of 1 percent. It will be recalled that the theory predicted a change of 11 percent.

When attempts were made to obtain an enrichment of Br^{81} chemical reaction of the C_2H_5Br with the duralumin rotor occurred. Apparently, under high centrifugal stress a sort of Grignard reaction was induced; the loss of C_2H_5Br was serious enough to prevent a successful separation of the last one cc. Recently it has been found that an alumilite coating (an anodic treatment of aluminum oxide) will protect the duralumin from reaction, at least for a while. It is hoped that this will permit long runs without reaction.

Conclusions

The agreement between the predicted and experimental values of the enrichment is not too significant in view of the rather spacious assumptions made in the theory and the wide spread of deviations found in the data. The major cause of these latter variations can be found in the photometric determination of line intensities in such a complex spectrum as Br_2. It is evident, though, that the agreement is good qualitatively and reasonably good quantitatively.

Compared with other methods for separating *heavy* isotopes the enrichment is sufficiently large to give some promise to centrifugation as a method of separating isotopes.

The author wishes to acknowledge his indebtedness to Professor Lars Onsager for assistance received with the theory here presented, and to Professor W. W. Watson for his direction of this research and for his able advice and assistance.

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The Accommodation Coefficient of Helium on Nickel*

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The thermal accommodation coefficient of helium on gas-free "A" nickel was measured at the temperatures 90, 195, 273 and 369°K, and was found to be 0.048, 0.060, 0.071 and 0.077, respectively (±0.004). In the presence of the gas the accommodation coefficient rose rapidly to the equilibrium values 0.413, 0.423, 0.360 and 0.343, respectively (±0.012). Using the theory of A. F. Devonshire and the observed values of α_0, calculations were made of the two constants of the interaction potential between a helium and a nickel atom. The results obtained were $\kappa=(0.75\pm0.05)\times10^8$ cm^{-1} for the exponential decay constant, and $D=(430\pm60)$ cal./mol for the heat of adsorption of helium on nickel. At the two lower temperatures the thermal conductivity of "A" nickel was measured. The values obtained were (0.74±0.04) watt/cm²/deg. at 90°K, and (0.71±0.04) watt/cm²/deg. at 195°K.

FOLLOWING the work of Roberts[1] who showed that the accommodation coefficient of a gas on a clean (that is, gas-free) metal surface was much smaller than that on a gas-covered surface, investigations of the exchange of energy between a gas and a hot solid have proceeded along two lines. In the first, interest is centered on the properties of the clean metal; in the second, on the detection and investigation of films of adsorbed gas. The present work belongs in the former category and is concerned with surface films only to the extent that they must be removed.

Experimental Details

1. Apparatus

In most respects the apparatus used and the procedure followed was similar to that of Roberts.[1]

The metal to be investigated was in the form

* This paper represents the publication in part of a dissertation submitted to the faculty of Bryn Mawr College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] J. K. Roberts, Proc. Roy. Soc. **A129**, 146 (1930); **A135**, 192 (1932); **A142**, 518 (1933).

of a filament of nickel "A" wire, 14.86 cm long and 0.00423 cm in diameter. The filament, held taut by tungsten springs, was mounted along the axis of a Pyrex tube 1 cm in diameter. The tube was enclosed in a constant temperature bath so that the walls of the tube and the ends of the wire were maintained at a fixed temperature while the wire was heated above its surroundings by the passage of an electric current. (Liquid air, CO_2-snow-and-acetone, shaved ice and water provided three fixed temperatures. For the highest temperature (369°K) an SAE 20 oil bath was used.) The bath temperature was measured by means of two chromel-alumel thermocouples placed less than 0.5 cm from the tungsten-to-glass seals of the experimental tube.

The potential drop across the tube and across a 10-ohm standard resistance in series with the tube was measured by means of a Queen Gray potentiometer. From these measurements the fundamental experimental quantities, namely, the resistance of the tube and the power input, were determined.

