium. Furthermore, the carbonate was only slightly soluble in water, and this fact lead him to believe he had found a new alkali element. The new element was called "Lithium" (from the Greek word $\lambda\iota\theta\omicron\varsigma$, meaning stone). Since it occurred in minerals, it was thus distinguished from the alkali elements sodium and potassium which at that time were thought to be found only in plants.

Other chemists soon started working on the preparation of pure lithium, and in 1818 Sir Humphry Davy (2, p. 8) prepared a minute amount of lithium metal by electrodecomposing moist lithium oxide. However, it was not until 1854 that any appreciable amount of lithium was produced. Bunsen and Matthiessen (2, p. 8) electrolyzed fused lithium chloride and obtained enough pure metal to enable them to determine some of its physical and chemical properties. It remained until 1893, when Guntz (2, p. 8) suggested the addition of potassium chloride to the fused lithium chloride bath, for a practical method of preparation to become available.

Lithium constitutes about 0.004 per cent of the earth's crust and is found widely distributed. It occurs mainly as silicates, phosphates, fluorides, and chlorides. The United States possesses the richest deposits of known lithium minerals in the world. The most important of these minerals are spodumene $[\text{LiAl}(\text{SiO}_3)_2]$, lepidolite (a lithium-orthosilicate), kryolithionite $[\text{Na}_3\text{Li}_3(\text{AlF}_6)_2]$, amblygonite $[\text{Li}(\text{Al},\text{F})\text{PO}_4]$, and petalite, the lithium-aluminum silicate studied by Arrvedson.

Lithium is extracted from its ores according to several methods. The phosphate ores are decomposed by either aqua regia or hydrochloric acid, and the lithium chloride formed is extracted by suitable methods. Silicate ores were formerly treated by a fusion method involving the addition of various carbonates and sulfates, but at present a process developed by the Metallgesellschaft A. G., Frankfurt-am-Main, Germany, is used. In this process the finely ground ore is mixed with excess K_2SO_4 , and the mixture heated to a temperature just below the lowest melting point of any component or possible product. Usually this minimum temperature is about 720°C ., which is the melting point of KLiSO_4 . One of the final products of this process is Li_2SO_4 , which is extracted from the mixture with water.

Reduction of the oxide with silicon under a vacuum will produce lithium metal. However, a more practical method is the electrolysis of a fused mixture of LiCl and KCl . KCl is added to increase the conductivity of the melt and to lower the melting point of the fused chlorides. Both the molten LiCl and molten lithium metal are extremely reactive, but despite this the metal is now being produced with a purity of 99.5 per cent metal and an efficiency of above 95 per cent, based on the amount of LiCl used.

Lithium is the first of the Group Ia elements in the periodic table. It displays properties similar to the elements in this group. However, some of its properties are more similar to the elements in Group IIa than they are to the alkali metals. At room temperatures, lithium metal can be handled as easily as calcium. It is not necessary to observe the extreme precautions required to manipulate the more active metals such as sodium, potassium, rubidium, and cesium. While these latter elements sometimes react violently in air, lithium reacts slowly. The primary reaction is probably with nitrogen to form Li_3N if enough water vapor is present to catalyze the reaction (2, p. 14). In an atmosphere of helium, argon, or low-molecular weight hydrocarbons, lithium can be melted and poured into molds without great difficulty. Lithium reacts with water to displace hydrogen rapidly, but not so violently as do the other alkali metals. Spontaneous combustion of the hydrogen or the metal does not occur, since lithium does not become molten (melting point 186°C .) as do Na, K, Rb, and Cs. The similarity of the basicity of lithium to the alkaline earths, rather than to the other alkali elements, is emphasized by the fact that the ionization potential, the value of which is 5.37 volts, places it between strontium and barium.

A stable compound, LiH , is formed when lithium and hydrogen react at elevated temperatures. It is ionic in character and very similar in properties to the halogen salts. The halides also are formed by direct union of the elements at high temperatures. The properties of the halides generally resemble the alkaline earth halides. Lithium reacts slowly with nitrogen to form the nitride which gives off NH_3 when allowed to react with water. It is a black compound melting at 845°C . Lithium oxide (Li_2O) is formed by direct union of the elements at high temperatures, and small amounts of Li_2O_2 are also found to be present in the product. The color of most lithium compounds is white.

