

## Isobaric and Isothermal Hysteresis in Metal Hydrides and Oxides

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An analysis is presented of the thermodynamics of both isothermal and isobaric hysteresis, leading to equations for the calculation of the irreversible entropy production and the loss of free energy in hysteresis cycles of both kinds. The status of 'apparent' enthalpies derived from the temperature dependence of isothermal data is examined and two extreme types of behaviour are identified. An analysis of experimental data shows that the palladium–hydrogen system exhibits characteristics lying between these extremes. However, this does not seriously affect the use of either isothermal or isobaric data to derive the entropy production and free-energy loss. Existing published work on rare-earth metal–oxygen systems is also analysed, but no firm conclusions can be drawn.

Many metal hydrides and oxides exist in two (or more) solid phases, conversions between which exhibit hysteresis. If the system is studied isothermally it is found that the pressure ( $p_f$ ) at which the phase richer in hydrogen (the hydride phase) or the higher oxide is formed is higher than that ( $p_d$ ) at which the reverse process occurs on lowering the gas pressure. Alternatively, the gas pressure may be held constant at a value greater than  $p_f$  at the lower experimental temperature. The temperature ( $T_d$ ) at which the hydride or oxide decomposes on raising the temperature is then higher than that ( $T_f$ ) at which the reverse change takes place on cooling.

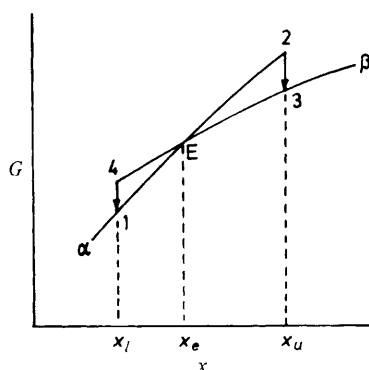
In this paper isothermal and isobaric hysteresis phenomena are considered, and the relationship between them is discussed. The conclusions are illustrated by experimental data for the palladium–hydrogen system, and compared with data on oxide systems from the literature. Two of the authors have previously presented a detailed model for isothermal hysteresis in metal hydrides,<sup>1,2</sup> and the work of another of the authors<sup>3</sup> and McKinnon<sup>4</sup> should also be referred to.

We begin with a discussion of the fundamental thermodynamic nature of hysteresis phenomena. Isothermal and isobaric hysteresis are then analysed in thermodynamic terms. The present treatment applies to relatively low pressures when non-ideality of the gas and hydrostatic effects on the solid can be neglected.

### General Thermodynamic Analysis of Hysteresis Phenomena

A thermodynamic interpretation of hysteresis phenomena may be based on the supposition that when an external (independent) variable ( $x$ ) is changed through the hysteresis region, the system can persist in a metastable state beyond the true equilibrium point up to some critical transition point at which it transforms irreversibly into an equilibrium state; on reversing the direction of change of the external variable, the system again overshoots the equilibrium position and the reverse transition also occurs irreversibly from a metastable state.

This sequence of events may be represented conveniently in terms of the variation of



**Fig. 1.** Schematic representation of free-energy curves for a systems exhibiting hysteresis in the interconversion of states  $\alpha$  and  $\beta$  brought about by variations in an external parameter  $x$ .

the free energy of the system  $G$  as a function of  $x$ , as indicated schematically in fig. 1.<sup>5</sup> The curves representing the free energies of the system in states  $\alpha$  and  $\beta$  intersect at E. In the absence of hysteresis the phase transition would occur reversibly at  $x_e$ . However, for systems in which hysteresis occurs, when  $x$  varies from  $x_e$  to  $x_u$  the system remains in a metastable  $\alpha$  state until at  $x_u$  it changes irreversibly to state  $\beta$ . Similarly, on reducing  $x$ , the system is metastable between  $x_e$  and  $x_l$ , and returns irreversibly to state  $\alpha$  at  $x_l$ .

