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DIFFUSION STUDIES IN LIQUID METALS

Martin Hsieh and R. A. Swalin

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Institute of Technology
University of Minnesota
Minneapolis, Minnesota 55455

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ABSTRACT

Self-diffusion coefficients were determined for liquid potassium and rubidium in order to test the validity of various theories of self-diffusion in liquid metals. The measurements were self-diffusion in K and Rb at atmosphere pressure, the effect of pressure on self-diffusion coefficients of K and Rb, and self-diffusion in K and Rb at constant volume. The temperature ranges of present investigations at atmosphere pressure were 345°K - 867°K and 337°K - 802°K respectively for K and Rb. The effect of pressure on self-diffusion coefficients in K and Rb was measured at 418°K from 1-3450 bar. Self-diffusion coefficients in K and Rb were determined up to 530°K . In the self-diffusion studies radioactive K^{42} and Rb^{86} isotopes were used as tracers and a recently developed capillary method was employed.

The self-diffusion coefficients in liquid K and Rb at one atmosphere pressure could be represented by the following expressions.

$$D_{\text{K}}(345^{\circ}\text{K}-867^{\circ}\text{K}) = (-2.443 \pm 0.346) \times 10^{-5} + (5.344 \pm 0.088) \times 10^{-10} (T^{\circ}\text{K})^2 \quad \text{cm}^2/\text{sec}$$

$$D_{\text{Rb}}(337^{\circ}\text{K}-802^{\circ}\text{K}) = (-1.479 \pm 0.238) \times 10^{-5} + (3.824 \pm 0.07) \times 10^{-10} (T^{\circ}\text{K})^2 \quad \text{cm}^2/\text{sec}$$

The empirical equation for both K and Rb may be expressed as

$$D/D_m = 1.665 [(T/T_m)^2 - 0.399]$$

in the range from melting point to about 873°K .

The linear dependence of $\ln D$ versus T^2 for both Rb and K, observed in present investigation, leads to support the prediction of the fluctuation theory proposed by Swalin. The experimental data also agree well with the dense-gas-like picture of Ascarelli and Paskin.

The effect of pressure on self-diffusion coefficients in K and Rb were observed to be small. The scatter of data is about $\pm 15\%$. This scatter of data may mask the observation of this small effect. However, the diffusion coefficients were observed to decrease with increasing pressure for both K and Rb by use of least square straight line fit in the plot of $\ln D$ versus P . The dependence of the diffusion coefficients on the pressure at 418°K could be expressed as

For potassium

$$\ln (D_K \times 10^5 \text{ cm}^2/\text{sec}) = (1.86 \pm 0.03) - (4.42 \pm 1.41) \times 10^{-5} P(\text{bar})$$

For rubidium

$$\ln (D_{\text{Rb}} \times 10^5 \text{ cm}^2/\text{sec}) = (1.66 \pm 0.02) - (3.43 \pm 1.02) \times 10^{-5} P(\text{bar})$$

The activation volumes calculated by the slope of $\ln D$ versus P at temperature 418°K were $1.5 \pm 0.5 \text{ cm}^3/\text{mole}$ and $1.2 \pm 0.4 \text{ cm}^3/\text{mole}$ for liquid K and Rb respectively.

The difference of self-diffusion ^{coefficients} between constant volume and constant atmosphere pressure were observed to be small.

1. INTRODUCTION

It has been recognized that one of the important keys to understanding of the liquid state is the diffusion process. The mechanism of self-diffusion in liquids has been of theoretical interest.⁽¹⁻⁸⁾ In order to understand the mechanism for the diffusion process in liquids and to test the concepts and models proposed for diffusion process in liquids, it is desirable to examine the temperature-dependence of the self-diffusion coefficients, since different theoretical approaches predict different temperature dependence of the self-diffusion coefficients in liquids.^(2,9) Accurate experimental data are relatively few in number, additional systematic measurements are needed to allow adequate theories to be tested, especially for experimental measurements over wide temperature range. The purpose of the present work is to investigate the nature of the mechanism of self-diffusion in liquid metals by measuring the temperature dependence of self-diffusion coefficients over a wide temperature range and to compare experimental results with theoretical models. As part of study of self-diffusion in liquid metals, it is of interest to know the effect of pressure on diffusion coefficients in liquid metals. The pressure effect on self-diffusions in principle offers information about the mechanism of diffusion in liquids. Furthermore, as some of the fundamental differences between the various theories involve the role of the free volume in liquid metals, it is desirable to obtain diffusion data under constant volume condition.

Liquid potassium and rubidium were chosen for several reasons as follows.

(a) Ozelton and Swalin⁽¹⁰⁾ measured the self-diffusion coefficient of sodium at constant volume using a long capillary technique and provided a severe test of the fluctuation theory. As a part of continuous studies in our laboratory,

therefore, it is interesting to measure self-diffusion coefficient in other alkaline metals.

(b) Potassium and rubidium have low melting points (336.8°K and 312.0°K respectively). One may therefore measure self-diffusion coefficient starting at low temperature without going to very high temperature. In addition, the effect of pressure on the diffusion coefficients in liquid metals can be measured by use of our present hydraulic system.

(c) Radioactive isotopes of potassium (K^{42}) and rubidium (Rb^{86}) are available and both emit gamma radiation of suitable energy, thus simplifying experimental measurements of concentration.

(d) The alkaline metals are monovalent and have simple electronic structures. This may simplify theoretical analysis.

(e) In alkaline metals, very few attempts have been made to study self-diffusion in liquid K and Rb. The available data are limited to narrow temperature ranges and thus one is unable to test theoretical models.

A new capillary method^(11, 12) was employed. Measurements of self-diffusion coefficients in K and Rb consist of three parts: self-diffusion in K and Rb at atmosphere pressure, the effect of pressure on diffusion coefficients in K and Rb at 418°K , and self-diffusion in K and Rb at constant volume.

