

Temperature Scale and Thermionic Emission from Rhodium

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molecules. The photometric curves of the Raman lines from the concentrated solutions appear however those of single lines. If one concludes that dissociation is complete, one may still find in the ideas concerning the structure of water of Bernal and Fowler,⁹ used also by Prins, a qualitative explanation of the difference with respect to Raman scattering between the behavior of the nitrates of sodium and cadmium on the one hand and silver and lead on the other. The sodium and silver ions are singly charged, but the sodium being smaller exerts a greater influence in maintaining or increasing a certain regularity in structure in the water. The cadmium and lead ions are doubly charged, so that although the cadmium ion is as large as silver it produces an effect more like that of sodium, but the still larger lead ion again has a smaller directing effect, and its presence may lead to a weakening

of the structure. This might be tested in a study of the water bands of small frequency shift referred to by Hibben¹⁰ as surely due to intermolecular interaction.

The NO₃ ion is considered to be plane, with the nitrogen at the center of an equilateral triangle, and the oxygen atoms at the corners. The Raman line studied here is ascribed to the radial vibration. The effect of the cations on this vibration would be indirect according to the point of view suggested here. Where there is a superarrangement of the cations, there are crystal-like groupings of molecules, and the symmetry makes for a higher vibration frequency, but if the water structure is weakened, and the cations are more at random, the central forces in the NO₃ ion may be weakened, and the frequency lowered.

Our thanks are due to Dorothy Franklin, who assisted considerably in measuring the plates.

⁹ Bernal and Fowler, *J. Chem. Phys.* **1**, 515 (1933).

¹⁰ Hibben, *J. Chem. Phys.* **5**, 166 (1937).

Temperature Scale and Thermionic Emission from Rhodium

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When rhodium is heated to incandescence in an atmosphere of air or oxygen, a coating forms on its surface. This is shown by a change in the emissivity. When the temperature is increased sufficiently this coating suddenly disappears, and when the temperature is lowered it reappears. This coating is probably an activated adsorption of oxygen, or an oxide of rhodium. It is found experimentally that the temperature and partial oxygen pressure at which the coating disappears are related by the Clausius-Clapyron equation:

$$(d \log_e P)/dT = L/RT^2.$$

P is the partial oxygen pressure, T the absolute temperature, and L the heat of vaporization of the surface. The electron work function of a clean rhodium surface is found to be $\phi = 4.80$ volts, and $A = 33$ amp./cm²/degree².

EMISSION AND TEMPERATURE SCALE

THE peculiarities of rhodium surfaces described below were first encountered when measurements of spectral emissivity were being taken.¹ A specimen of rhodium in the shape of a V wedge 6 cm long, 4 mm wide on a side, and about 0.04 mm thick was mounted inside a brass

chamber which was evacuated to a pressure of $1-2 \times 10^{-6}$ mm. The true temperature was measured by an optical pyrometer sighted inside the wedge, and the apparent temperature by another pyrometer sighted on the outside surface.

A typical sequence of readings is shown in Fig. 1. When the temperature was first raised, a series of values shown by the lower curve was found. Upon lowering the temperature there was

¹ L. V. Whitney, *Phys. Rev.* **48**, 458 (1935).

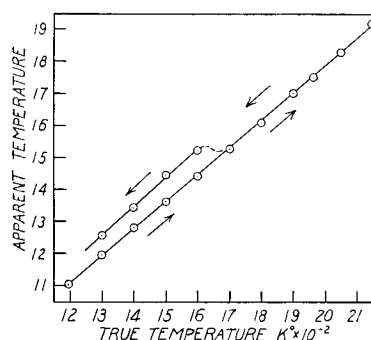


FIG. 1.

a sudden shift to the upper curve. The emissivity as calculated from points of the lower curve ranged from about 0.22 to 0.29 for $\lambda=6698\text{\AA}$; that from points of the upper curve was about 0.60. High emissivities were always found with this chamber at low temperatures after the temperature had once been raised beyond the transition point, the initial low emissivities at low temperatures never being found again after the first set of readings. The change from one curve to the other was always abrupt. If the temperature were being raised slowly, a critical point would be reached at which the emissivity would change and the true temperature flash up 100 to 150 degrees. The sudden rise in temperature was due to the fact that a low emissivity surface replaced the high emissivity surface.

It was difficult to take readings in the neighborhood of the critical point, and a shorter wedge, about 13 mm long, was therefore substituted. Because of the steep temperature gradient along this wedge, it was possible to have the center hot enough to show a low emissivity while the extremities showed a high emissivity. Figs. 2 to 5 are photographs of this wedge at various temperatures.