Lithium hydroxide is less hygroscopic than either NaOH or KOH . A finely powdered mono-hydrate, $\text{LiOH}\cdot\text{H}_2\text{O}$, crystallizes from aqueous solution. Lithium hydroxide is approximately one fifth as soluble by weight in water as NaOH and KOH . It is nearly one hundred times more soluble in water than CaO . LiOH melts at 445°C ., and its vapor pressure is 760 mm. of Hg at 925°C . Lithium metal alloys readily with Ag, Al, Cd, Bi, Hg, Mg, Pb, Sn, Tl, and Zn. A great many intermetallic compounds are formed in the alloys. It is the only alkali element that alloys with silicon.

Osborg (2, p. 17) listed some physical and chemical properties of lithium metal, and these agree with an AEC publication on lithium properties prepared by Jesseman (3). The main properties of the metal are listed in Table 1.

No large quantities of lithium compounds or the metal were used commercially before 1941. Since that time, however, many uses have been found. In the chemical industry many of its compounds now have wide application. One of the more recent applications is the use of organo-lithium compounds in organic syntheses. The alloys formed by lithium are of considerable importance in today's metallurgical industry. Lithium performs the function of degassing, deoxidizing, desulfurizing, and in general, purifying many commonly used non-ferrous alloys. At this time, however, the largest user of lithium is the ceramic industry (4).

Walter M. Fenton of the Metalloy Corporation (5) summarizes the commercial uses of lithium and its compounds.

Ceramic industry	- low-melting porcelain enamels
Lubricating grease	- multipurpose greases
Pharmaceuticals	- production of synthetic vitamin A and other applications of the "Lithium Grignard reaction"
	use of lithium amide in the production of antihistamines

Table 1

Physical and Chemical Properties of Lithium Metal

Atomic number	3
Isotopes	7 and 6 ($\text{Li}^7/\text{Li}^6 \cong 12/1$)
Atomic weight	6.940
Specific gravity at 20°C.	0.534
Crystal structure	body centered cubic
Color	silvery white
Hardness, Mohs' scale	0.6
Melting point	186°C
Boiling point	1336°C $\pm$ 5°
Specific heat at 0°C	0.7951
Average specific heat, 0° - 157°C	1.3215
Heat of fusion	32.81 cal./gm.
Heat of vaporization	35.4 kcal./gm. atom
Coefficient of thermal expansion (cubic) between 18° and 180°C	1.801 x 10 ⁻⁴
Electrical Conductivity	11.7 recip. ohm/cu. cm.
Characteristic spectrum lines	6,708 Å (red) 6,103 Å (orange)

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Metallurgy	- use of lithium copper cartridges for degasification and scavenging of copper and copper alloys
Metallurgy (light metals)	- use of lithium halides in brazing fluxes and welding rods for brazing and welding alumina
Electronics	- use of lithium in the formation of ferrites

B. Rate Laws for Gas-metal Reactions

In studying the reactions occurring between metals and gases, correlation of many variables is necessary to explain the reaction rates observed. These variables involve the characteristics of the metal and particularly the nature of the reaction-product film which is deposited on the metal surface. Many reactions between metals and oxygen have been reported in the literature. As a result of these studies, an extensive theory has developed to explain the observations made. The reaction between lithium metal and water vapor takes place with the formation of a reaction-product film on the metal surface, and thus rate observations should be explainable by the same laws governing reactions involving oxygen and metals.

Gulbransen (6) listed the following variables as being important in any systematic study of the kinetics of the oxidation process for a particular metal or alloy: (1) time, (2) temperature, (3) gas pressure, (4) surface preparation, including chemical treatments, (5) composition of the oxidizing atmosphere, (6) concentration of the inert gas in the lattice of the metal, (7) crystal orientation in the metal surface, (8) surface area, (9) cycling procedures in temperature, (10) rate of gas flow, and (11) vacuum effect. However, he stated that the three most important variables from the point of view of reaction kinetics are time, temperature, and pressure.