The vacuum system was designed so that the pressure in the experimental tube was controlled by means of two stopcocks, A and B, in series, placed between the high and low vacuum sides of the mercury diffusion pump. When stopcock A was closed the pressure in the tube was maintained at about 10^{-6} mm Hg. When stopcock A was open, helium circulated through the tube at a pressure (of the order of 10^{-3} mm Hg) determined by the setting of stopcock B. Pressures were measured by means of a McLeod gauge in shunt with the tube.[2] The helium was purified by circulation over a misch metal arc. After a few hours of operation the helium was spectroscopically pure, except for the presence in the misch metal bottle of mercury vapor which was prevented from reaching the tube by the interposition of traps. These traps were filled with liquid air when tube measurements at that temperature were being made; at other times CO_2-snow-and-acetone was used as the refrigerant.

[2] The values of the accommodation coefficient reported here differ somewhat from those presented in a preliminary report (Phys. Rev. **55**, 684 (1939)) because later consideration showed that a different pressure correction should have been applied, to take into account the difference in temperature between the McLeod gauge and the tube.

2. Procedure

After the initial bake-out at 450°C the wire was flashed repeatedly in vacuum until further flashing at 950°C produced no further change in the resistance at 0°C. Some of the difficulties encountered in this process of aging the nickel wire have been described in a previous paper.[3] When, after prolonged heat treatment, the wire became stable, the vacuum system was cut off from the fore pump and helium introduced. The system was then ready for the investigation proper.

It has been amply shown[1, 4] that, at the temperatures at which the present work was done (under 400°K), the surface of the metal cannot be kept free from contamination in the presence even of spectroscopically pure helium. It is necessary, therefore, to begin either with a hot wire or with a previously cleaned wire in vacuum, and to measure the accommodation coefficient as a function of time, in order that α_0, the accommodation coefficient for a clean wire, may be determined by extrapolation. The former method has been used by Roberts;[1] the latter, by Mann and Newell.[5] Both have been tried by the author and the second found to possess distinct advantages.

Whichever method is adopted the primary measurement is that of the variation of the resistance of the wire with time. If the wire is flashed in the presence of the gas, and the zero of time taken when the flashing current is cut off, then the resistance drops rapidly because of the cooling of the wire at the same time that it drops because of the gradual increase in the accommodation coefficient which results from the building up of a surface film on the metal. Even if a determination is made of the time taken for the disturbance due to flashing to die down (in Roberts' case this was about four minutes), and if only later values of the resistance are used to determine α, it is still necessary, in order to find α_0, to extrapolate over a considerable interval (about four minutes) during which the accommodation coefficient can be expected to have been changing most rapidly. If, on the other

[3] B. Raines, Phys. Rev. **54**, 481 (1938).
[4] W. B. Mann, Proc. Roy. Soc. **A146**, 776 (1934).
[5] W. B. Mann and W. C. Newell, Proc. Roy. Soc. **A158**, 397 (1937).

hand, after flashing in vacuum, the resistance is measured as a function of time until it becomes stable, and *then* gas is admitted, any change in resistance thereafter is due to the additional heat loss to the gas. This loss is proportional to αp (the product of accommodation coefficient and pressure) and is known to be zero at the time the gas was admitted. A simple auxiliary experiment suffices to determine the variation of pressure with time after admission of the gas. Hence α, the ratio of the ordinates of the αp and p curves, can be determined for times as little as 15 sec. after the time of admission of the gas. Although αp and p both approach zero as time approaches zero, their ratio does not, and the intercept value (see Fig. 2) gives α_0, the required accommodation coefficient for the gas on a clean wire. The results reported in the present paper were obtained by this method.

Figure 1 shows a typical curve for the variation of the resistance of the tube with time after flashing.* It can be seen that the change in resistance due to cooling took place over a longer time than did the change in resistance due to increasing heat loss to the gas. Hence, in this work, it was impossible to use the first method of determining α_0.