In any process in a closed system the change in entropy ( $dS$ ) is given by

$$dS = d_e S + d_i S \quad (1)$$

where  $d_e S$  is the entropy transferred to or from the surroundings and is equal to  $dQ/T$  (where  $dQ$  is the amount of thermal energy transferred), and  $d_i S$  is the entropy produced in any internal irreversible processes.<sup>6</sup> The production of entropy is associated with an irreversible dissipation of free energy:

$$-T d_i S = d_i G.$$

Thus in fig. 1

$$\Delta_i S(2 \rightarrow 3) = [G^\alpha(x_u) - G^\beta(x_u)]/T \quad (2a)$$

and

$$\Delta_i S(4 \rightarrow 1) = [G^\beta(x_l) - G^\alpha(x_l)]/T. \quad (2b)$$

If, after a cycle of hysteresis, the system returns to the same state, *i.e.* in Bridgman's terms<sup>7</sup> the state is recoverable, then  $\Delta S = 0$  and

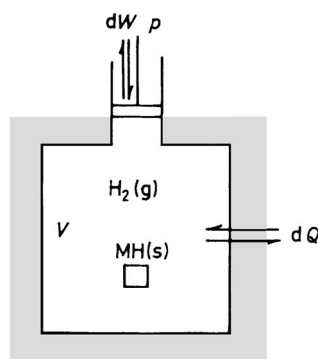
$$\oint d_i S = -\oint d_e S = -\oint dQ/T = \oint (-d_i G/T). \quad (3)$$

The total entropy production is the sum of the contributions from the internal irreversible steps, in each of which a certain amount of free energy is dissipated. The irreversibly produced entropy in the cycle is transferred to the surroundings and appears as a net 'production of heat'.

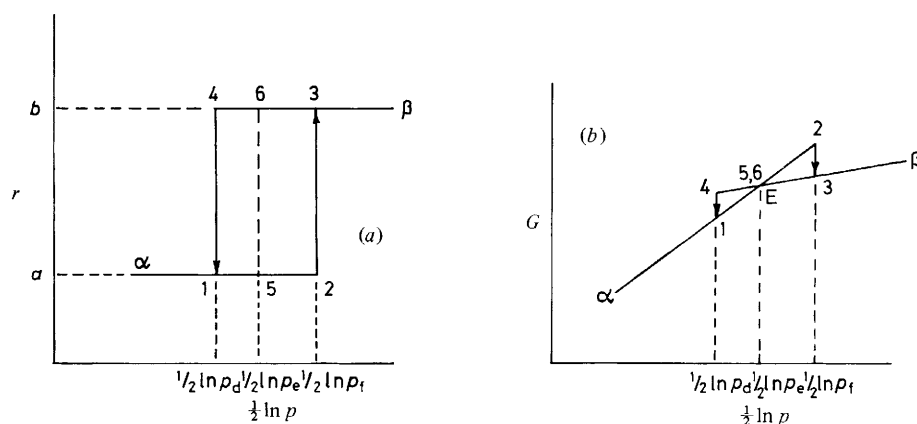
It is important to stress that, in general, it is not possible experimentally to identify the equilibrium state, so that only the total entropy production in a cycle can be obtained.<sup>†</sup>

In most instances of hysteresis the transitions are not sharp, but are spread out over

<sup>†</sup> In some special cases, *e.g.* supercooling of a liquid, it may be possible to show that one of the transitions takes place reversibly under equilibrium conditions, but in the systems considered here this is not the case. In other instances experimental observations may suggest the location of the equilibrium state, but the arguments employed are not firmly based on thermodynamic considerations. The relation between supercooling phenomena and hysteresis is discussed in more detail by Everett and Whitton.<sup>5</sup>



**Fig. 2.** Definition of system in discussing metal–hydrogen systems. The system contains 1 mol of  $\frac{1}{2}\text{H}_2$  and 1 mol of metal (M). The solid hydride MH(s) coexists with gaseous hydrogen at a pressure  $p$  in a volume  $V$ . In a process in which an amount of work  $dW$  is exchanged with the surroundings, a transfer  $dQ$  of thermal energy occurs.



