

PtCl₆. This was subsequently decomposed to platinum metal. The same procedure was repeated a third time in an attempt to prepare platinum entirely free of iron, iridium, gold, and copper.

APPENDIX II: CHEMICAL PURIFICATION OF THE IRIDIUM FRACTION

The filtrate from the (NH₄)₂PtCl₆ precipitation contained any iridium present, including some added as a carrier before the precipitation with NH₄Cl. Small amounts of palladium and rhodium were added, the solution diluted to 400 ml, and the palladium precipitated with dimethylglyoxime. After standing one hour, the precipitate was separated by filtration and washed with dilute (1:99) HCl and hot water.

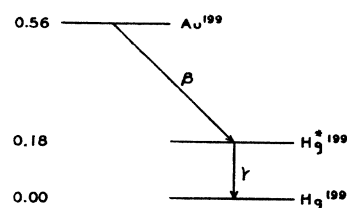


FIG. 7. Disintegration scheme of gold (199).

To the filtrate was added sodium nitrite, then Na₂CO₃ to make the solution neutral. After boiling, the solution was slightly acidified and Na₂S solution added to precipitate rhodium sulfide. The filtrate containing iridium was made alkaline with Na₂CO₃ and iridium sulfide was precipitated with Na₂S. The iridium precipitate was washed and ignited.

Second-Order Transformations in Two-Component Systems. Application to Solutions of He³ in He⁴

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A thermodynamic treatment has been made of a second-order transformation in two-component systems. In addition to the requirement that there be no heat of transformation and no volume change, it turns out that the composition is equal in the two phases. Equations have been developed for $(dT/dx)_P$, $(dx/dP)_T$, and $(dP/dT)_x$ along the equilibrium curves. If we assume that the transformation of liquid helium remains second-order on the addition of a mole fraction x of He³ to a He⁴ solution, then for the limit of very dilute solutions

$$(dT/dx)_P = 21 \text{ deg.} \quad \text{and} \quad (dx/dP)_T = 6 \times 10^{-4} \text{ atmos.}^{-1}.$$

I. INTRODUCTION

IN order to give a thermodynamic treatment of the change in temperature of the lambda-point of liquid helium with pressure, Ehrenfest¹ was led to the concept of thermodynamic transitions of higher order. In the usual phase transitions there is a discontinuity in the temperature and pressure derivatives of the free energy (the entropy and volume, respectively) but the free energy is equal in the two phases. Such a transformation was called first-order by Ehrenfest. At the lambda-point of liquid helium the free

energy and its first derivatives are equal on both sides of the transformation but there is a discontinuity in the second derivatives of the free energy in crossing a line in the pressure-temperature plane along which the transformation occurs. This was called a transformation of the second order. Similarly, a transformation of the n th order is one in which a discontinuity first appears in the n th derivative of the free energy.

Recent experimental investigations of the properties of dilute solutions of the isotope He³ in ordinary helium make it of interest to investigate the thermodynamics of higher order transitions in systems of more than one com-

¹ P. Ehrenfest, Comm. Leiden Suppl. No. 75b.

ponent. The treatment given will, for reasons of brevity and simplicity, be confined to two-component systems and to a second-order transition. The same methods can be extended to more complicated systems and to higher order transitions.

We take as variables the pressure, P , temperature, T , and the mole fraction of component two in each phase, $x(I)$ and $x(II)$. Of these four variables any two may be independently chosen when the phases are in equilibrium. The conditions for equilibrium between the phases is that the partial molal free energies of each component be equal in the two phases,

$$\bar{G}_1(I) = \bar{G}_1(II) \quad \text{and} \quad \bar{G}_2(I) = \bar{G}_2(II), \quad (1)$$

and that for any variation

$$d\bar{G}_1(I) = d\bar{G}_1(II) \quad \text{and} \quad d\bar{G}_2(I) = d\bar{G}_2(II), \quad (2)$$

if the two phases are to remain in equilibrium.