After taking the data for the curve shown in Fig. 1, the resistance R was measured as a function of power input Q. The temperature excess of the wire was always less than 10°C, so that $R=f(Q)$ was a straight line whose intercept value gave R_0, the resistance of the wire at bath temperature. In this connection it should be noted that all measurements of resistance were taken with the current flowing first in one and then in the reverse direction, in order to eliminate errors due to thermal e.m.f.'s. The order of magnitude of these e.m.f.'s was such that when this precaution was not observed, the curve of (apparent) resistance against power showed large departures from linearity. The tube was then re-evacuated and its resistance in vacuum again determined. In each case $(R-R_0)$ agreed closely with that found just before the gas was admitted, showing that the wire had returned to its former condition, and that the contamination had been superficial.

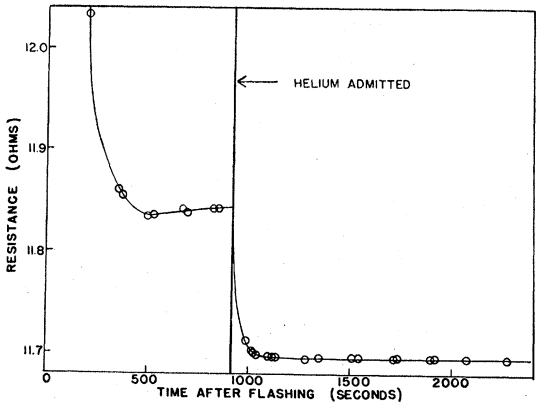

FIG. 1. Variation of the resistance of the wire (273°K) with time after flashing. The drop in resistance after helium is admitted is due entirely to loss of heat to the gas.

RESULTS

The equation for the distribution of temperature along a current-bearing wire whose ends are maintained at a fixed temperature has been developed by Roberts and extended by Michels and Cox[6] to a filament supported by springs. Michels and Cox, however, made no correction for the increase in resistivity due to heating of the wire. When this correction is made, and account is taken of heat lost to the gas as well as by radiation and by conduction through the ends, the differential equation obtained

$$d^2t/dx^2-At+B=0,$$

and the solution:

$$t=\frac{B}{A}\left[1+\frac{\sinh A^{\frac{1}{2}}(x-L)-\sinh A^{\frac{1}{2}}x}{\sinh A^{\frac{1}{2}}L}\right]$$

remain the same in form, but the constants A and B have the values

$$A=\frac{8e\sigma T^3}{aK}+\frac{2}{aK}\left(\frac{2R}{\pi\mu T}\right)^{\frac{1}{2}}\alpha p-\frac{I^2\rho_0 c}{\pi^2a^4K}$$

and

$$B=I^2\rho_0/\pi^2a^4K-A\Delta T$$

for the filament, and

$$A_s=\frac{8e_s\sigma T^3}{a_sK_s}+\frac{2}{a_sK_s}\left(\frac{2R}{\pi\mu T}\right)^{\frac{1}{2}}\alpha p-\frac{I^2\rho_{s0}c_s}{\pi^2a_s^4K_s}$$

* The slight but unmistakable increase in resistance between 500 and 900 sec. is to be attributed to a real change in the resistivity of the wire. This creep of the resistance of the nickel to a stable value was always observed after flashing. In this curve it is unnoticeable after 900 sec. but it sometimes persisted longer.

[6] W. C. Michels and M. Cox, Physics **7**, 153 (1935).

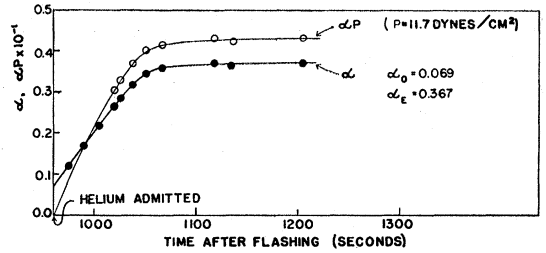

FIG. 2. The αp curve shows the variation with time of the heat lost to the gas. The α curve is obtained by dividing αp by the pressure which attains its equilibrium value (11.7 dynes/cm²) one minute after admission of the gas.

and

$$B_s = I^2\rho_{s0}/\pi^2 a_s^4 K_s$$

for the springs.