**Fig. 3.** Isothermal hysteresis. (a) Phase diagram for metal–hydrogen system which can exist in two states  $\alpha$  and  $\beta$ . The hydrogen:metal ratio ( $r$ ) in state  $\alpha$  is  $a$ , and in state  $\beta$ ,  $b$ . Irreversible transition from  $\alpha$  to  $\beta$  occurs at  $p_t$  ( $2 \rightarrow 3$ ), and from  $\beta$  to  $\alpha$  at  $p_d$  ( $4 \rightarrow 1$ );  $p_e$  is the (hypothetical) equilibrium transition pressure. (b) Schematic representation of free energies of states  $\alpha$  and  $\beta$  as function of logarithm of hydrogen pressure, showing irreversible fall in free energy in the steps  $2 \rightarrow 3$  and  $4 \rightarrow 1$ .

a relatively narrow range of values of  $x$ . One of the authors and his coworkers<sup>8</sup> have interpreted this by suggesting that the system may be thought of formally as a mosaic of ‘domains’, the transition points  $x_u$  and  $x_l$  varying from domain to domain. However, in the present discussion we shall begin by simplifying the problem by supposing that the transitions occur throughout the system at well defined values of  $x_u$  and  $x_l$ .

### Isothermal Hysteresis in Metal–Hydrogen Systems

For definiteness we consider metal–hydrogen systems, although essentially the same arguments apply to metal–oxygen systems. The thermodynamic system under consideration is shown in fig. 2. Furthermore, we make the additional simplification of representing the composition–pressure isotherms as in fig. 3(a). State  $\alpha$  consists of  $(1 - a)$

mol of  $\frac{1}{2}\text{H}_2(\text{g})$  and 1 mol of  $\text{MH}_a^\alpha(\text{s})$ , while state  $\beta$  contains  $(1-b)$  mol of  $\frac{1}{2}\text{H}_2(\text{g})$  and 1 mol of  $\text{MH}_b^\beta(\text{s})$ . ( $\text{M}$  denotes the metal). The free energy of the system when all of the metal is in the  $\alpha$ -phase, *i.e.* along the line 1–2 (fig. 3), is given by

$$G^\alpha = \mu_{\text{MH}_a}^\alpha + \frac{1}{2}(1-a)RT \ln(p_{\text{H}_2}/p^\ominus) \quad (4)$$

where the standard gaseous state is  $p^\ominus$  and the gas is assumed to be ideal. Similarly, for the state  $\beta$ , *i.e.* along the line 3–4 (fig. 3),

$$G^\beta = \mu_{\text{MH}_b}^\beta + \frac{1}{2}(1-b)RT \ln(p_{\text{H}_2}/p^\ominus). \quad (5)$$

These free-energy curves may be represented graphically as in fig. 3(b). As indicated above, the  $\alpha$  and  $\beta$  states are in stable equilibrium with hydrogen gas in the regions 1–E and 3–E, and in metastable equilibrium with respect to the other phase in E–2 and E–4. Irreversible transitions from  $\alpha$  to  $\beta$  and from  $\beta$  to  $\alpha$  occur *via* steps 2–3, at  $p_t$  and 4–1, at  $p_d$ , and are accompanied by the entropy productions (and losses of free energy) given by

$$T\Delta_i S(2 \rightarrow 3) = \frac{1}{2}(b-a)RT \ln(p_t/p_e) = -\Delta_i G(2 \rightarrow 3) \quad (6)$$

$$T\Delta_i S(4 \rightarrow 1) = \frac{1}{2}(a-b)RT \ln(p_d/p_e) = -\Delta_i G(4 \rightarrow 1) \quad (7)$$

where  $p_e$  is the equilibrium pressure. However, since  $p_e$  is generally unknown, all that can be obtained experimentally is the total entropy production, and total loss of free energy in the cycle: the latter is equal to the net work done by the surroundings on the system. Thus

$$\begin{aligned} -\Delta_i G(\text{cycle}) = T\Delta_i S(\text{cycle}) &= T[\Delta_i S(2 \rightarrow 3) + \Delta_i S(4 \rightarrow 1)] = \frac{1}{2}(b-a)RT \ln(p_t/p_d) \\ &= \Delta W(\text{cycle}) \end{aligned} \quad (8)$$

the work done in the step  $2 \rightarrow 3$ ,  $(b-a)RT$ , being exactly cancelled by that done in  $4 \rightarrow 1$ ,  $(a-b)RT$ .