$$\begin{aligned} & [\partial\bar{G}_1(I)/\partial T]dT + [\partial\bar{G}_1(I)/\partial P]dP \\ & + [\partial\bar{G}_1(I)/\partial x(I)]dx(I) \\ & = [\partial\bar{G}_1(II)/\partial T]dT + [\partial\bar{G}_1(II)/\partial P]dP \\ & + [\partial\bar{G}_1(II)/\partial x(II)]dx(II) \end{aligned} \quad (3)$$

with a similar equation for \bar{G}_2 . By eliminating $dx(II)$ between the two equations one obtains

$$\begin{aligned} & [(\bar{S}_1(I) - \bar{S}_1(II))(\partial\bar{G}_2/\partial x(II)) \\ & - (\bar{S}_2(I) - \bar{S}_2(II))(\partial\bar{G}_1/\partial x(II))]dT \\ & - [(\bar{V}_1(I) - \bar{V}_1(II))(\partial\bar{G}_2/\partial x(II)) \\ & - (\bar{V}_2(I) - \bar{V}_2(II))(\partial\bar{G}_1/\partial x(II))]dP \\ & - [(\partial\bar{G}_1/\partial x(I))(\partial\bar{G}_2/\partial x(II)) \\ & - (\partial\bar{G}_2/\partial x(I))(\partial\bar{G}_1/\partial x(II))]dx(I) = 0, \end{aligned} \quad (4)$$

where the substitutions

$$\partial\bar{G}/\partial T = -\bar{S}, \quad \text{the partial molal entropy,} \quad (5)$$

and

$$\partial\bar{G}/\partial P = \bar{V}, \quad \text{the partial molal volume,} \quad (6)$$

have been made. Using the Gibbs-Duhem equation,

$$x(\partial\bar{G}_2/\partial x) + (1-x)(\partial\bar{G}_1/\partial x) = 0. \quad (7)$$

Equation (4) becomes

$$\begin{aligned} & [(1-x(II))\Delta\bar{S}_1 + x(II)\Delta\bar{S}_2]dT \\ & - [(1-x(II))\Delta\bar{V}_1 + x(II)\Delta\bar{V}_2]dP \\ & - [1 - (x(II)/x(I))] \\ & \quad \times [\partial\bar{G}_1/\partial x(I)]dx(I) = 0, \end{aligned} \quad (8)$$

where Δ indicates the difference between phases

I and II . For a first-order transformation the coefficients of dT , dP , and $dx(I)$ will be finite, and one may immediately write down the expressions for $(dP/dT)_{x(I)}$, $(dx(I)/dT)_P$, and $(dx(I)/dP)_T$. Also, since there is a similar expression for $dx(II)$, the coefficients $(dx(I)/dx(II))_P$ and $(dx(I)/dx(II))_T$ may be obtained.

In a second-order transition the coefficients of dT , dP , and $dx(I)$ will be zero. If the coefficient of $dx(I)$ vanishes, $x(I)$ must equal $x(II)$ or the composition must be equal in the two phases. The coefficient of dT then becomes

$$(1-x)\Delta\bar{S}_1 + x\Delta\bar{S}_2 = \Delta S,$$

where S is the total entropy per mole. Likewise, the coefficient of dP becomes $-\Delta V$. The requirement that the coefficients of dT , dP , and $dx(I)$ vanish is equivalent to saying there is no entropy change (or no latent heat) and no volume change. $\Delta\bar{S}_1$, $\Delta\bar{S}_2$, $\Delta\bar{V}_1$, and $\Delta\bar{V}_2$ are not individually zero, but are related by the expressions

$$\Delta\bar{S}_1/\Delta\bar{S}_2 = \Delta\bar{V}_1/\Delta\bar{V}_2 = x/(x-1), \quad (9)$$

and from the Gibbs-Duhem relation

$$\begin{aligned} x/(x-1) & = [\partial\bar{G}_1/\partial x(I)]/[\partial\bar{G}_2/\partial x(I)] \\ & = [\partial\bar{G}_1/\partial x(II)]/[\partial\bar{G}_2/\partial x(II)] \\ & = [\Delta\partial\bar{G}_1/\partial x]/[\Delta\partial\bar{G}_2/\partial x]. \end{aligned} \quad (10)$$