2. EXPERIMENTAL

The experimental procedure consisted essentially of preparing samples which is a column of liquid metal with a "thin layer" of radioactive tracer at one end, diffusion annealing, sectioning and analyzing samples for the concentration of radioactive tracer along the length of each sample. Some details of the experimental procedure are described as follows.

2.1 Preparation of Samples

The method used was analogous to the standard "thin layer" slicing method in the solid state. Following Larsson and Lodding's technique⁽¹¹⁾ of preparing samples, a small amount of radioactive tracer (a cylinder one mm long) was introduced to the bottom of a long precision bore capillary. The rest of the capillary was filled with non-radioactive pure metal under vacuum of 10^{-4} mm of Hg or less. This filling process is similar to that used by Ozelton and Swalin.⁽¹⁰⁾

The pure potassium (99.95+%) and rubidium (99.9+%) were supplied by MSA Research Corporation. The radioactive tracers used in present investigation were K^{42} and Rb^{86} in pure elemental form. Both tracers were prepared by encapsulating pure metals in tubes and then irradiated by suitable neutron flux through the Radioactive Materials Corporation.

Both fused quartz and type 316 stainless steel precision capillaries with 1 mm i. d. were used in containing liquid metals. The latter are required for annealing above 523°K, since quartz begins to react appreciably in liquid rubidium and potassium at higher temperature. The length of each precision tube is about 7 to 8 cm for fused quartz capillaries, and about 8 to 10 cm for stainless steel tubes.

After preparing samples, the capsules were transferred to a container which contained silicone oil and were ready to use in diffusion annealing. A more elaborate process was needed for samples with stainless steel precision capsules: a stainless steel sample container was used to contain these capsules during the diffusion annealing process. The stainless steel container was partially filled with the liquid metal to be studied. Three to four stainless steel capsules were

put inside each container. The open ends of the capsules were inserted into the metal in container. The steel container was sealed in purified argon atmosphere.

2.2 Diffusion Annealing

2.2.1 Self-diffusion at one atmosphere pressure and below 523°K

A silicone oil annealing bath was employed during experiments. When the desired temperature of the bath was achieved, the sample was introduced. It was held vertically by a sample holder which has six cylindrical holes drilled vertically and had the bottom ends closed. The sample holder was fixed on a horizontal plate which can be moved up and down by use of two rods. These rods slide in guides and can be fixed at the desired position by tightening two bolts on the two guides. A chromel-alumel thermocouple housed with a protecting alumina tube was put into a hole of the sample holder adjacent to that where the sample located. After the proper diffusion time, the sample was taken out of the diffusion annealing bath and quenched in liquid nitrogen.

For the self-diffusion of liquid rubidium, a single sample was usually put into the diffusion annealing bath each time. In the case of liquid potassium, three samples were introduced into the diffusion annealing bath each time in order to decrease the total diffusion annealing time due to the short half-life of K-42.

2.2.2 Self-diffusion at one atmosphere pressure and temperature above 523°K

For diffusion anneals above 523°K, a furnace with kanthal wire winding was used. Three to four samples were placed in sample container. The temperature of the samples did not reach the desired temperature immediately after introducing the samples and sample container into the furnace but took about ten minutes for the samples to reach the steady state temperature. During diffusion annealing, the temperature close to the center portion of the sample container of the furnace

was monitored with the chromel-alumel thermocouple. At the end of the diffusion annealing, the steel container was pulled out from the furnace and was quenched immediately in liquid nitrogen. After a suitable time, the sample container was put into the vacuum dry box. This sealed container was opened and checked to ensure freedom from leakage. Samples were removed from the container for radiological analysis.

2.2.3 Self-diffusion at high pressure

The high pressure vessel was preheated to the desired steady state temperature before the diffusion annealing was initiated. For self-diffusion in liquid rubidium, a sample was put into the high pressure vessel. The high pressure vessel was quickly connected to the high pressure system and the pressure was applied to the desired value. The pressure range used during the present experiment was from 1 to 3450 bar.

A few experiments were carried out to determine the magnitude of error introduced by the process of applying pressure at the initial stage of diffusion annealing. The sample with an iron tube outside was held inside of the high pressure tube where the temperature was kept below the melting point of the metal investigated. When the temperature and the pressure reached the steady state, this sample was dropped into the high pressure vessel and rested on the sample holder inside the vessel. The diffusion annealing was performed under the steady state condition, thus eliminating the error due to the process of applying pressure. From the experimental results, it seems that the error due to the process of applying pressure was within the experimental error of other sources and thus this error may be neglected.

For the rubidium work, a single sample was put into the high pressure vessel for each experiment. For the potassium work, three to four samples were used for each experiment in order to shorten the total experimental time due to the availability of isotope and short half-life of K-42.

At the end of diffusion anneal, the high pressure furnace was removed from the bottom of the high pressure vessel and the high pressure vessel was quenched by use of liquid nitrogen.

The pressure required to maintain a constant volume over the temperature range was obtained from the P-T curves for liquid potassium and rubidium measured by Lien.⁽¹³⁾ The constant volume maintained is that at the melting point of liquid metal.

2.3 Determination of Diffusion Coefficient

From the "thin film" solution of Fick's second law of diffusion the activity, I, along the capillary varies according to the equation⁽¹⁴⁾

$$I = (\text{constant}/Dt) \exp(-x^2/4Dt) \quad (1)$$

where x is the distance along the cylinder axis from the closed end and t is the annealing time. The diffusion coefficient D was calculated by the slope, S, of the straight line in the plot of $\ln I$ versus x^2 , i. e.

$$S = \frac{d \ln I}{dx^2} = - \frac{1}{4Dt} \quad (2)$$

Each sample was cut into ten to fifteen sections of approximately equal length. The metal in each section was dissolved in 2 ml distilled water in a scintillation vial. The relative tracer concentration of each section was analyzed by use of scintillation well counters. The peak at 1.52 Mev for K⁴² and the peak at 1.08 Mev for Rb⁸⁵ were used for counting. The decay correction was made.