Several laws have been proposed to explain the time variation of the oxidation of metals. The most important of these are (1) the linear law, (2) the parabolic law, and (3) the logarithmic or exponential law. In 1922 Tammann and Koster (7) found that the interference color changes on the surface of zinc heated to 400°C in air followed an exponential law. This was stated

$$t = Ae^{by} - A, \quad (1)$$

where y = film thickness as obtained from the interference color observations, t = time, and A and b are constants. The following year Pilling and Bedworth in a now classic work (8) proposed the linear and parabolic rate laws to explain the rate of oxidation of copper, cadmium, zinc, and other metals at high temperatures. Which of these laws were applicable to a particular reaction depended upon the ratio of the molecular volume of the metallic oxide to that of the metal. Thus, for values of Md/mD (where M is the molecular weight of the oxide; D , its density; m , the molecular weight of the metal; and d , its density) less than one, the oxide coat is porous or may not adhere to the metal; and a linear law,

$$y = kt + A, \quad (2)$$

is followed. When this ratio is greater than one, an adherent oxide film is formed, and a parabolic rate law,

$$y^2 = kt + A, \quad (3)$$

is followed. In equations (2) and (3) " k " is a constant, and the other symbols are the same as those in equation (1). Pilling and Bedworth were able to explain these laws on the basis of the fact that the rate-limiting step during the reaction was diffusion of some species in the reaction coat. Recently Wagner and Grunewald (9), Mott (10), and Miley (11) have proposed similar explanations for these two laws.

Bangham and Stafford in 1925 (12) observed that an empirical rate law,

$$\frac{dy}{dt} = kt^{-(1-A)},$$

fitted the data obtained when zinc reacted with oxygen at temperatures below 400°C . The extensive investigation of this reaction by Vernon, Akeroyd, and Stroud (13) was reported in 1939 for the temperature range 25° to 400°C . These workers found that a logarithmic law,

$$w = k \log(at + c), \quad (4)$$

best fitted their data, where w = weight gain due to the oxide film; t = time; and k , a , and c are constants. For c equal to unity, $1/a$ equal to A , w equal to y , and $1/k$ equal to b , this law is the same as that of Tammann and Koster. Thus, the logarithmic law was discovered independently by Tammann and Koster in 1922 and by Vernon, Akeroyd, and Stroud in 1939.

Because Tammann's pioneering work was based on measurements obtained by a simple color method, the results were not considered highly accurate.

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Consequently, the work of Vernon attains considerable importance. The logarithmic law was derived by him on the basis of the following assumptions. If N_0 is the number of oxygen atoms incident on the outer oxide surface of a metal per second, a certain fraction p of these will succeed in penetrating the first layer of metal oxide molecules. If the same fraction penetrates the second layer of oxide molecules, $p^2 N_0$ atoms are incident on the third layer, and so on. If at any time t there are n layers of oxide, then the number of oxygen atoms reacting at the metal surface per second equals $p^n N_0$. If this oxygen combines with the metal to form fresh oxide, the weight-increment per second will be proportional to $p^n N_0$.

Thus,
$$\frac{dw}{dt} = kp^n N_0.$$

Since $n \propto w$,

$$\frac{dw}{dt} = kp^{k_2 w} N_0 = k' p^{k_2 w},$$

$$\frac{dw}{p^{k_2 w}} = k' dt,$$

and integrating $w = k \log(at + c). \quad (5a)$

Since the condition that $w = 0$ when $t = 0$ requires that $c = 1$, it follows that

$$w = k \log(at + 1). \quad (5b)$$

More recently Brodsky and Cubicciotti (14) have found that the oxidation of silicon at high temperatures follows the logarithmic law. These workers, following the method of Tammann and Koster, derived the logarithmic law from Fick's law of diffusion. This law states that

$$\frac{dw}{dt} = D \frac{dc}{dx},$$

where w = amount of diffused substance, c = concentration of the diffusion species at a distance x from the starting point, t = time, and D = the diffusion coefficient. If the diffusion of some species through the growing oxide layer is the rate-determining step for the reaction and if the diffusion paths through the oxide are blocked in some statistical

manner, the concentration of the diffusing species in the coat will decrease exponentially. Stated mathematically,

$$c = c_0 e^{-bx},$$

where c_0 and b are constants. Therefore, the concentration gradient will be

$$\frac{dc}{dx} = -c_0 b e^{-bx}.$$

Since the total thickness of the oxide, x , is related to w by a gravimetric factor ($w = gx$),

$$\frac{dw}{dt} = D \frac{dc}{dx} = -Dc_0 b e^{-wb/g}.$$

Integrating, $W = g/b \log(-Dc_0 b^2 t/g + c')$

or $w = k \log(at + c').$

The condition that when $w = 0$, $t = 0$, requires that $c' = 1$. Hence,

$$w = k \log(1 + at),$$

which is the logarithmic rate law.