Figure 2 shows the outer surface of the wedge below the critical point, after it had previously been conditioned above it. The apparent temperature at the center is about 1500°K , and the surface has a high emissivity. Fig. 3 shows the wedge when the apparent temperature at the center is about 1790°K ; this center part has low emissivity, while high emissivities obtain nearer the ends. Fig. 4 shows the appearance of the wedge when the temperature was slightly lower than it was in Fig. 3; the central low emissivity region is shorter. Fig. 5 shows the inside of the wedge when the outside had the appearance of Figs. 3 and 4.

Figure 6 shows the same wedge after it had burned out. Five zones are distinguishable. The central zone had a blue appearance when cold, but at the time of burning out it had low emissivity characteristic of temperatures above the critical point. Zones adjacent to the center

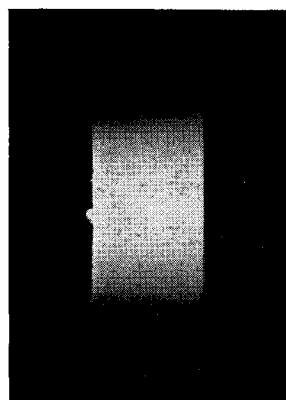


FIG. 2.

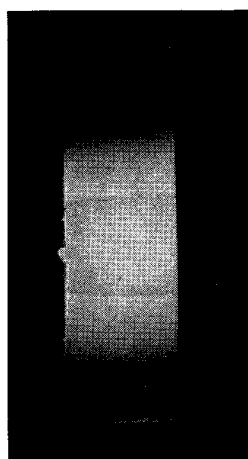


FIG. 3.

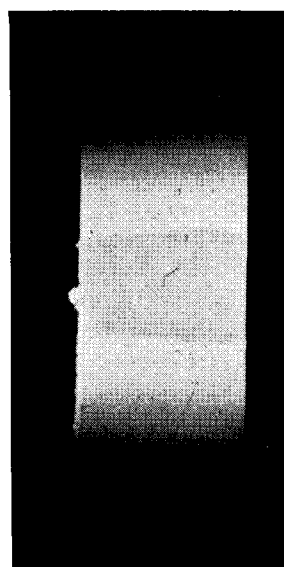


FIG. 4.

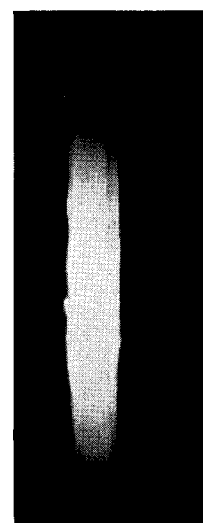


FIG. 5.

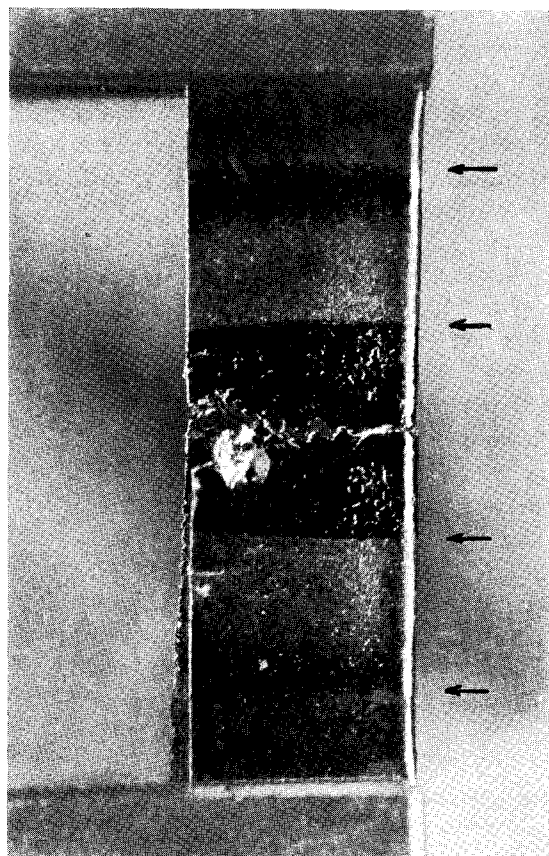


FIG. 6.

had high emissivity, and the top and bottom zones low emissivity. (These last zones are not as clearly marked as the others and are not visible in Figs. 3 and 4.) These end zones had never become hot enough to pass the critical point and thus had kept their initial low emissivity throughout the experiment. X-ray pictures taken of the high and low emissivity surfaces showed no crystalline differences in the metal.