The mean temperature excess for the filament is*

$$\bar{t} = \frac{B}{A}\left[1 + \frac{2(1-\cosh A^{\frac{1}{2}}L)}{A^{\frac{1}{2}}L \sinh A^{\frac{1}{2}}L}\right]$$

and for the springs,*

$$\bar{t}_s = \frac{a^2K}{a_s^2K_s}\frac{B}{A^{\frac{1}{2}}}\frac{(\cosh A^{\frac{1}{2}}L-1)}{\sinh A^{\frac{1}{2}}L}\frac{(1-\operatorname{sech} A_s^{\frac{1}{2}}L_s)}{A_sL_s} + \frac{B_s}{A_s}\left[1 - \frac{\tanh A_s^{\frac{1}{2}}L_s}{A_s^{\frac{1}{2}}L_s}\right].$$

The temperature excess at the junction of filament and springs is:*

$$\Delta T = \frac{a^2K}{a_s^2K_s}\frac{B}{A^{\frac{1}{2}}}\frac{(\cosh A^{\frac{1}{2}}L-1)}{\sinh A^{\frac{1}{2}}L}\frac{\tanh A_s^{\frac{1}{2}}L_s}{A_s^{\frac{1}{2}}} + \frac{B_s}{A_s}(1-\operatorname{sech} A_s^{\frac{1}{2}}L_s).$$

In order to compute the heat loss to the gas, from which αp and then α are determined, it is necessary to know the losses due to radiation and to conduction through the ends. In addition to easily-measured properties of the nickel wire (such as resistance and diameter), these losses depend, respectively, on the total emissivity (e) and the thermal conductivity (K) of the wire. When the pressure is reduced to about 10^{-6} mm Hg, the gas loss is negligible, and (from the value of $(R-R_0)$ just before the gas was admitted) either the radiation loss (and hence e) or the conduction loss (and hence K) can be determined provided the other is known.

A search of the literature revealed no data on the total emissivity of nickel in the required temperature range, and it therefore remained to select from the many determinations of the thermal conductivity of nickel (above room temperature) the set of data most likely to be representative of the specimen of nickel used in this experiment. The data of van Dusen and Shelton[7] on commercial malleable nickel were chosen and after making a slight extrapolation to 0°C, the values of total emissivity shown by the circles of curve I, Fig. 3, were obtained. For the two lower temperatures (195 and 90°K), the radiation loss is small, and it was therefore thought preferable to estimate e and to compute K. Hence a smooth curve (curve I, Fig. 3) was passed through the computed points and (0, 0), roughly following the variation to be expected if $e \propto (\rho T)^{\frac{1}{2}}$. As questionable as the procedure looks at first glance, in all probability it produces a very small error, for the variation in e indicated by the dotted lines of curve I, Fig. 3 would cause only a two-percent variation in K.

The mean values of thermal conductivity found were 0.74 watt/cm²/deg. at 90°K and 0.71 watt/cm²/deg. at 195°K. The internal consistency was about one percent, but the probable error can conservatively be estimated at five percent to allow for systematic errors. It can be seen (curve II, Fig. 3) that the values

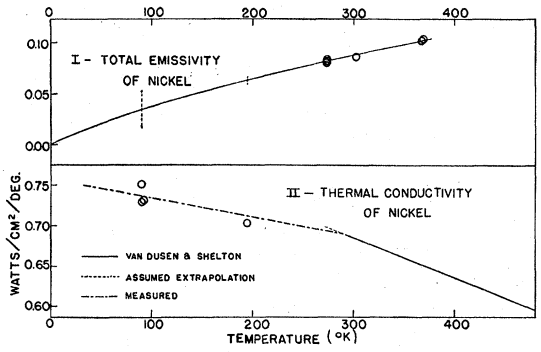

FIG. 3. At 273°K and above, the total emissivity of nickel was determined, using values of thermal conductivity obtained by van Dusen and Shelton. Below 273°K the thermal conductivity was determined, using values of the total emissivity from curve I.