At present, the exact mechanisms of the three oxidation laws are still not well established. However, Evans (15) summarized the various theories of these rate laws in 1943, and no major changes have as yet been proposed.

(1) The Linear Law, $y = kt + A$, occurs when the films formed on metals are porous or non-continuous or in those cases where the film falls completely away from the metal as it is formed. Thus, a continually renewed metallic surface is available for reaction.

(2) The Parabolic Law, $y^2 = kt + A$, is followed when non-porous films possessing ionic and electronic conductivity are formed and is governed by ionic migration under a potential gradient.

(3) The Logarithmic Law, $y = k \log(at + c)$, is followed when the above conditions for the parabolic law are absent, and is believed to be due to the migration of interstitial matter through flaw-paths or zones of loose structure in the outer part of the oxide film. Thus, the actual rate of passage along a given path depends upon the rate of crossing a less pervious inner film of constant thickness and is independent of the thickness of the outer film, provided that no obstruction occurs

in the path through the outer film. If such an obstruction occurs, however, passage along the path in question becomes impossible, and the chance of obstruction of a given path will increase with the film thickness. It can be shown that the growth rate will fall off with film thickness in accordance with the logarithmic law.

Pilling and Bedworth (8) first formulated an empirical expression relating temperature and oxidation rate, but it was soon discarded, since no physical significance could be attached to it. Later Dunn (16) applied the Arrhenius equation to the oxidation of metals as a function of temperature. The use of this equation,

$$\frac{d \ln w}{dT} = \frac{-Q}{RT^2} \text{ or } w = Ae^{-Q/RT}, \quad (6)$$

where w = oxidation rate, T = absolute temperature, and A and Q are constants, was justified by Dunn's work with several metals. Arrhenius (17) originally derived this equation starting with the van't Hoff equation. In the latter the variation of the equilibrium constant with temperature was given as

$$\frac{d \ln K_c}{dT} = \frac{\Delta E}{RT^2}. \quad (7)$$

Since K_c is equal to k/k' , it follows that

$$\frac{d \ln k}{dT} - \frac{d \ln k'}{dT} = \frac{\Delta E}{RT^2}, \quad (8)$$

where k and k' are the velocity constants of direct and reverse reactions. Van't Hoff suggested equation (8) could be split up to give

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} + A \quad \text{and} \quad \frac{d \ln k'}{dT} = \frac{E'}{RT^2} + A, \quad (9)$$

where $E - E'$ is equal to ΔE and A is a constant. It was found experimentally that A was equal to zero. Thus,

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \quad \text{or} \quad \ln k = -E/RT + \text{constant}. \quad (10)$$

Equation (10) is identical with equation (6), where E is the energy of activation. E may be determined by plotting $\ln k$ against $1/T$ and solving for E from the slope, which is equal to $-E/R$. It is, therefore, possible to calculate a value for the energy of activation of a gas-metal reaction, providing the Arrhenius equation holds for the data.

The influence of pressure on the oxidation rate has been studied by several workers, but no general laws have been proposed as was the case with time and temperature. Wilkins (19) suggested the idea of limiting pressures, both minimum and maximum, outside of which no definite rate law is followed. He proposed that outside of this range the rate would depend on other factors, such as the rate at which the gas molecules are impinging onto the surface, the accommodation coefficient of the gas molecules on the surface, the rate of diffusion of metal ions, the evaporation of gas molecules from the surface, and the mobility of the absorbed gas molecules on the surface.

IV. EXPERIMENTAL INVESTIGATION

A. Apparatus

It was found that the reaction between lithium metal and water vapor could be followed by measuring the pressure increase due to hydrogen in a closed system. This fact follows from the reaction

which indicates that hydrogen is produced quantitatively. The rate of the above reaction was determined by introducing water into a suitable evacuated vessel containing lithium metal and measuring the pressure change due to evolved hydrogen. The apparatus is shown in Figure 1. The reaction vessel was constructed of 45-mm.-outside-diameter pyrex tubing and was approximately 15 cm. in height. Its volume was about 250 ml. Connected at the bottom of the flask was a water-inlet tube which extended above taper B. At the top of the inlet tube was a serum bottle rubber stopper, covered with a pool of mercury, through which water could be injected into the system by means of a hypodermic syringe. The taper B was a 29/26 ground glass joint, the outer member of which was sealed off to serve as a cap. A glass hook extended down into the reaction vessel from inside the cap. The lithium sample could thus be suspended in the vessel as shown in the diagram. At C was a 10-mm. high-vacuum stopcock. This lead to a vacuum pump through a dry-ice trap.