The mass of each section of the sample was accurately determined by chemical titration. The length of each section was calculated by knowledge of the uniform cross-section area and the density of liquid metals at annealing temperature.

For diffusion measurements in K and Rb at one atmosphere pressure and below 523°K, samples were directly put into the silicone oil at the beginning of diffusion annealing and were immediately quenched in liquid nitrogen at completion of diffusion annealing. The correction of the diffusion annealing time during heating and cooling process was small and, therefore, negligible. For diffusion measurements at one atmosphere pressure and above 523°K, a correction of the diffusion annealing time was made due to the heating process. For the diffusion experiments at high pressure, a correction of the diffusion annealing time was done because of the non-zero cooling process.

For a diffusion experiment, the slope of the plot of $\ln I$ versus x^2 is related to the product of diffusion annealing time and diffusion coefficient by equation (2). The correction of diffusion annealing time was made during heating (or cooling) process by finding out an effective diffusion annealing time, t_{eff} , according to equation

$$D(T_0) t_{\text{eff}} = \int_0^{t_0} D(T) dt \quad (3)$$

where T_0 is the steady state temperature of diffusion annealing, t_0 is total diffusion annealing time.

3. RESULTS

The typical penetration profiles obtained from these experiments are presented in Figure 1. The self-diffusion coefficients obtained at one atmosphere are listed in Table 1 for potassium and Table 2 for rubidium. The results obtained

at constant volume are tabulated in Table 3 for potassium and Table 4 for rubidium. The self-diffusion coefficients obtained both at one atmosphere and constant volume are shown in Figure 2 for potassium and Figure 3 for rubidium, plotted conventionally as $\ln D$ versus $1/T$. By examining the temperature-dependence of the self-diffusion coefficients, it appears that the plot of D versus T^2 at one atmosphere pressure yields the best straight line fit for both potassium and rubidium. Figure 4 and Figure 5 show the plot of D versus T^2 for potassium and rubidium respectively. A least square straight line fit⁽¹⁵⁾ for the diffusion coefficients in potassium and rubidium yields the following temperature dependence for the diffusion coefficients in K and Rb.

In K, in the temperature range 345-868°K

$$D \times 10^5 = (-2.44 \pm 0.35) + (5.34 \pm 0.09) \times 10^{-5} T^2 (K^\circ)^2$$

cm²/sec (4)

In Rb, in the temperature range 337-801°K

$$D \times 10^5 = (-1.48 \pm 0.24) + (3.82 \pm 0.07) \times 10^{-5} T^2 (K^\circ)^2$$

cm²/sec (5)

The present result for K is compared with the measurements of Rohlin and Lodding⁽¹⁶⁾ and Larsson, Roxberg, and Lodding,⁽¹⁷⁾ as shown in Figure 6 in an Arrhenius plot. In Figure 7, the result of Rb is shown in an Arrhenius plot and compared with the measurements of Nordén and Lodding⁽¹⁸⁾ and the corrected results of Nordén and Lodding by Larsson et al.⁽¹⁷⁾

Results of the effect of pressure on diffusion coefficients are listed in Tables 5 and 6. Self-diffusion coefficients were measured at average temperature 418.6^{+2}_{-1} °K and 418.2^{+1}_{-3} °K for Rb. Results are plotted as $\ln (D_{avg})$ versus P in Figure 8 for potassium and Figure 9 for rubidium, where D_{avg} is the average

value of D obtained at each pressure. The effect of pressure on diffusion coefficients of K and Rb was analyzed by the least square straight line fit to yield the following expressions:

In K, in the pressure range 1-3450 bar, temperature 418.6°K

$$\ln (D \times 10^5 \text{ cm}^2/\text{sec}) = (1.86 \pm 0.03) - (4.42 \pm 1.41) \times 10^{-5} P(\text{bar}) \quad (6)$$

In Rb, in the pressure range 1-3450 bar, temperature 418.2°K

$$\ln (D \times 10^5 \text{ cm}^2/\text{sec}) = (1.66 \pm 0.02) - (3.43 \pm 1.02) \times 10^{-5} P(\text{bar}) \quad (7)$$

Table 1

Self-diffusion of liquid potassium at one atmosphere pressure

T (°K)	t×10 ⁻³ (sec)	Dx10 ⁵ (cm ² /sec)
346 [±] 0.5	13.62	4.52
		4.49
		4.02
376 [±] 0.5	12.12	5.27
		5.24
418 [±] 0.5	11.04	5.91
		6.36
		6.44
420 [±] 0.5	17.64	5.99
		6.89
472 [±] 0.5	9.00	9.07
		9.57
519 [±] 0.5	13.20	12.19
		13.37
521 [±] 0.5	6.30	10.52
		12.13
598 [±] 1.5	9.00	17.37
		16.86
691 [±] 1	9.00	22.58
778 [±] 1.5	8.46	28.52
		30.21
		32.13
867 [±] 1.5	6.48	36.75
		38.13
		38.51