If we require that the transformation remain second-order then the coefficients of dT , dP , and $dx(I)$ in Eq. (8) must remain zero along the transition line. If we call A the coefficient of dT then

$$\begin{aligned} (dA/dx(I))_P = 0 & = (\partial A/\partial x(I)) \\ & + (\partial A/\partial x(II))(dx(II)/dx(I))_P \\ & + (\partial A/\partial T)(dT/dx(I))_P. \end{aligned}$$

Since $(dx(I)/dx(II))_P = 1$ along the transition line, we obtain

$$(dx/dT)_P = \Delta C_P/T(\Delta\bar{S}_1 - \Delta\bar{S}_2).$$

The coefficient of $dx(I)$ in Eq. (8), represented by C , when differentiated in the same fashion as A above does not give a determinate equation since

$$\partial C/\partial T = 0$$

and

$$(\partial C/\partial x(I)) + (\partial C/\partial x(II))(dx(II)/dx(I))_P = 0.$$

However, the requirement that C remains zero

is that $x(I)$ remain equal to $x(II)$, or that $dx(I) = dx(II)$ along the transition curve. Substituting in Eq. (3), we obtain

$$(dx/dT)_P = \Delta\bar{S}_1/(\Delta\partial\bar{G}_1/\partial x) = \Delta\bar{S}_2/(\Delta\partial\bar{G}_2/\partial x) \\ = (\Delta\bar{S}_1 - \Delta\bar{S}_2)/(\Delta\partial\bar{G}_1/\partial x - \Delta\partial\bar{G}_2/\partial x).$$

In a similar fashion one obtains the equations summarized below.

$$(dT/dx)_P = \Delta(\partial\bar{G}_1/\partial x)/\Delta\bar{S}_1 = \Delta(\partial\bar{G}_2/\partial x)/\Delta\bar{S}_2 \\ = [\Delta(\partial\bar{G}_1/\partial x) - \Delta(\partial\bar{G}_2/\partial x)]/ \\ [\Delta\bar{S}_1 - \Delta\bar{S}_2] \\ = T(\Delta\bar{S}_1 - \Delta\bar{S}_2)/C_P \\ = -(\Delta\bar{V}_1 - \Delta\bar{V}_2)/\Delta(\partial V/\partial T), \quad (11)$$

$$(dx/dP)_T = -\Delta\bar{V}_1/\Delta(\partial\bar{G}_1/\partial x) \\ = -\Delta\bar{V}_2/\Delta(\partial\bar{G}_2/\partial x) \\ = -[\Delta\bar{V}_1 - \Delta\bar{V}_2]/ \\ [\Delta(\partial\bar{G}_1/\partial x) - \Delta(\partial\bar{G}_2/\partial x)] \\ = -\Delta(\partial V/\partial T)/(\Delta\bar{S}_1 - \Delta\bar{S}_2) \\ = \Delta(\partial V/\partial P)/(\Delta\bar{V}_1 - \Delta\bar{V}_2), \quad (12)$$

$$(dP/dT)_x = \Delta\bar{S}_1/\Delta\bar{V}_1 = \Delta\bar{S}_2/\Delta\bar{V}_2 \\ = (\Delta\bar{S}_1 - \Delta\bar{S}_2)/(\Delta\bar{V}_1 - \Delta\bar{V}_2) \\ = \Delta C_P/T\Delta(\partial V/\partial T) \\ = -\Delta(\partial V/\partial T)/\Delta(\partial V/\partial P). \quad (13)$$