Below stopcock C a recording mercurial monometer F was connected to the system. This manometer, following the design of Svec and Gibbs (18), was used to measure continuously the total gas pressure in the system. It consisted of a large bulb mercury monometer with a length of resistance wire (No. 30 Chromel A) placed concentrically in the mercury column. The resistance wire was included in a direct current bridge circuit, and the degree of unbalance of the bridge was followed with a recording potentiometer. Operation of the device required that the bridge first be balanced when the pressure in the apparatus was zero. Then, as the mercury column rose due to increasing pressure, the resistance of the concentric wire was shorted, causing the potentiometer pen to drive up scale.

From a suitable calibration curve, chart readings were converted to pressure. A slowly increasing gas pressure could thus be followed over a period of several hours.

During any particular experiment the entire reaction system was placed in a constant temperature water bath, with the water level being just up to the vacuum stopcock C (see Figure 1). Included in the bath were a stirring motor, two 750-watt heating units connected to auto transformers, one 250-watt knife-type intermittent heater controlled by a mercury to tungsten thermo-regulator and relay, a constant level float connected to an overhead water reservoir, and a 0° to 100°C thermometer calibrated in tenths of degrees. The bath could be controlled to 0.01°C over a range of 30° to 80°C.

Experiments were carried out to determine the time required for thermal equilibrium to be obtained between the lithium and the water bath. This was accomplished by placing the bulb of a thermometer in an aluminum cylinder having the same dimensions as the lithium cylinders used and sealing the cylinder and the thermometer into the reaction apparatus. It was found that with a gas present in the apparatus, thermal equilibrium was reached within 5 to 15 minutes, depending upon the initial temperature difference between bath and metal and upon the gas pressure. A relationship was also found for the time of temperature equilibration when the reaction vessel was evacuated. The results of these experiments showed that under any conditions keeping the vessel containing the lithium in the water bath for 30 minutes was sufficient for the metal to attain the bath temperature. Therefore, in all experiments described in this thesis, 30 minutes were allowed for temperature equilibration of the metal samples before water was introduced into the reaction vessel to initiate the metal-water vapor reaction.

B. Procedure

Lithium metal was obtained from the Metalloy Corp., Minneapolis, Minn., in the form of extruded rods one-half inch in diameter and about 6 inches in length. Spectrographic analysis made by the analytical section of the Ames Laboratory indicated that the total impurities were less than 0.1 per cent, occurring as Al, Ba, Ca, Mg, Mn, and Si. Cylinders approximately 2 inches in length and slightly less than one-half inch in diameter were prepared by machining under sodium-dried turbine oil. Machining conditions were carefully controlled and repeated for each cylinder to insure a uniform metal surface for the entire group of samples used in this study. As a results of these precautions, a smooth-appearing, shiny surface was obtained on the cylinders with no apparent tarnishing. The freshly machined cylinders were stored under sodium-dried turbine oil until used. While the samples were

Fig. 1—Apparatus for studying kinetics of the reaction between lithium and water vapor.

normally used in the experiments as soon as possible after the machining operation, it was observed that lithium metal stored under these conditions would maintain its metallic appearance for as long as 24 hours. All handling of the cylinders was by means of rubber-tipped forceps or surgical gloves which had been dipped in dry turbine oil. This precaution was necessary to obviate the formation of active centers on the metal surface.

Immediately preceding the experimental reactions, the dimensions of the cylinders were measured using machinists' calipers. The oil was removed from the lithium using a rinse of sodium-dried Skelly B followed by one in sodium-dried diethyl ether. During this latter rinse operation, a stainless steel hook was fastened to the top of the cylinder, by means of which it could be hung vertically in the reaction vessel as shown in Figure 1. Apiezon W was applied along the lower part of the inner member of taper B, and the vessel was flushed with argon gas. The lithium cylinder was attached to the hook connected to the outside member of taper B, and the latter was placed in position on the vessel as shown in Figure 1.

