Diffusion and Desorption of Metal Impurities in Platinum*

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Activation energies for the volume diffusion of certain impurities in polycrystalline platinum samples have been obtained by studying the ions released from their surfaces at temperatures above 1000°C. For one Pt sample these energies were 4.7±0.2 ev for the diffusion of Na, 4.4±0.2 ev for K, and 3.7±0.2 ev for Ca. For a second sample, however, all the energies were 10–15% higher. After periods of inert gas ion bombardment at room temperature, bursts of K^+ and Na^+ ions were released at temperatures of about 600°C and 700°C, respectively. Activation energies associated with this release were 1.9±0.1 ev for K^+ and 2.6±0.1 ev for Na^+. In this case there was close agreement between the two different samples.

INTRODUCTION

POSITIVE ions are emitted from metal surfaces (a) at elevated temperatures (thermionic emission),[1-5] (b) at intermediate temperatures following a period of ion bombardment (activated thermionic emission),[6-8] and (c) at any temperature during ion bombardment (secondary ion emission).[5,9,10] Mass spectrometric studies have shown that the thermionic positive ions are mainly of alkali metal impurities and—if the temperature is sufficiently high—of the base metal itself. Similar studies have shown that secondary ions include, in addition to the above, various species and fragments of surface compounds and "reflected" ions of the bombarding beam. There has been some question as to the nature and origin[6] of the activated ions, but in the experiments to be described it is clear that they were certain bulk impurities that became uncovered during the bombardment and were then free to desorb (as ions) during the subsequent heat treatment.

A study of positive ion emission from metals provides information on various thermally activated processes occurring within the metals and on their surfaces. The present paper describes a study of the thermionic and activated thermionic emission of certain alkali metal and calcium impurity ions from a Pt surface. Activation energies for diffusion and desorption of these impurities were obtained from the study.

EXPERIMENTAL

The experimental arrangement has already been described in detail in a previous paper.[10] For reference purposes we include here only a diagram of the ion source region of the sector field mass spectrometer (Fig. 1). The metal being investigated—in this case platinum—is located on the axis of the instrument so that ions released from its surface may be accelerated and mass analyzed. Thermionic positive ion emission is studied by heating the metal to any desired temperature by an electric conduction current—the temperature being measured by an optical pyrometer. Secondary ion emission is studied by bombarding the platinum surface with inert gas ions of any energy up to 1000 ev. Activated thermionic emission is studied by first bombarding the surface at room temperature and then heating it to any desired temperature.

RESULTS AND DISCUSSION

A. Thermionic Emission and Volume Diffusion

Volume diffusion in a solid is a thermally activated process[11] and follows a rate law of the form:

$$R = R_0 e^{-Q_{VD}/kT},$$
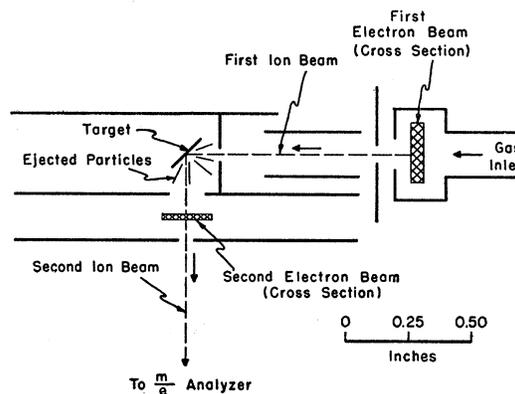
FIG. 1. Diagram showing the electrode geometry in the ion source region of the mass spectrometer. The "target" is a platinum foil which may be heated by an electric conduction current and/or bombarded by an inert gas ion beam. Ions released from the target are accelerated and mass analyzed in a magnetic field (not shown).

[1] O. W. Richardson, *The Emission of Electricity from Hot Bodies* (Longman's, Green and Company, New York, 1921).
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[8] A. Riddoch and J. H. Leck, Proc. Phys. Soc. (London) **72**, 467 (1958).
[9] R. E. Honig, J. Appl. Phys. **29**, 549 (1958).
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[11] R. M. Barrer, *Diffusion in and through Solids* (University Press, Cambridge, 1951), p. 207.

where R is the rate, R_0 depends on the gradient of the concentration of the diffusing material but is essentially constant for a constant gradient, Q_{VD} is the activation energy for volume diffusion—that is, the height of the potential energy barrier which a particle must surmount in order to move to another site, k is Boltzmann's constant, and T is the absolute temperature.

When a refractory metal such as platinum is heated to a high temperature the alkali metal impurities diffuse to the surface and immediately desorb as positive ions. This is the thermionic emission previously referred to. The emission is initially very high (microamperes) because the more or less uniform distribution of impurities in a fresh sample results in a steep concentration gradient right at the surface. After the sample has aged for several hours at a high temperature the emission has dropped several orders of magnitude and is no longer rapidly changing with time, indicating that the gradient at the surface is also changing only slowly with time as the impurities become depleted.

To study emission rates as a function of temperature it is necessary to use a well aged sample and to operate at temperatures low enough so that the concentration gradient (and hence R_0) remains essentially constant during the time required to make a series of measurements. The reproducibility of the data serves to indicate whether or not these conditions are adequately being fulfilled.