Table 2

Self-diffusion of liquid rubidium at one atmosphere pressure

T (°K)	$t \times 10^{-3}$ (sec)	$D \times 10^5$ (cm ² /sec)
337 $\pm$ 0.5	22.20	3.19
345 $\pm$ 0.5	31.32	3.57
352 $\pm$ 0.5	26.10	2.93
352 $\pm$ 0.5	26.10	3.25
375 $\pm$ 0.5	18.60	4.10
374 $\pm$ 0.5	19.80	3.59
375 $\pm$ 1	18.90	3.50
379 $\pm$ 0.5	24.00	4.28
397 $\pm$ 0.5	19.50	4.56
404 $\pm$ 0.5	22.02	4.57
412 $\pm$ 0.5	17.40	4.73
417 $\pm$ 1	37.20	5.46
417 $\pm$ 0.5	34.56	4.97
439 $\pm$ 0.5	22.20	6.28
450 $\pm$ 0.5	24.42	6.34
451 $\pm$ 1	21.60	5.57
457 $\pm$ 0.5	17.40	6.02
477 $\pm$ 0.5	20.16	6.79
488 $\pm$ 0.5	21.60	7.78
continued		

Table 2 (continued)

T (°K)	$t \times 10^{-3}$ (sec)	$D \times 10^5$ (cm ² /sec)
497±0.5	11.34	7.27
523±0.5	14.16	8.12
523±0.5	26.20	9.09
605±1.5	9.54	10.83
605±1.5	9.54	11.66
698±1.5	7.92	17.55
698±1.5	7.92	18.50
777±1	4.50	23.49
802±2.5	7.92	25.99
802±2.5	7.92	26.26
802±2.5	7.92	26.54

Table 3

Self-diffusion of liquid potassium at constant volume

Pressure (bar)	T (°K)	$t \times 10^{-3}$ (sec)	$D \times 10^5$ (cm ² /sec)
240 ⁺⁷ ₋₇	370 ^{+0.5} _{-0.5}	14.40	4.35
			4.62
			4.96
585 ⁺⁷ ₋₇	419 ^{+0.5} _{-0.5}	10.86	5.53
			5.80
			6.25
			5.76
860 ⁺⁷ ₋₇	456 ^{+0.5} _{-0.5}	11.10	7.88
			8.08
			8.13
			8.18
1110 ⁺⁷ ₋₇	491 ^{+1.5} ₋₃	11.22	8.47
			8.77
			8.94
1400 ⁺⁷ ₋₇	530 ^{+0.5} _{-0.5}	11.16	9.18
			10.51
			14.39

Table 4

Self-diffusion of liquid rubidium at constant volume

Pressure (bar)	T (°K)	$t \times 10^{-3}$ (sec)	$D \times 10^5$ (cm ² /sec)
790±7	446±0.75	9.84	5.64
940±7	470±0.5	15.96	6.06
1080±7	493±0.5	9.90	5.77
1110±4	499±0.25	11.52	7.37
1140±7	503±0.5	9.24	8.07
1150±7	505±0.5	13.62	7.55
1150±14	506±0.5	12.84	7.50
1220±7	517±0.75	11.70	6.79
1230±10	518±0.1	11.34	7.11

Table 5

Effect of pressure on self-diffusion coefficient of liquid potassium
at constant temperature ($T_{\text{average}} = 418^{\circ}\text{K}$)

Pressure (bar)	T ($^{\circ}\text{K}$)	$t \times 10^{-3}$ (sec)	$D \times 10^5$ (cm^2/sec)
1	$418_{-0.5}^{+0.5}$	11.04	5.91
			6.36
			6.44
1	$420_{-0.5}^{+0.5}$	17.64	5.99
			6.89
690_{-34}^{+7}	419_{-1}^{+1}	17.28	6.54
			7.47
690_{-14}^{+4}	$418_{-0.75}^{+0.75}$	10.56	5.66
			5.78
			6.46
1380_{-20}^{+14}	$418_{-0.5}^{+0.5}$	10.80	6.12
			6.05
2070_{-70}^{+70}	$418_{-0.5}^{+0.5}$	11.58	6.37
2070_{-70}^{+70}	418_{-1}^{+1}	7.02	6.50
			5.37
2760_{-34}^{+34}	$419_{-0.5}^{+0.5}$	15.24	5.26
			6.10
3450_{-34}^{+34}	418_{-1}^{+1}	17.22	5.05
			5.27
3450_{-34}^{+34}	$420_{-0.5}^{+0.5}$	12.24	5.37
			6.18

Table 6

Effect of pressure on self-diffusion coefficient of liquid rubidium
at constant temperature ($T_{\text{average}} = 418^{\circ}\text{K}$)

Pressure (bar)	T ($^{\circ}\text{K}$)	$t \times 10^{-3}$ (sec)	$D \times 10^5$ (cm^2/sec)
1	417 ± 0.5	11.52	4.62
1	418 ± 1	16.14	4.81
1	418 ± 0.5	14.64	5.15
1	417 ± 0.5	11.52	5.48
1	417 ± 0.5	11.52	6.18
635 ± 7	419 ± 0.25	14.82	4.36
635 ± 7	419 ± 0.5	13.26	4.47
635 ± 17	419 ± 0.25	14.40	4.61
635 ± 7	419 ± 0.5	11.40	5.14
635 ± 28	420 ± 0.5	13.86	5.70
635 ± 7	418 ± 0.25	12.48	6.22
1380 ± 7	416 ± 0.25	14.16	4.57
1380 ± 10	419 ± 0.25	14.04	5.05
1380 ± 7	418 ± 0.25	14.40	5.27
1380 ± 7	420 ± 0.5	16.44	5.45
1380 ± 14	419 ± 0.75	13.56	5.75
continued			

Table 6 (continued)