Evacuation of the apparatus was begun immediately while the taper and wax were warmed to insure a vacuum-tight seal. The evacuation was continued for at least 30 minutes. During this time the apparatus was partially lowered into the water bath to bring the lithium to thermal equilibrium with the bath. After the 30-minute interval, stopcock C was closed and the system lowered the rest of the way into the bath. The position of the system was adjusted until the monometer was perfectly vertical as determined with a spirit level. The chart switch of the recording potentiometer was turned on, and the potentiometer pen was zeroed at a chart reading previously selected when calibrating the monometer. Two ml. of an aqueous solution of lithium chloride were then introduced into the vessel through the serum bottle stopper. As the reaction between water vapor and lithium then proceeded, the pressure of the hydrogen evolved was recorded. Observations were made at 35.0°, 45.0°, 55.0°, 65.0°, and 75.0°C.

Because two of the rate variables, vapor pressure and temperature, are not independent, a method was needed for varying one and holding the second variable constant for a set of reactions. The lowering of the vapor pressure of the water used in the reactions with an electrolyte, lithium chloride, proved to be satisfactory for the purpose. It was possible, by the addition of this salt, to lower the vapor pressure of water to about 40 per cent of that of pure water. One series of aqueous solutions was prepared having varying vapor pressures at any particular temperature. Other solutions were prepared, by means of which it was possible to vary the temperature and maintain a constant vapor pressure. The vapor pressures of these solutions were determined at the various temperatures by introducing 2 ml. of solution into the evacuated system as in a regular run. Table 2 lists the measured vapor pressures which were used in the hydrogen pressure calculations.

Table 2

Vapor Pressures of LiCl Aqueous Solutions

LiCl conc., gms LiCl/100 gms H ₂ O	Temp., °C.	Measured v.p., mm. Hg	Literature v.p.,* mm. Hg
0	35.0	42.2	42.2
0	45.0	72.5	71.9
20	45.0	52.0	-
40	45.0	34.0	-
55	45.0	22.0	-
0	55.0	118.0	118.04
40	55.0	58.0	-
55	55.0	39.0	-
0	65.0	184.0	187.54
55	65.0	58.0	-
0	75.0	285.0	289.1
55	75.0	100.0	-

* Lange, N. A., "Handbook of Chemistry," 7th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 1483-86.

V. EXPERIMENTAL RESULTS

As each reaction between lithium metal and water vapor proceeded, it was observed that a definite trend was followed. The film formed on the surface of the cylinder appeared first to be black or very dark and metallic, changing to white as the reaction proceeded. The pressure due to the liberated hydrogen increased slowly, and it appeared that a protective coat was being formed. In order to know the composition of this coat, samples of lithium with flat surfaces were prepared. They were allowed to react with water vapor in the system as in regular runs. The black and white compounds which formed on the surfaces were then analyzed by means of a recording X-ray diffractometer. The only compounds of lithium present as indicated by the diffraction patterns were LiOH and a small amount of $\text{LiOH} \cdot \text{H}_2\text{O}$. No lines ascribable to oxide or nitride were present. Another check on the products of the lithium-water vapor reaction was an analysis of the gas produced. This was done by allowing the gas in the reaction system after a reaction had been completed to expand into an evacuated sample bulb. The water vapor present in the sample was frozen out with dry ice, and the remainder was analyzed by means of a mass spectrometer. Only hydrogen was found to be present in the gas except for a trace of residual water vapor.

Since the reaction of lithium with water vapor proceeds with the formation of a LiOH surface film, the reaction rate data are expected to fit one of the three gas-solid rate laws stated in equations (2), (3), or (4). A comparison of these three laws is presented in Figure 2 to determine which law best describes the data obtained from a typical experiment. The weight of water vapor in mg. reacted per cm^2 of lithium surface is plotted against the appropriate function of the time. The water-vapor weight values were obtained from hydrogen pressures by determining the total volume of the reaction system, the volume and surface area of the lithium cylinders, and by then utilizing the ratio of hydrogen produced to water vapor reacted as determined from the chemical equation involving the reaction of lithium with water vapor. The hydrogen pressures were obtained by subtracting the vapor pressures of water at the temperature being studied from the total pressure. It was assumed that the surface areas used for these calculations were only minimum areas and could well have had actual values equal to twice those of the calculated areas. This could be due to surface unevenness formed in the machining process and to the nature of the metal. It was assumed, however, that the true surface areas were proportional to the calculated areas by a fairly constant factor. This was substantiated by the reproducibility of the data obtained from the experiments. From Figure 2 a straight line is observed for the logarithmic treatment of the data. The curves, concave upward for the parabolic plot and concave downward for the linear plot, emphasize the conclusion that a logarithmic rate law is followed. Similar plots of data from other experiments corroborate this conclusion.