It is also instructive to follow an essentially equivalent procedure by calculating the entropy difference between states 2 and 3 (which are interconvertible experimentally only by the irreversible step  $2 \rightarrow 3$ ) through the sequence of steps  $2 \rightarrow 5$ ,  $5 \rightarrow 6$ ,  $6 \rightarrow 3$ . Of these  $2 \rightarrow 5$  and  $6 \rightarrow 3$  are, respectively, the reversible expansion of  $(1-a)$  mol of gas and the reversible compression of  $(1-b)$  mol of gas. Step  $5 \rightarrow 6$  is not experimentally realisable, but consists of a hypothetical reversible absorption of  $(b-a)$  mol of  $\text{H}_2$  at  $p_e$ :†

$$\left. \begin{aligned} \Delta S(2 \rightarrow 5) &= \frac{1}{2}(1-a)R \ln(p_t/p_e) = \Delta Q(2-5)/T \\ \Delta S(5 \rightarrow 6) &= (b-a)\Delta_f H/T \\ \Delta S(6 \rightarrow 3) &= \frac{1}{2}(1-b)R \ln(p_e/p_t) = \Delta Q(6-3)/T \end{aligned} \right\} \quad (9)$$

where  $\Delta_f H$  is the molar enthalpy for hydride formation [*i.e.* for the absorption of 1 mol of  $\frac{1}{2}\text{H}_2(\text{g})$ ].  $\Delta S(2-3)$  is given by the sum of the changes in eqn (9)

$$\Delta S(2 \rightarrow 3) = S(3) - S(2) = (b-a)\Delta_f H/T + \frac{1}{2}(b-a)R \ln(p_t/p_e). \quad (10)$$

When 2–3 occurs irreversibly

$$\Delta S(2-3) = \Delta_e S(2 \rightarrow 3) + \Delta_i S(2 \rightarrow 3). \quad (11)$$

† A question can be raised about the validity of the above procedure, which rests on the assumption that states 2 and 3 are recoverable in the Bridgman sense.<sup>7</sup> This seems to be justified experimentally by the observation that hysteresis cycles (sometimes omitting the first) are repeatable. In terms of one molecular interpretation,<sup>1</sup> in which hysteresis in these systems is attributed to the plastic deformation needed to accommodate the volume changes accompanying hydride formation and decomposition, it is suggested that the dislocation densities in the metal in states 2 and 3 are the same in successive cycles.

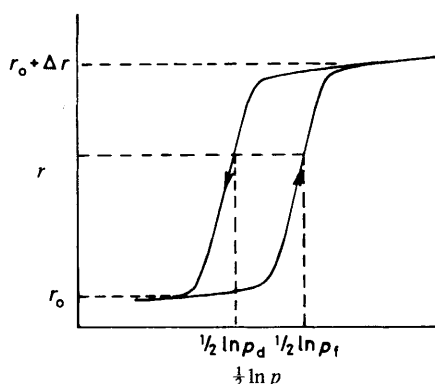


Fig. 4. General form of isothermal hysteresis loop for metal-hydrogen system showing diffuse transitions.

The heat flow in the irreversible process at constant pressure is  $(b-a)\Delta_f H$ , so that  $\Delta_e S(2 \rightarrow 3) = (b-a)\Delta_f H/T$ , and comparing eqn (10) and (11) we may identify†

$$\Delta_i S(2 \rightarrow 3) = \frac{1}{2}(b-a)R \ln(p_f/p_e) \quad (12)$$

which is the same as eqn (6). Furthermore, from eqn (9)

$$\Delta_i S(2 \rightarrow 3) = \Delta Q(2 \rightarrow 5)/T + \Delta Q(6 \rightarrow 3)/T \quad (13)$$

where  $\Delta Q(2 \rightarrow 5)$  and  $\Delta Q(6 \rightarrow 3)$  are positive and negative quantities, respectively. For the cycle  $5 \rightarrow 2 \rightarrow 3 \rightarrow 6 \rightarrow 5$  (fig. 3),  $\Delta S = 0$ . Since the enthalpies of formation (2–3) and decomposition (6–5) cancel, the overall entropy exchange  $\Delta_e S(\text{cycle})$ , which carries away the irreversibly produced entropy in step  $2 \rightarrow 3$  is made up of the contributions from the reversible compression and expansion of the gas in steps  $5 \rightarrow 2$  and  $3 \rightarrow 6$ . Of the amount of heat  $\Delta Q(5 \rightarrow 2)$  evolved during the compression  $p_e \rightarrow p_f$ , a lesser amount of heat  $\Delta Q(3 \rightarrow 6)$  has to be absorbed during the expansion  $p_f \rightarrow p_e$  in order to compensate for the entropy production in the hydride formation step 2–3.