Pressure (bar)	T (°K)	$t \times 10^{-3}$ (sec)	$D \times 10^5$ (cm ² /sec)
2070 ⁺⁷ ₋₇	415 ^{+0.5} _{-0.5}	13.32	4.00
2070 ⁺¹⁴ ₋₁₄	418 ^{+0.5} _{-0.5}	26.22	4.17
2070 ⁺¹⁴ ₋₁₄	418 ^{+0.5} _{-0.5}	16.14	4.95
2070 ⁺⁷ ₋₇	418 ^{+0.5} _{-0.5}	13.02	5.71
2760 ⁺⁷ ₋₇	419 ^{+0.3} _{-0.3}	11.82	3.76
2760 ⁺⁷ ₋₇	418 ^{+0.5} _{-0.5}	16.92	4.20
2760 ⁺⁷ ₋₇	419 ^{+0.15} _{-0.15}	11.22	4.50
2760 ⁺¹⁰ ₋₁₀	419 ^{+0.3} _{-0.3}	12.00	5.55
2760 ⁺⁷ ₋₇	419 ^{+0.25} _{-0.25}	15.30	5.71
3450 ⁺⁷ ₋₇	419 ^{+0.25} _{-0.25}	16.44	4.05
3450 ⁺⁷ ₋₁₄	419 ^{+0.25} _{-0.25}	11.70	4.21
3450 ⁺¹⁰ ₋₁₀	418 ^{+0.25} _{-0.25}	13.62	4.88
3450 ⁺¹⁴ ₋₁₄	418 ^{+0.75} _{-0.75}	11.04	5.37

4. DISCUSSION

4.1 Self-diffusion at Atmosphere Pressure

The experimental results of self-diffusion in liquid K and Rb at one atmosphere pressure are plotted in Figure 6 and Figure 7 respectively. The results of self-diffusion in Rb may be plotted as a straight line fit in the curves of $\ln D$ versus $1/T$, D versus T , and D versus T^2 in the low temperature range (from the melting point of Rb to about 523°K); for the wide temperature range from melting point to 761°K, however, the results from this investigation do not yield a straight line fit in the curve of $\ln D$ versus $1/T$, D versus $T^{1/2}$, D versus T and D versus $T^{3/2}$. It is seen that the linear relation of the plot of D versus T^2 is well followed. The results of self-diffusion in K yield the best straight line fit in the plot of D versus T^2 over the temperature range from 345°K to 867°K. The results for both K and Rb may be expressed as a linear relation between D and T^2 .

Our agreement with the data obtained by Larsson, Roxbergh and Lodding is very good and within experimental error. The agreement with the data measured by Rohlin and Lodding is good at the lowest temperature, but only fair at the highest temperature of their measurement. The investigation of Rohlin and Lodding was probably affected by convection due to the temperature fluctuation effect. (17)

The agreement with the Rb data obtained by Nördén and Lodding is fair. However, the agreement between two slopes within the temperature range investigated by Nördén and Lodding is very good.

Recent theoretical models of self-diffusion in liquids have postulated that diffusive motion is not an activated process. It is questionable to use the

"activated state" formalism to treat diffusion in liquid state. Nevertheless, the Arrhenius formalism was used merely as a convenient way to present experimental data. The parameter Q in the Arrhenius formalism, $D = D_0 \exp(-Q/RT)$ was employed to present the slope of experimental data on a plot of $\ln D$ versus $1/T$ in liquid diffusion.

An increase in "activation energy," Q , with temperature of self-diffusion in liquid metals has been observed in some of the earlier investigations.^(2, 11) No direct proportionality exists between Q and the mean temperature. Larsson and Lodding⁽¹¹⁾ observed the abrupt increase of Q , in their measurement of self-diffusion in liquid Ga, from 1 to 2 Kcal/mole. The abrupt change of Q in Ga was observed at about 343°K. The Arrhenius plot of self-diffusion coefficient in Ga yields an "activation energy" of 1.1 Kcal/mole below 343°K. The activation energy is about 2.1 Kcal/mole at higher temperature.

The present result for rubidium may also be presented in two straight lines on a plot of $\ln D$ versus $1/T$ as shown in Figure 7. The "activation energy" is about 1.95 Kcal/mole for temperature below about 603°K, and 4.11 Kcal/mole at temperature above about 603°K.

For potassium the data did not fit two straight line segments in the plot of $\ln D$ versus $1/T$. No well defined straight line can be obtained due to the scatter of experimental data as shown in Figure 6.

It appears, in the present investigation, that a small deviation from straight line in the plot of $\ln D$ versus $1/T$ may be observed even in the narrow temperature range from 370°K to 557°K in which the investigation was made by Larsson et al. If the present potassium data^{are} fitted by two straight line segments,

the average "activation energy" is 2.04 Kcal/mole for temperature below about 523°K, and 2.93 Kcal/mole for temperature above 523°K.

Nachtrieb⁽²⁾ has plotted the activation energy of eleven liquid metals. He found that a relation exists between Q and T_m , the melting point of the metal ($Q=3.55 RT_m$). Also a linear relation between Q and T_m has been proposed earlier by Saxton and Sherby⁽¹⁹⁾ ($Q=3.0 RT_m$ for liquid metals). From the present results, the "activation energy" near melting point may be expressed as $3.04 RT_m$ for K and $3.14 RT_m$ for Rb. The measurements of Lodding et al result the value $Q/RT_m = 3.10$ for alkaline metals. Thus the measurements of alkaline metals near melting point predict the value $Q/RT_m=3.10$ which is between that of Nachtrieb and that of Saxton and Sherby and agree with the results of Lodding et al.