Fig. 2— Comparison of three rate laws for gas-metal reactions using lithium-water vapor data.

The value of the constant a in the logarithmic equation was set equal to 0.4 by Brodsky and Cubicciotti (14) in silicon-oxygen reaction rate studies, but its magnitude under the conditions of this research was empirically determined by finding that value which best fitted the experimental data. Different values of a , ranging from 0.2 to 0.8, were applied in a series of plots involving the weight of water reacted versus the logarithmic time function. A value of 0.45 provided the best of the straight lines obtained, although the function is relatively insensitive to the value of a .

Graphs were prepared for each reaction with mg. H_2O reacted per $cm.^2$ plotted against $\log(1 + 0.45t)$, where t is time in hours. Values of the logarithmic rate constants k were found as the slopes of the initial part of the curves, where definite straight lines were evident. Table 3 lists the slopes in $mg./cm.^2-hr.$ for each run and lists the average slopes at each temperature and vapor pressure. Typical examples of the plots are shown in Figures 3 and 4. Figure 3 contains plots of the reaction data obtained using pure water in each case in the temperature range 35.0° to $75.0^\circ C$. It should be noted that with increasing temperature the water vapor pressure is also increasing. Figure 4 shows reactions in the temperature range 45.0° to $75.0^\circ C$. using solutions of 55 gms. $LiCl/100$ gms. H_2O as a source of water vapor. While the vapor pressures of these solutions still increase as the temperatures increase, much lower values for the vapor pressure are obtained than for pure water. It should be noted that on extending the data in Figures 3 and 4 over a longer time, definite changes or breaks were observed in the slopes of the curves, appearing at a time corresponding to a certain coat thickness. These sudden breaks seemed to be dependent on the temperature and pressure, but nothing definite can be said about the rate law after these periods.

In order that the vapor pressure effect on the reaction rates might be determined, reactions were run at $45.0^\circ C$ with varied vapor pressures. Figure 5 shows plots of the data obtained in these experiments. It is clearly indicated that there is a certain pressure below which no further decrease in rate of reaction is observed. This pressure appears to be in the vicinity of 50 mm. Hg at $45.0^\circ C$. It can also be observed from Table 3 that a similar limiting vapor pressure at $55.0^\circ C$ occurs in the region of 60 mm. Hg. Figure 6 shows the values of the rate constants plotted against temperatures, the lower curve being for the 55 gms. $LiCl/100$ gms. H_2O solutions and the upper curve being for the reactions when pure water was the source of water vapor. If the limiting pressure assumption is true, it is probable that there is no pressure dependence evident from the lower curve until a temperature of 75.0° is reached. This fact is observed on the graph between $65.0^\circ C$ and $75.0^\circ C$ where a deviation appears on the curve. An extrapolation serves to estimate what the pressure-independent rate constant would be at $75.0^\circ C$. The upper curve shows the same type of deviation after $55.0^\circ C$., and an

Table 3

Lithium-water Vapor Reaction Data

Run	Temp., °C.	Vapor press., mm. Hg	Wt. H ₂ O reacted after 90 min., mg./cm.	Slope k, mg./cm. ² -hr.	Ave. slope k, mg./cm. ² -hr.
I-1	35.00	42.2	2.187	7.78	7.92
I-2	35.00	42.2	2.130	7.78	
I-3	35.00	42.2	2.164	7.39	
I-4	35.00	42.2	2.512	9.15	
I-5	35.00	42.2	2.098	7.50	
II-1	45.00	71.9	3.449	10.40	9.74
II-2	45.00	71.9	3.107	9.92	
II-3	45.00	71.9	2.352	8.89	
II-4	45.00	71.9	2.077	9.75	
III-1	45.00	52.0	1.561	5.00	5.06
III-2	45.00	52.0	1.835	5.55	
III-3	45.00	52.0	1.279	4.63	
IV-1	45.00	34.0	1.055	3.63	5.34
IV-2	45.00	34.0	1.765	6.67	
IV-3	45.00	34.0	1.527	5.74	
V-1	45.00	22.0	1.231	5.29	4.73
V-2	45.00	22.0	1.118	4.17	
VI-1	55.00	118.0	3.331	12.29	12.81
VI-2	55.00	118.0	3.473	12.91	
VI-3	55.00	118.0	3.611	13.23	
VII-1	55.00	58.0	1.744	6.60	6.37
VII-2	55.00	58.0	1.554	6.15	
VIII-1	55.00	39.0	2.053	5.21	6.08
VIII-2	55.00	39.0	2.933	8.33	
VIII-3	55.00	39.0	1.202	4.70	
IX-1	65.00	184.0	3.863	13.90	28.20
IX-2	65.00	184.0	7.524	40.00	
IX-3	65.00	184.0	6.829	30.60	
X-1	65.00	58.0	3.521	9.33	9.03
X-2	65.00	58.0	2.143	9.09	
X-3	65.00	58.0	1.293	7.00	
X-4	65.00	58.0	2.492	10.70	