II. APPLICATION TO DILUTE SOLUTIONS

In the limit of very dilute solutions the preceding equations may be simplified. In the limit of $x=0$, $\bar{S}_1=S$ and $\bar{V}_1=V$ so that $\Delta\bar{S}_1$ and $\Delta\bar{V}_1$ both are zero for a second-order transition. We can also use Henry's law, $f=Kx$, where f is the fugacity.² Then, using the well-known thermodynamic treatment of dilute solutions, at $x=0$,

$$\partial\bar{G}_2/\partial x = (RT/x) + RT(\partial \ln K/\partial x), \quad (14) \\ (\partial\bar{G}_1/\partial x) = -RT,$$

$$\Delta\bar{S}_2 = -RT\Delta(\partial \ln K/\partial T), \quad (15)$$

$$\Delta\bar{V}_2 = RT\Delta(\partial \ln K/\partial P). \quad (16)$$

Then Eqs. (11) to (13) become

$$\left(\frac{dT}{dx}\right)_P = \frac{\Delta(\partial \ln K/\partial x)}{\Delta(\partial \ln K/\partial T)} = \frac{RT^2\Delta(\partial \ln K/\partial T)}{\Delta C_P} \\ = \frac{RT\Delta(\partial \ln K/\partial P)}{\Delta(\partial V/\partial T)}, \quad (17)$$

² See G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923) Chapters XVII and XX for the definition of fugacity and the discussion of the laws of the dilute solution.

$$\left(\frac{dx}{dP}\right)_T = -\frac{\Delta(\partial \ln K/\partial P)}{\Delta(\partial \ln K/\partial x)} \\ = -\frac{\Delta(\partial V/\partial T)}{RT\Delta(\partial \ln K/\partial T)} \\ = -\frac{\Delta(\partial V/\partial P)}{RT\Delta(\partial \ln K/\partial P)}, \quad (18)$$

$$\left(\frac{dP}{dT}\right)_x = \frac{\Delta(\partial \ln K/\partial T)}{\Delta(\partial \ln K/\partial P)} = \frac{\Delta C_P}{T\Delta(\partial V/\partial T)} \\ = -\frac{\Delta(\partial V/\partial T)}{\Delta(\partial V/\partial P)}. \quad (19)$$

III. CHANGE TO A FIRST-ORDER TRANSITION

We have treated the case where the transition remains second-order over a finite range of pressure, temperature, and composition. We may consider that the difference in free energy between the two phases is expanded in a Taylor's series around a point where the transition is second-order. The coefficients of the first-order derivatives will be zero and the requirement that they remain zero involves the vanishing of a discriminant of the coefficients of the second-order terms.^{3,4}

This condition is expressed by the equality of the various terms in Eqs. (17), (18), and (19). If this condition is not met, then the transition is second-order at only one point and changes to a first-order transition when the composition is changed. For convenience we assume that the singular point is at $x=0$. The fugacities are equal in the two phases so $x(I)K(I) = x(II)K(II)$. Then Eq. (8) becomes

$$\Delta SdT - \Delta VdP \\ + RT[1 - (K(I)/K(II))]dx(I) = 0. \quad (20)$$

The coefficients of dT , dP , and $dx(I)$ are zero, i.e., the transition is second-order, at $x=0$. To determine the slope of the equilibrium line we must determine the limit of the ratios of the coefficients as x approaches zero.

$$K(I)dx(I) + x(I)dK(I) \\ = K(II)dx(II) + x(II)dK(II)$$

³ P. S. Epstein, *Textbook of Thermodynamics* (John Wiley and Sons, Inc., New York, New York, 1937), pp. 128-133.