Available theories of self-diffusion in liquids do not predict D to vary with temperature simply according to Arrhenius-type relation as for diffusion in solid state. The suggested expression can usually be reduced to the form

$$D = AT^n \exp(-B/RT) \quad (8)$$

where A , B and n are constants, B may be zero, and n generally lies between $1/2$ and about 2. When such an expression is plotted as $\ln D$ versus $1/T$, a temperature dependent slope is obtained which has an apparent activation energy $Q=B+nRT$. The possibility that B may be zero and n may be 2 is seen from Figures 6 and 7. If the present empirical relations, equation (4) for K and equation (5) for Rb, are extrapolated to the melting point, one may obtain, for the diffusion coefficients at melting points, $D=3.62 \times 10^{-5} \text{ cm}^2/\text{sec}$ for K and $D=2.244 \times 10^{-5} \text{ cm}^2/\text{sec}$ for Rb. If the units, D_m and T_m , are used in the expressions between D and T , one may express equations (4) and (5) alternatively as

$$\underline{K}, \quad \frac{D}{D_m} = 1.675 \left[\left(\frac{T}{T_m} \right)^2 - 0.403 \right] \quad (9)$$

$$\underline{Rb}, \quad \frac{D}{D_m} = 1.659 \left[\left(\frac{T}{T_m} \right)^2 - 0.397 \right] \quad (10)$$

It is seen that these two equations differ only little from each other. The difference in slopes of these two equations in fact is about 1%. Thus the data of K and Rb may be expressed together in the plot of D/D_m versus T/T_m .

The combined results may be expressed as

$$D/D_m = 1.665 \left[(T/T_m)^2 - 0.399 \right] \quad (11)$$

from T_m to about 873°K.

Several theories of self-diffusion in liquids have been developed during recent years and have contributed to our understanding of the liquid structure. It has been postulated that diffusive motion in liquids is not activated as in the case for the solid state and further that a high degree of cooperative motion exists between neighboring atoms. It has been suggested by several investigators^(2, 5, 7, 20) that mean displacements are probably considerably smaller than interatomic distances, and that the jump frequencies may approach those of thermal oscillation.

Swalin^(4, 6) has proposed a fluctuation model for the self-diffusion in liquid metals based on the concept that atom may make diffusive movements into voids through local density fluctuations over a continuous distribution of distances. By use of a Morse potential function, the following temperature dependence is predicted:

$$D = 1.29 \times 10^{-8} (T^2 / \Delta H v_A^2) \quad \text{cm}^2/\text{sec} \quad (12)$$

where ΔH_v is the molar heat of vaporization in Kcal mole⁻¹, and α is a measure of the curvature of the potential energy versus distance curve of the liquid.

The linear dependence of $\ln D$ versus T^2 for both Rb and K, observed in present investigation, leads to support the prediction of the fluctuation theory proposed by Swalin.

Ascarelli and Paskin presented a theory for the self-diffusion of liquid metals based on a dense-gas hard sphere approximation. By use of the Percus-Yevick hard-sphere equation of state and assumption that all simple metallic and non-metallic liquids have the same packing fraction, they obtained the hard-sphere dense-fluid formula.

$$D = 0.28 \, r_m (kT/m)^{1/2} (y_m/y) (10T_m \rho / T \rho_m)^{-1} \quad (13)$$

where r_m is the atomic radius at melting point, y the packing fraction, y_m the packing fraction at melting point, ρ the density, ρ_m the density at melting point, k is Boltzmann's constant, m is the atomic mass, T is the temperature, and T_m is the temperature at the melting point. The temperature dependence of formula (13) is in good agreement with experiments for liquid mercury, indium, tin⁽⁸⁾ and gallium.⁽¹¹⁾ The present results of K and Rb are shown in Figure 10 and Figure 11, plotted as D versus T^2 for potassium and rubidium respectively, and compared as with the theory calculated by use of equation (13).

For self-diffusion of liquid potassium, the value predicted by the Ascarelli and Paskin for the dense-gas formulation in the liquid metals, equation (13), is in agreement with the present experimental value over the temperature range from melting point to about 873°K. The deviation of theory from the least square straight line fit with experimental data for K, plotted as

D versus T^2 , as shown in Figure 10, is about 9% higher at about 873°K and about 12% lower at temperature about 603°K. For self-diffusion of liquid rubidium, the value predicted by equation (13) agrees with the experimental value within the experimental error from melting point to about 723°K. The deviation of the theory from the least square straight line fit of the plot of D versus T^2 for Rb, as shown in Figure 11, is about 15% higher at about 813°K. In general, the calculated values of the self-diffusion coefficients of potassium and rubidium are in very good agreement with the experimental values. In view of the model used by Ascarelli and Paskin, it seems that the dense-gas-like behavior of ions in a liquid metal yields the self-diffusion coefficient which agrees with experimental value very well. This dense-gas-like picture implies that the attractive potential between ions is indeed small. The van der Waals slowly varying attractive potential is suitable to liquid metals and this attractive potential is suitable to liquid K and Rb and this attractive potential can be approximated very well by a uniform negative potential.

4.2 Effect of Pressure on the Self-diffusion Coefficient

The results of the effect of pressure on the self-diffusion coefficient are shown in Figures 8 and 9 for potassium and rubidium respectively. The scatter of the data is about $\pm 10\%$ for K and $\pm 15\%$ for Rb. This scatter of the data may mask the observation of the small effect of pressure on self-diffusion coefficients. However, some small effect was observed both in potassium and rubidium by use of least square straight line fit in the plot of $\ln D$ versus P . The self-diffusion coefficients decrease with increasing pressure.