Further investigation showed that prolonged outgassing affected the temperature of the critical point. This indicated a surface layer dependent on the temperature and pressure conditions. The brass chamber was therefore discarded and a study made of this effect in an all Pyrex system where better vacuum conditions could be obtained. At high vacua (2×10^{-8} mm) the effect disappeared entirely, and the low emissivity 0.242, corresponding presumably to the clean metal surface, was obtained at all temperatures.

The temperature scale for this emissivity and for a wave-length of 6698Å is given in Table I.

When air was introduced into the system the transition phenomenon immediately reappeared. This suggests very strongly that the high emissivity surface is covered by a surface layer which disappears at high temperature. Readings were taken of the temperatures of the critical point for various pressures of air, oxygen, nitrogen, and hydrogen. There was a marked difference between these results in Pyrex glass and those obtained in the brass chamber; the pressures necessary to obtain the transition in the all-Pyrex system were greater by a factor of 10^6 or more. Perhaps the wax, which was used in sealing the brass chamber together, saturated the atmosphere about the hot filament and acted similar to a catalytic agent. When wax was purposely introduced into the Pyrex system the layer formed at lower pressures, but it is questionable whether conditions duplicated those inside the brass chamber.

Figure 7 shows the transition temperatures obtained when gases were introduced into the Pyrex system. It is evident that the temperature of breakdown of what is apparently a surface layer is a function of the partial oxygen pressure, since the readings for air reduced to partial oxygen pressures fall on the curve found for pure oxygen. The readings for nitrogen indicate a small oxygen content, but the temperatures of the transition point were so low they could not be read accurately. No surface layer appeared when hydrogen was introduced into the system.

Figure 8 is a graph of the logarithm of the oxygen pressure to the base e plotted against the reciprocal of the transition temperature. The

TABLE I.

TRUE TEMPERATURE	APPARENT TEMPERATURE
1200°K	1111°K
1300	1197
1400	1282
1500	1365
1600	1447
1700	1528
1800	1609
1900	1689
2000	1768
2100	1847

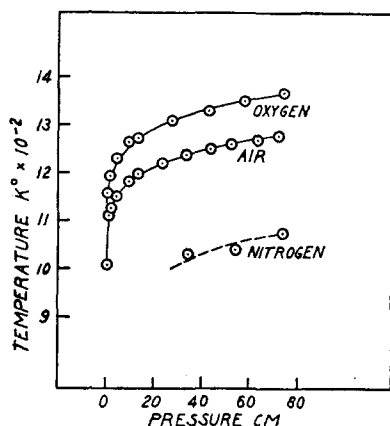


FIG. 7.

equation of this line is

$$\log_e P = -L/RT + b,$$

and the slope gives the value of L/R . The heat of vaporization of the surface, (L), was found from this graph to be 6.15×10^4 calories per g mole.

THERMIONIC EMISSION

A straight strip of rhodium 3 mm wide, 0.07 mm thick, and 10 cm long was mounted in a conventional type two-guard ring tube such as that described by Wahlin and Reynolds.² The tube was evacuated and the glass baked for 700 hours. During this baking the temperature of the filament was gradually raised to a value above the transition point. As soon as the furnaces were removed a thermionic determination was made. The Richardson plot showed a definite break at the transition point, the low temperature slope being the greater and corresponding to a work function higher by 3/10 volt. The high tempera-

² H. B. Wahlin and J. A. Reynolds, Phys. Rev. **48**, 751 (1935).

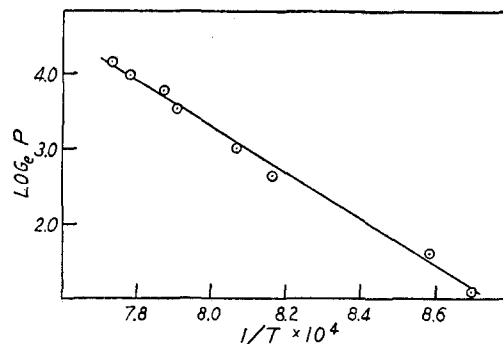


FIG. 8.

ture portion of the plot gave a work function slightly greater than that of a clean surface. Continued heat treatment at a temperature above the transition point caused the break to disappear gradually and after 1100 hours the values $\phi = 4.80$ volts, $A = 33$ amp./cm² degrees² were obtained. At this time a final pressure of 2×10^{-8} mm was reached. Additional heat treatment for 500 hours caused no further change. Two other specimens of rhodium gave the same values.

This value of the work function is not in agreement with that reported by Dixon.³ He observed, however, an abnormal variation of the work function with temperature which can best be explained as due to incomplete outgassing. He also found definite changes in the thermionic properties of the metal at 1100°C, which he attributed to a change in the structure of the metal. In view of the x-ray findings reported here, such a conclusion seems untenable.

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³ E. H. Dixon, Phys. Rev. **37**, 60 (1931).