⁴ P. W. Bridgman, *Phys. Rev.* **70**, 425 (1946).

along the equilibrium line, so when x is small

$$dx(II)/dx(I) = K(I)/K(II) = 1, \quad (21)$$

and we need not distinguish between $dx(I)$ and $dx(II)$.

$$\begin{aligned} (dT/dx)_P &= \lim_{x \rightarrow 0} RT[(K(I)/K(II)) - 1]/\Delta S \\ &= [RT\Delta(\partial \ln K/\partial x) \\ &\quad + RT\Delta(\partial \ln K/\partial T)(dT/dx)_P] / \\ &\quad [-RT\Delta(\partial \ln K/\partial T) \\ &\quad + (\Delta C_P/T)(dT/dx)_P] \end{aligned}$$

or

$$\begin{aligned} (dT/dx)_P &= [RT\Delta(\partial \ln K/\partial T) \\ &\quad \pm [(RT\Delta(\partial \ln K/\partial T))^2 \\ &\quad + \Delta C_P R \Delta(\partial \ln K/\partial x)]^{1/2}] / \\ &\quad (\Delta C_P/T). \quad (22) \end{aligned}$$

In a like fashion

$$\begin{aligned} (dP/dx)_T &= [-RT\Delta(\partial \ln K/\partial P) \\ &\quad \pm [(RT\Delta(\partial \ln K/\partial P))^2 \\ &\quad - \Delta(\partial V/\partial P)RT\Delta(\partial \ln K/\partial x)]^{1/2}] / \\ &\quad \Delta(\partial V/\partial P), \quad (23) \end{aligned}$$

$$\begin{aligned} (dP/dT)_x &= [-\Delta(\partial V/\partial T) \pm [(\Delta(\partial V/\partial T))^2 \\ &\quad + (\Delta C_P/T)\Delta(\partial V/\partial P)]^{1/2}] / \Delta(\partial V/\partial P). \quad (24) \end{aligned}$$

In these expressions the double sign of the square root corresponds to the existence of two equilibrium lines in the (T, x) , (T, P) , or (P, x) planes. These lines mark first-order transitions between the phases and at their intersection the transition becomes second-order. If one of the quantities under the square root sign in Eqs. (22)–(24) is zero, then in the corresponding plane the two lines coincide and the transition is second-order in that plane. If any two of the discriminants are zero then the third must be also and Eqs. (17)–(19) are obtained.

If one of the products in a discriminant is zero, then one of the lines in the corresponding plane becomes parallel to an axis. Thus, for example, if in Eq. (22) $\Delta(\partial \ln k/\partial x) = 0$, then one of the lines is $(dT/dx)_P = 0$.

When the transition is second-order along an equilibrium line, then the extrapolation of the free energies of the two phases would yield the result that one phase is stable on both sides of the line and the other can exist only along the line itself. We must therefore say there is some

physical reason not included in the thermodynamic treatment that one phase becomes unstable. This point has been discussed by Bridgman⁴ and Keesom.⁵ When the transition is second-order only at a point and changes to first-order along two equilibrium lines, we perhaps must discard some regions on the basis of a physical argument.

IV. APPLICATION TO LIQUID HELIUM

The recent measurements of Fairbank, Lane, Aldrich and Nier⁶ on the distribution of He³ between liquid and vapor He⁴ may be used for a thermodynamic calculation of the initial slope of the temperature-composition curve for the lambda-transformation. These authors measured C_V/C_L , the ratio of the concentration of He³ in the vapor and the liquid, as a function of temperature for both helium *I* and *II*. We may with sufficient accuracy treat the gases as ideal in which case the fugacity equals the pressure. The solutions were very dilute, around one part per million of He³, so the limiting laws may be used. Then $f_3 = Kx$, $f_4 = P$, the vapor pressure of He⁴, $C_V = f_3/P$, $C_L = x = f_3/K$, or $C_V/C_L = K/P$. Then

$$\begin{aligned} d \ln(C_V/C_L)/d(1/T) &= [d \ln K/d(1/T)] - [d \ln P/d(1/T)] \\ &= -[(H_3(\text{gas}) - \bar{H}_3)/R] \\ &\quad + [(H_4(\text{gas}) - H_4(\text{liq.}))/R]. \end{aligned}$$