In the diffusion of liquids, the diffusion coefficient may be expressed according to the activated state formalism as

$$\begin{aligned} D &= D_0 \exp(-\Delta H/RT) = \gamma_0 a^2 \gamma \exp(\Delta S/R) \exp(-\Delta H/RT) \\ &= \gamma_0 a^2 \gamma \exp(-\Delta F/RT) \end{aligned} \quad (14)$$

where γ_0 is a dimensionless statistical quantity such as $\gamma_0 a^2$ is equal to $\overline{j^2}$, the mean square jump distance in a given direction. ΔF is the molar activation free energy for the transport process. The "activation volume" ΔV^* is defined as the isothermal pressure variation of the activation free energy for the transport process.

$$\begin{aligned} \Delta V^* &= (\partial \Delta F / \partial P)_T = -RT \left[\partial \ln (D / \gamma_0 a^2) / \partial P \right]_T \\ &= -RT (\partial \ln D / \partial P)_T + 2RT (\partial \ln a / \partial P)_T \\ &\quad + RT (\partial \ln \gamma / \partial P)_T \end{aligned} \quad (15)$$

From equation (15), one may obtain

$$\Delta V^* = -RT \left[(\partial \ln D / \partial P)_T + (2\beta/3) - \gamma_G \beta \right] \quad (16)$$

where β is volume compressibility, γ_G is Gruneisen constant. The second and third terms on the right hand of equation (16) arise from the change in mean jump distance and mean frequency with pressure respectively, their net contribution to the "activation volume" is small and may be neglected.

The calculation of the "activation volume" in K and Rb is based on the assumption that the plot of $\ln D$ versus P at constant temperature yields a straight line which has been observed for Hg and Ga. ^(21, 22) The calculation of the "activation volume" of liquid Na is based on the data at constant pressure and constant volume ⁽¹⁰⁾ and the calibration curve of pressure and temperature relation at constant volume for Na measured by Lien. ⁽¹³⁾

The results of "activation volume" can be expressed as

$$\begin{aligned}\Delta V_{\text{Na}}^* &= 4.3 \text{ cm}^3/\text{mole} \\ \Delta V_{\text{K}}^* &= 1.5 \pm 0.5 \text{ cm}^3/\text{mole} \\ \Delta V_{\text{Rb}}^* &= 1.2 \pm 0.4 \text{ cm}^3/\text{mole}\end{aligned}\tag{17}$$

Earlier measurements of effect of pressure on self-diffusion by Nachtrieb and Petit yielded the "activation volume" $0.55 \text{ cm}^3/\text{mole}$ for liquid Ga and $0.59 \text{ cm}^3/\text{mole}$ for Hg.

The relative activation volumes (the activation volume divided by the molar volume) for self-diffusion in Na, K, Rb, Ga, Hg are shown in Table 7.

An interesting feature of the present results is the small magnitude of the activation volumes for liquid K and Rb in comparison with the same metals in the solid state. In the solid alkaline metals the ratio V^*/V_m is about 0.5. By contrast, V^*/V_m is about 0.02 for Rb, 0.03 for K, 0.04 for Hg and 0.05 for Ga. The relative activation volume for liquid Na, 0.17, appears to be unusually high in comparison with other liquid metals. Similarly, this small relative activation volume has been observed for liquid halides as well as nitrates.⁽²³⁾ It seems to imply a very significant difference in the mechanism of diffusion between solid and liquid metals. The average diffusive displacements in liquid appear to be considerably smaller than the interatomic distances, and the jump frequency may approach those of thermal oscillations. This may be explained by "activation volume" measurement according to fluctuation theory.

Table 7

The relative "activation volumes" for self-diffusion^(#)

Metal	$(V^*/V_m)_s$	$(V^*)_l \text{ cm}^3/\text{mole}$	$(V_m)_l \text{ cm}^3/\text{mole}$	$(V^*/V_m)_l$
Na	0.52 ⁽⁵⁶⁾ 0.40 ⁽⁵⁵⁾	4.3	24.9 ⁽⁵⁶⁾	0.17
K	0.57 ⁽⁵⁶⁾	1.5	48.7 ⁽⁵⁶⁾	0.03
Rb	—	1.2	59.9 ⁽⁵⁶⁾	0.02
Ga	—	0.55 ⁽⁸⁾	11.46 ⁽⁵⁷⁾	0.048
Hg	—	0.59 ⁽⁷⁾	14.85 ⁽⁵⁷⁾	0.040

(#) The subscripts s and l represent solid and liquid respectively.

V_m is molar volume.

According to Swalin's theory, there is no activation energy for the diffusion process of liquid state; the activation volume for diffusion in liquids needs redefinition. Theoretically the activation volume is given by equation (15). Since in Swalin's theory, $\Delta F=0$, the effect of pressure on the diffusion coefficient D must have a different meaning. ΔV^* has been defined as the effect of pressure on the size distribution of the fluctuation.⁽⁵⁾ It is different from the definition associated with an activated process in which ΔV^* represents the excess volume associated with an atom in an activated state. The root mean square jump distance is predicted according to this model to be much smaller than the interatomic distance for many metals and as a result very large jump frequencies are needed in order to yield a significant diffusion constant. It is believed that the evidence of the measurement of the pressure dependence of diffusion made by Nachtrieb and Petit^(21, 22) tends to support the general features of this theory. Nachtrieb and Petit found that the activation volume for the self-diffusion in liquid mercury is $0.98 \text{ \AA}^3$. This value is considerably smaller than the atomic volume of mercury. If a local volume fluctuation occurs a neighboring atom may diffuse into a space approximated by a segment of prolate spheroid. The average volume of this segment is

$$V = (1/6) \pi d^2 (\overline{j^2})^{1/2} \quad (18)$$

where d is the diameter of a segment atom and $(\overline{j^2})^{1/2}$ is the root mean square jump distance. Assuming that the activated state theory can be applied at all, the value of V may correspond approximately with the activation volume of self-diffusion. The measurement of pressure dependence of diffusion in liquid mercury yields an experimental root mean square jump distance $(\overline{j^2})^{1/2}$ of $0.18 \text{ \AA}$

from equation (18). The calculated root mean square distance by Swalin is $0.13 \text{ \AA}$ which is in good agreement with the experiment.