* Because of typographical or algebraic errors in the Michels and Cox paper, the expressions for $\bar{t}$, $\bar{t}_s$ and ΔT are incorrectly printed. They should read as above.

[7] M. S. van Dusen and S. M. Shelton, Nat. Bur. Stand. J. Research **12**, 429 (1934).

obtained join fairly smoothly onto those of van Dusen and Shelton.

The Accommodation Coefficient

The results for the accommodation coefficient of helium on grade "A" nickel are shown in Table I.

The results are in fair agreement with Roberts'[1] observed value of 0.085 for α_0 (He on Ni) for a temperature somewhat above room temperature. Nevertheless, the fact that he gets a bigger α_0 for a smaller equilibrium value (0.20) lends point to the argument that changes in α might have been more rapid, during the first four minutes after flashing, than was indicated by the best extrapolation that could be made.

That the wire was stable when the measurements (of Table I) were made can be inferred not only from the consistency of the determinations at one temperature, but from the smooth variation from highest to lowest temperature, despite the chronological order in which the determinations were made.

Among the many theories of the thermal accommodation coefficient which have appeared in recent years, that of Devonshire[8] is the only one which takes into account, as an integral part of the development, the attractive field which is known to exist between a solid and a gas. Hence the interpretation of the results presented here will be confined to considerations suggested by his treatment. His formula for the thermal accommodation coefficient contains as parameters two constants of the interaction potential between a gas and a solid atom: D, the heat of adsorption of the gas on the solid, and κ, the exponential decay constant. Using $\kappa=0.75\times10^8$ cm^{-1}, $D=428$ cal./mol, and applying the correction factor 1.04 to raise slightly the absolute values of α_0, one obtains theoretical values for the accommodation coefficient which are in striking agreement with the experimental results. This is shown clearly in Table II. The estimation of the precision of this determination of the field constants is, however, a matter of some difficulty. On the one hand, the experimental values of the accommodation coefficient have not been corrected for the roughness of the surface of the wire. They are therefore too high by a factor which is larger than 1, and possibly larger than 2.[1] On the other hand, as Devonshire points out, because of his use of a one-dimensional model, the theoretical values are too large by a factor between 1 and 2. Hence it was thought advisable to find another pair of values of D and κ which would give the observed temperature variation as before, but which would require a correction factor of approximately 1.5 to bring the absolute values into agreement with experiment. Then the difference between these two sets of values could be used as an estimate of the probable error. The values $\kappa=0.70\times10^8$ cm^{-1}, $D=373$ cal./mol were found to satisfy these requirements. On this basis, the constants of the interaction potential between helium and nickel can be given as $\kappa=(0.75\pm0.05)\times10^8$ cm^{-1} and $D=(430\pm60)$ cal./mol.

In conclusion it is a pleasure to thank Professor Walter C. Michels for his interest and advice during the course of this work. I am indebted also to a bequest of the late Marion E. Reilly which made possible the purchase of some of the essential apparatus.

Table I. *Accommodation coefficient of helium on nickel.*

	Accommodation Coefficient		
T°K	α_0 gas-free surface	α_e equilibrium value, gas-covered surface	Chronological order of determinations
369	0.077±0.004	0.343±0.012	7
273	0.069	0.357	1
	0.073	0.362	2
195	0.060	0.423	3
90	0.056	0.395	4
	0.046	0.417	5
	0.042	0.426	6

Table II. *Comparison of observed accommodation coefficients with those computed from Devonshire's theory.*

	Accommodation Coefficient He-Ni		
		Computed (Devonshire's theory)	
T (°K)	Observed (mean values)	$\kappa=0.75\times10^8$ cm^{-1} $D=428$ cal./mol corr. fact. 1.04	$\kappa=0.70\times10^8$ cm^{-1} $D=373$ cal./mol corr. fact. 1.56
369	0.077	0.077	0.080
273	0.071	0.070	0.071
195	0.060	0.061	0.060
90	0.048	0.047	0.044

[8] A. F. Devonshire, Proc. Roy. Soc. **A158**, 269 (1937).