Table 3 (continued)

Run	Temp., °C.	Vapor press., mm. Hg	Wt. H ₂ O reacted after 90 min., mg./cm. ²	Slope k, mg./cm. ² -hr.	ave. slope k, mg./cm. ² -hr.
XI-1	75.00	285.0	-	59.10	61.20
XI-2	75.00	285.0	-	63.30	
XII-1	75.00	100.0	4.348	16.10	14.10
XII-2	75.00	100.0	1.891	12.10	

extrapolation to 65.0°C was made. It is slightly more difficult to justify this latter extrapolation, since the pressures are well above 50 and 60 mm. Hg. However, the fact that the vapor pressure of water rises exponentially with temperature and that a sudden deviation is observed in the graph seems to justify an extrapolation of at least 10 degrees. It is very probable that this pressure-independent region is also bounded at the lower end at some pressure as has been observed several times in oxygen-metal studies (6, 8, and 19), but none of the lithium-water vapor studies made here were extended to low enough pressures to observe this effect.

It was stated that a form of the Arrhenius expression, equation (10), could be used to determine the activation energy for the reaction. This is accomplished by plotting $\log k$ against $1/T$ and determining the slope, where k is the rate constant and T , the absolute temperature. E , the activation energy, is equal to $-2.303 \times R \times \text{slope}$. In order that all conditions be similar, data from runs at different temperatures, but with vapor pressures in the same range, were used. Figure 7 shows two sets of data for runs which obey the above conditions, one set with vapor pressures of approximately 50 mm. of Hg and the other set in the 100 mm. of Hg range. Table 4 lists the necessary values for plotting $\log k$ against $1/T$. These plots are shown in Figure 8. It is observed that two straight lines are formed, the slopes of which have similar values. From Figure 8 values for the activation energy of the reaction between lithium metal and water vapor are estimated to be 6.2 kcal./mole and 5.5 kcal./mole when the water vapor pressures are 50 mm. Hg and 100 mm. Hg, respectively. Since the difference between these two values cannot be explained solely upon the basis of experimental error, it must be concluded that there is a pressure effect which influences the activation energy of this reaction.

Fig. 3—Logarithmic plot of the lithium-water vapor data in which pure H_2O solutions are used.

Fig. 4—Logarithmic plot of the lithium-water vapor data in which 55 gms. LiCl/100 gm. H₂O solutions are used.

Fig. 5—Logarithmic plot of average lithium-water vapor data at 45.0°C with varying water vapor pressures.

Fig. 6—Effect of temperature on rate constants from lithium-water vapor data.

Fig. 7—Logarithmic plot of lithium-water vapor data used in calculating activation energies.

Fig. 8—Log k versus $1/T$ from lithium-water vapor data.

Table 4
Lithium-water Vapor Reaction Data for
Use in Determining Activation Energy

Run	Vapor pressure, mm. Hg	Temp., °A.	1/T., °A.	Slope k	Log k
III	52.0	318.18	.003143	5.06	.70424
VII	58.0	328.18	.003047	6.37	.80448
X	58.0	338.18	.002957	9.03	.95569
XII'	-	348.18	.002872	11.00*	1.94139
II	71.9	318.18	.003143	9.74	.98856
VI	118.0	328.18	.003047	12.81	1.10755
IX'	-	338.18	.002957	16.00*	1.20412

* Extrapolated values from Figure 6

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