By similar arguments

$$\Delta_i S(4 \rightarrow 1) = \Delta Q(1 \rightarrow 5)/T + \Delta Q(6 \rightarrow 4)/T = \frac{1}{2}(b-a)R \ln(p_e/p_d). \quad (14)$$

As stressed above, the hypothetical steps 5–6 and 6–5 are not realizable in practice, so that one must consider the cycle around the whole hysteresis loop (or a closed scan from  $p_f$  to  $p_d$  and back again or *vice versa*), when

$$\Delta_i S(\text{cycle}) = \Delta Q(1 \rightarrow 2)/T + \Delta Q(3 \rightarrow 4)/T = \frac{1}{2}(b-a)R \ln(p_f/p_d). \quad (15)$$

The net heat change in the complete isothermal cycle now consists of the contributions from the reversible compression of the gas from  $1 \rightarrow 2$  and the decompression  $3 \rightarrow 4$  and this compensates for the irreversible changes in  $2 \rightarrow 3$  and  $4 \rightarrow 1$  so that  $\Delta S(\text{cycle}) = 0$ .

We stress that not only the entropy of the system, but also the enthalpy and free energy must return to the same values at the end of the cycle since the system is recoverable, at least for hysteresis cycles after the first, which are the ones of concern here. Thus for the simplified behaviour of fig. 3, the enthalpy of transition  $2 \rightarrow 3$  is equal in magnitude to that of the reverse transition  $4 \rightarrow 1$ . The quantities which do not return to the same values (and are not functions of state) are the work done on the system and the heat exchanged with the surroundings. It is this fact which leads to the general thermodynamic concept that because of hysteresis the net work done on the system is dissipated as heat.

† This involves the assumption that  $\Delta_f H$  at  $p_e$  is the same as that at  $p_f$ .

So far we have discussed the simple case of a rectangular loop. It is readily shown<sup>9</sup> (see fig. 2) that in the more general case of fig. 4 that

$$\begin{aligned}
 -\Delta_i G(\text{cycle}) = \Delta W(\text{cycle}) &= \oint p \, dV = \frac{1}{2} RT \oint \ln p \, dr \\
 &= \frac{1}{2} RT \int_{r_0}^{r_0 + \Delta r} \ln(p_t/p_d) \, dr = T \Delta_i S(\text{cycle}) \quad (16)
 \end{aligned}$$

where  $r = [H]/[M]$  and  $p_t$  and  $p_d$  are the pressures on the two branches of the hysteresis loop at a given  $r$ . Thus the entropy production in an isothermal cycle is given by the area of the loop plotted in  $R \ln p^{\frac{1}{2}}$  against  $r$  coordinates. The free-energy loss per unit quantity of H involved in the cycle is obtained by dividing the terms in eqn (16) by  $\Delta r$ .

### Isobaric Hysteresis

Here again it is instructive to consider the problem in terms of the free energies of states  $\alpha$  and  $\beta$ . However, instead of maintaining constant temperature, the system is now in contact with a series of heat reservoirs covering a range of temperatures, while the applied pressure is constant. The composition–temperature diagram is taken as a simple rectangle [fig. 5(a)], while the free energies of the two states are sketched as functions of temperature in fig. 5(b).

In general, for the reaction of 1 mol of  $\frac{1}{2}H_2$  converting  $MH_a^\alpha$  into  $MH_b^\beta$ , denoted by  $\Delta_r$ , we have from the Gibbs–Helmholtz equation (assuming  $\Delta_r C_p$ , the isobaric heat-capacity change of reaction, to be constant)

$$\frac{\Delta_r G(T)}{T} = \frac{\Delta_r H(T)}{T} - \frac{\Delta_r H(T_e)}{T_e} - \Delta_r C_p \ln \frac{T}{T_e} \quad (17)$$