The experimental procedure here consisted simply of measuring the peak height of each impurity as a function of the temperature of the well aged platinum sample. Figure 2 shows the experimental data for a typical run, and Fig. 3 is the same data replotted on a semilog scale. The straight lines indicate that the rate law was of the expected form. Activation energies for volume diffusion of the various species are obtained from the slopes of these lines and are listed in Table I.

It is curious that the values obtained for the two different platinum samples differ from each other by such a large amount (10–15%). Possibly this is due to the fact that neither sample was a single crystal, and therefore, the relative importance of bulk and grain boundary diffusion may have been different for the two cases. Diffusion along grain boundaries is believed to

FIG. 2. Peak height vs temperature for the various impurity ions.

require a lower activation energy than diffusion through the grains.[12]

Published activation energies for volume diffusion in solids are usually less than 3 ev[13]; thus for Cu in Pt, Ni in Pt, and vacancies in Pt, the values are 2.4, 1.9, and 1.1 ev, respectively.[14,15] These are considerably lower than the values in Table I. However, energies of 4 or 5 ev have occasionally been reported,[16] especially for the more refractory metals. Furthermore, we observed activation energies of approximately 2 ev on applying this technique to a copper sample. The method is therefore probably quite reliable.
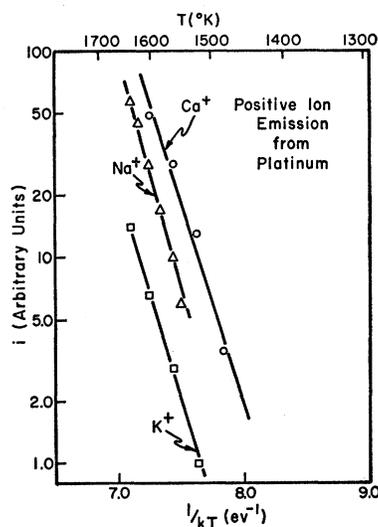
FIG. 3. The data of Fig. 2 plotted on a semilog scale. Q_{VD}, the activation energy for volume diffusion, is equal to the slope of the line for each species.

TABLE I. Activation energies in electron volts for volume diffusion of certain impurities in platinum. Probable errors in the values are estimated to be about ±0.2 ev.

Impurity	First sample	Second sample	Ionic radius[a] (angstroms)
Na	4.7	5.3	0.95
K	4.4	4.9	1.33
Ca	3.7	4.5	1.00

[a] See reference 17.

[12] C. J. S. Smithells, *Metals Reference Book* (Interscience Publishers, Inc., New York, 1949), p. 392.

[13] W. Seith, *Diffusion in Metallen* (Springer-Verlag, Berlin, 1955), p. 43.

[14] O. Kubaschewski and H. Ebert, Z. Elektrochem. **50**, 138 (1944).

[15] F. J. Bradshaw and S. Pearson, Phil. Mag. **1**, 812 (1956).

[16] I. Langmuir, Phys. Rev. **20**, 113 (1922); S. Dushman *et al.*, Phys. Rev. **29**, 903 (1927); I. A. M. van Liempt, Rec. trav. chim. **64**, 239 (1945).

Desorption
K$^+$ from Pt

T = 870° K
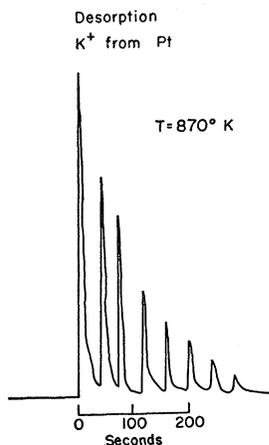
FIG. 4. A recorder trace of a set of sweeps across the K^+ peak following a period of inert gas ion bombardment.

0   100   200
Seconds

T(°K)

FIG. 6. A plot of logτ vs $1/kT$. Q_d, the activation energy for desorption, is equal to the slope of the straight line.

The activation energies for the three impurities are not in the same order as their atomic or ionic sizes.[17] Na and Ca are very nearly the same size, yet the activation energy for the diffusion of Na is 20–30% higher than that for Ca. The activation energy for K, the largest atom (or ion) of the three, lies between the other two.

B. Activated Thermionic Emission and Desorption

Desorption is also a thermally activated process. It can generally be studied separately from diffusion because the activation energies (and hence the temperature ranges in which measurements are made) are usually quite different for the two processes. For example, in the present instance Na and K desorbed readily from Pt at temperatures several hundred degrees below that for which diffusion was appreciable. For Ca, however, the temperature ranges overlapped.

In order to study the desorption of the impurity atoms, it was first necessary to get them onto the surface. Ordinarily this is accomplished by evaporation
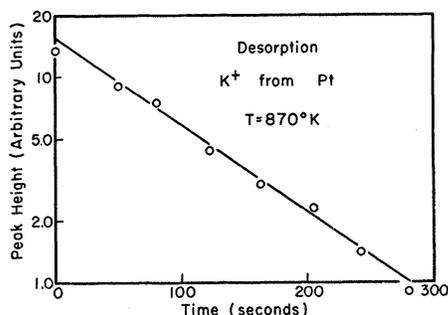
FIG. 5. The peak heights of Fig. 4 plotted on a semilog scale. The time constant τ is equal to the reciprocal of the slope of the straight line.