When $\ln(C_V/C_L)$ is plotted against $1/T$ one obtains two straight lines which, within the accuracy of the measurements, intersect at the lambda-point, but which are very different in slope. From the data of Fairbank, Lane, Aldrich, and Nier⁶ one obtains from the slope above the lambda-temperature,

$$\begin{aligned} H_4(\text{gas}) - H_4(\text{liq.}) - (H_3(\text{gas}) - \bar{H}_3) \\ = 14 \text{ cal. mole}^{-1}. \end{aligned}$$

Taking the heat of vaporization of He⁴,

$$H_4(\text{gas}) - H_4(\text{liq.}) = 22 \text{ cal. mole}^{-1}$$

at the lambda-temperature, then the partial molal heat of vaporization of He³, from helium *I*, $H_3(\text{gas}) - \bar{H}_3 = 8 \text{ cal. mole}^{-1}$. From the slope

⁴ W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., Amsterdam and London, 1942), Chapter V.

⁶ Fairbank, Lane, Aldrich, and Nier, *Phys. Rev.* **73**, 729 (1948).

below the lambda-temperature

$$H_4(\text{gas}) - H_4(\text{liq.}) - (H_3(\text{gas}) - \bar{H}_3) \\ = -147 \text{ cal. mole}^{-1},$$

and at the lambda-temperature

$$H_3(\text{gas}) - \bar{H}_3 = 169 \text{ cal. mole}^{-1}.$$

Above the lambda-point the heat of vaporization of He³ from the solution is less than that of He⁴ as one might expect from the greater zero-point energy of the lighter isotope. The very large heat of vaporization below the lambda-point is unexplained. It should be pointed out that \bar{H}_3 is a measure of the change in enthalpy on the addition of an infinitesimal amount of He³ to a He⁴ solution, and the large energy effect may be because the addition of an atom of He³ causes a lowering in energy of a large number of He⁴ atoms.

The data of Fairbank, Lane, Aldrich, and Nier⁶ indicate that at the lambda-point C_V/C_L is equal in the two phases, or that $K(I) = K(II)$. The coefficient of $dx(I)$ in Eq. (20) is therefore zero. ΔS and ΔV are also zero for He⁴, and, in fact, remain zero along a curve in the P, T plane, but their derivatives are finite along this curve.

$$\Delta \bar{H}_3 = T \Delta \bar{S}_3 = -RT^2 \Delta(\partial \ln K / \partial T) \\ = 161 \text{ cal. mole}^{-1}.$$

The value $\Delta C_P = -7.6 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ has been chosen by Keesom⁵. Although it is not possible

to assign a very exact value on the basis of the experimental measurements, the value chosen proved to be consistent with the observed discontinuity in $\partial V / \partial T$ and the observed change of the lambda-temperature with pressure as related by Eq. (19). If we assume that the transition remains second-order along a line in the T, x plane, then by Eq. (17) $(dT/dx)_P = 21 \text{ deg.}$ And taking $(dP/dT)_x = -80.8 \text{ atmos. deg.}^{-1}$ from Keesom,⁵ by Eqs. (18) and (19), $(dx/dP)_T = 6 \times 10^{-4} \text{ atmos.}^{-1}$. It should be emphasized that these values apply only to the limiting case of very dilute solutions.

Thus the initial slope of the temperature-composition curve for the lambda-point will be an increase in temperature of about 0.2° per mole percent of He³ added. The accuracy of the experimental data is not high, but unless the vapor-liquid equilibrium measurements on He II are very much in error one can definitely conclude that the lambda-temperature will be raised by the addition of small amounts of He³, provided the transition remains second-order. There are no available measurements on $\Delta(\partial \ln K / \partial x)$ so the possibility that the transition goes over to a first-order one in the T, x plane in accordance with Eq. (22) cannot be excluded.

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