Table 8 shows the root mean square jump distance $(\bar{j}^2)^{1/2}$ of Na, K, Rb, Ga, Hg calculated from the measurement of pressure dependence of self-diffusion coefficient, the "activation volume" of liquid metals according to fluctuation theory. It appears that the mean displacements for self-diffusion in liquid metals are about $0.1 \text{ \AA}$ to $0.5 \text{ \AA}$. Therefore, our model predicts that liquid diffusion may occur by very small jump distance and that the jump frequencies may approach those of thermal oscillations.

4.3 Self-diffusion at Constant Volume

The experimental results for self-diffusion in K and Rb at constant volume are plotted in Figures 2 and 3. The results are compared with the data at constant atmosphere pressure and only slight differences were observed. The self-diffusion coefficient in K at constant volume is slightly lower than that at constant atmosphere pressure. Similar result was observed for Rb. The result that the difference between constant volume and constant atmosphere pressure data is small agrees with the result of isothermal pressure measurement in which that pressure effect is observed to be small. This small difference between self-diffusion at constant volume and at constant atmosphere pressure enables us, as an approximation, to test various theories which involve the role of the "free volume" by the data at constant atmosphere pressure.

This observation may be explained as follows. According to the hole theory of liquids, the total enthalpy of activation for diffusion, ΔH_{total} , consists two terms^(24, 26), the energy required to form a hole in the liquid, ΔH_h ,

Table 8

The root mean square jump distance $(\bar{j}^2)^{1/2}$
calculated from the "activation volume" of liquid metals

Metal	Atomic diameter (Å)	ΔV^* (activation volume (cm ³ /mole))	$(\bar{j}^2)^{1/2}$ (Å)
Na	3.8	4.3	0.58
K	4.62	1.5	0.23
Rb	4.88	1.2	0.16
Ga	2.70	0.55	0.24
Hg	3.2	0.59	0.18

and the energy of activation needed for the particle to jump into an adjacent hole, ΔH_j . At constant volume, the total number of holes in one mole of liquid remains constant so that $\Delta H_j = -R \left(\frac{\partial \ln D}{\partial (1/T)} \right)_V$. Hence, the energy of hole formation is

$$\begin{aligned} \Delta H_h &= \Delta H_{\text{total}} - \Delta H_j \\ &= -R \left[\left(\frac{\partial \ln D}{\partial (1/T)} \right)_P - \left(\frac{\partial \ln D}{\partial (1/T)} \right)_V \right] \end{aligned} \quad (19)$$

If the hole theory is correct, the predominant term in ΔH_{total} is the energy to form a hole, i.e., ΔH_h and that ΔH_j contribute very little to the total activation energy. Present results do not support this argument.

The fluctuation theory considers that the mean jump distance is smaller than the interatomic distance and hence it removes the emphasis from the role played by holes. Therefore, ΔH_{total} is approximately equal to ΔH_j , and ΔH_h is small. This is seen from the small difference in slope of the plot of $\ln D$ versus T at constant atmosphere pressure and constant volume.

The results of self-diffusion at one atmosphere pressure and at constant volume are compared with the predictions of the theory of dense-gas formulation proposed by Ascarelli and Paskin as shown in Figure 12 and 13. The agreement between the observed values and the calculated results for self-diffusion at one atmosphere pressure and constant volume is very good.

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FIGURES

- 1 Penetration profile for self-diffusion of liquid rubidium at temperature 418°K and one atmosphere pressure
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- 3 Self-diffusion of liquid rubidium at one atmosphere pressure and at constant volume
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Figure 1
Penetration profiles for self-diffusion of liquid rubidium
at temperature 418°K and one atmosphere pressure

Figure 2

Self-diffusion of liquid potassium at one atmosphere pressure and at constant volume

Figure 3

Self-diffusion of liquid rubidium at one atmosphere pressure
and at constant volume

Figure 4

Self-diffusion of liquid potassium at one atmosphere pressure,
plotted as D versus T^2

Figure 5

Self-diffusion of liquid rubidium at one atmosphere pressure,
plotted as D versus T^2

Figure 6

Self-diffusion of liquid potassium at one atmosphere pressure, plotted as $\ln D$ versus $1/T$ and compared with the measurements of Rhodin and Lodding and Larsson, Roxberg and Lodding

—— Rhodin and Lodding
 ——— Larsson, Roxbergh and Lodding

..... present result
 Present result

Figure 7

Self-diffusion of liquid rubidium at one atmosphere pressure, plotted as $\ln D$ versus $1/T$ and compared with the measurements of Norden and Lodding, and the results of Norden and Lodding corrected by Larsson et al

----- Norden and Lodding
 ----- Norden and Lodding corrected by Larsson et al

----- present result
 ----- present result

Figure 8
Effect of pressure on self-diffusion coefficient of liquid potassium
at constant temperature 418°K, plotted as $\ln(D_{\text{average}})$ versus P

Figure 9

Effect of pressure on self-diffusion coefficient of liquid rubidium at constant temperature 418°K, plotted as $\ln(D_{\text{average}})$ versus P

Figure 11
Self-diffusion of liquid rubidium, plotted as D versus T^2
and compared with the theory of dense-gas formulation by Ascarelli and Paskin

Figure 12

Self-diffusion of liquid potassium at one atmosphere pressure and constant volume, plotted as $\ln D$ versus $1/T$ and compared with the theory of dense-gas formulation by Ascarelli and Paskin

- experimental data (one atmosphere pressure)
- - - experimental data (constant volume)
- Ascarelli and Paskin (one atmosphere pressure)
- - - Ascarelli and Paskin (constant volume)

Figure 13

Self-diffusion of liquid rubidium at one atmosphere pressure and constant volume, plotted as $\ln D$ versus $1/T$ and compared with the theory of dense-gas formulation by Ascarelli and Paskin

- experimental data (one atmosphere pressure)
- experimental data (constant volume)
- - - Ascarelli and Paskin (one atmosphere pressure)
- - - Ascarelli and Paskin (constant volume)