[17] Handbook of Chemistry and Physics, edited by C. D. Hodgman (Chemical Rubber Publishing Company, Cleveland, 1948), thirtieth edition, p. 2628.

from some external source.[18] In the present experiment the bulk material itself served as the source, and the impurities were brought to the surface not by heating, for this required a temperature well above the desorption temperature, but by ion bombardment. The mechanism involved here was undoubtedly one of erosion. That is, the sputtering away of surface layers by the ion bombardment caused subsurface impurity atoms to become exposed. These were then free to desorb as positive ions upon heating. Judging from the desorption currents, the number which were exposed by the bombardment was more or less proportional to the length of time the beam was on for periods up to five minutes. This suggests that within these periods the surface concentration of impurities was considerably less than a monolayer, which is of significance here because activation energies for desorption are independent of coverage only if the coverage is very low.

The experimental procedure for all desorption runs consisted of (1) flashing the Pt to 1350°C for 30 seconds to clean its surface, (2) bombarding it at room temperature for two minutes with a 10 μa/cm^2—1000 ev inert gas ion beam to expose the impurities, and (3) heating it (without bombardment) to some predetermined temperature T while simultaneously measuring the peak heights of the impurities as a function of time.

TABLE II. Activation energies in electron volts for desorption of certain impurities from platinum. Probable errors in the values are estimated to be about ±0.10 ev.

Impurity	First sample	Second sample
Na	2.60	2.61
K	1.85	1.92

[18] See, for example, F. L. Hughes et al., Phys. Rev. 113, 1023 (1959).

Figure 4 shows a typical desorption run. At time $t=0$ the Pt sample, which had previously been flashed and bombarded as specified above, was suddenly heated from room temperature to 870°K. It can be seen that the K^+ peak decayed exponentially with time in accordance with the relation

$$i = i_0 e^{-t/\tau}.$$

The characteristic time constant τ is obtained from the slope of the straight line in Fig. 5, the same data replotted on a semilog scale.

The activation energy for desorption Q_d is related to

τ by the expression

$$\tau = \tau_0 e^{Q_d/kT}.$$

Thus, by measuring τ for several different temperatures and plotting $\log\tau$ vs $1/kT$, one obtains Q_d directly from the slope of the resulting straight line. Figure 6 is such a plot and the desorption energies for K and Na are recorded in Table II. Reliable values for Ca were not obtained.

It is interesting to note that although the volume diffusion energies were appreciably different for the two samples, the desorption energies were very nearly the same.

Ionic Conductivity of Gamma Irradiated Sodium Chloride*

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Single crystals of NaCl were subjected to about 5×10^5 roentgens of Co^{60} gamma irradiation at 5°C, and then rapidly heated and maintained at a fixed temperature in the range 65°C to 135°C. The dc ionic conductivity at this temperature was measured by means of a vibrating reed electrometer as a function of time. It decreased in the temperature range 65°C to 80°C during a period of several hours to a value that was less than the preirradiation conductivity by a factor which was typically about 30. The conductivity is presumed to be a direct measure of the number of positive ion vacancies. The data fit a rate equation describing the bimolecular process $A+B \rightarrow AB$, with an activation energy approximately equal to that of the mobility of the positive ion vacancies. This confirms the supposition that the change of conductivity reflects the clustering of the positive ion vacancies with other imperfections at a rate controlled by the diffusion of these vacancies. Above 100°C, many of the clusters appear to break up again with an accompanying increase of conductivity. The conducting vacancies appear to be localized in a rather small fraction of the total volume of the crystal.

I. INTRODUCTION

SEVERAL studies have been made of the ionic conductivity of NaCl and KCl which were irradiated with ionizing radiations.[1-5] In such crystals, whether irradiated or not, it has been accepted that the current is ordinarily due to the motion of free positive ion vacancies, each having an apparent negative charge. The presence of positive divalent impurities and the requirement of charge neutrality necessitates that there are many more positive than negative ion vacancies

below temperatures (about 500°C in ordinary so-called "pure" crystals) at which the number of vacancies is primarily intrinsic. In addition, positive ion vacancies are considerably more mobile and thus conductivity can be taken as a direct measure of their number.

Measurements of density changes and of coloration[6] which occur when crystals are irradiated with x rays indicate creation of new vacancies. In an apparent contradiction with this increase of vacancy concentration there have been observed decreases in diffusion[7] and in ionic conductivity resulting from irradiation. Of particular interest here are studies[2-4] in which NaCl and KCl crystals were exposed to either 350-Mev protons or 2-Mev gamma rays and then their conductivity measured while the temperature increased at a constant rate (1–2°C/min) from room temperature to about 400°C. Typical results[4] are illustrated in Fig. 1, which shows the ratio of the conductivity σ of irradiated crystals to the conductivity, σ_0, of unirradiated crystals at the same temperature. It is important to remark that,

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