The states  $\beta$  and  $\alpha$  are thermodynamically stable in the regions  $1 \rightarrow E$  and  $3 \rightarrow E$ , respectively, and metastable in the regions  $E \rightarrow 2$  and  $E \rightarrow 4$ . Irreversible entropy production occurs in the decomposition step  $2 \rightarrow 3$  on raising the temperature to  $T_d$ , and in  $4 \rightarrow 1$  when state  $\alpha$  is reformed at  $T_f$ , the losses in free energy being, respectively,  $\Delta_d G(T_d)$  and  $\Delta_f G(T_f)$ . Hence

$$\Delta_i S(2 \rightarrow 3) = \frac{-\Delta_d G(T_d)}{T_d} = (b-a) \left( \frac{\Delta_r H(T_d)}{T_d} - \frac{\Delta_r H(T_e)}{T_e} - \Delta_r C_p \ln \frac{T_d}{T_e} \right), \quad (18)$$

$$\Delta_i S(4 \rightarrow 1) = \frac{-\Delta_f G(T_f)}{T_f} = -(b-a) \left( \frac{\Delta_r H(T_f)}{T_f} - \frac{\Delta_r H(T_e)}{T_e} - \Delta_r C_p \ln \frac{T_f}{T_e} \right) \quad (19)$$

where  $\Delta_r H = -\Delta_d H$ .

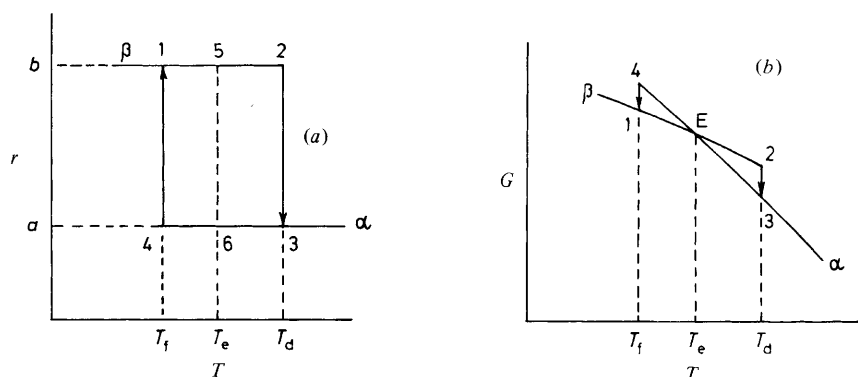
In the cycle

$$\Delta_i S(\text{cycle}) = (b-a) \left( \frac{\Delta_r H(T_d)}{T_d} - \frac{\Delta_r H(T_f)}{T_f} - \Delta_r C_p \ln \frac{T_d}{T_f} \right). \quad (20)$$

The corresponding free-energy loss in the cycle is

$$-\Delta_i G(\text{cycle}) = T_d \Delta_i S(2 \rightarrow 3) + T_f \Delta_i S(4 \rightarrow 1). \quad (21)$$

Since both  $\Delta_i S(2 \rightarrow 3)$  and  $\Delta_i S(4 \rightarrow 1)$  involve  $T_e$  it follows that  $\Delta_i G(\text{cycle})$ , unlike  $\Delta_i S(\text{cycle})$ , depends on  $T_e$ . Thus while  $\Delta_i S(\text{cycle})$  can be calculated from experimental data,  $\Delta_i G(\text{cycle})$  for isobaric hysteresis is not amenable to direct evaluation in the absence of knowledge of the equilibrium temperature, or of an approximate method of locating the equilibrium state.



**Fig. 5.** Isobaric hysteresis: (a) Phase diagram for metal–hydrogen system which transforms from the low temperature state  $\beta$  to  $\alpha$  at  $T_d$ , and reforms  $\beta$  at  $T_f$ .  $T_e$  is the (hypothetical) equilibrium temperature. (b) Schematic representation of free energies of states  $\alpha$  and  $\beta$  as function of temperature, showing irreversible fall in free energy in the steps  $2 \rightarrow 3$  at  $T_d$  and  $4 \rightarrow 1$  at  $T_f$ .

Alternatively we may calculate the external entropy exchange in the separate steps  $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$ :

$$\begin{aligned} \Delta_e S(1 \rightarrow 2) &= \int_{T_f}^{T_d} \frac{dQ}{T} = \int_{T_f}^{T_d} \frac{C_p(\text{MH}_b^\beta) + \left(\frac{1-b}{2}\right) C_p(\text{H}_2)}{T} dT \\ &= \left[ C_p(\text{MH}_b^\beta) + \left(\frac{1-b}{2}\right) C_p(\text{H}_2) \right] \ln \frac{T_d}{T_f} \end{aligned} \quad (22)$$

$$\Delta_e S(2 \rightarrow 3) = (a-b) [\Delta_f H(T_d)] / T_d; \quad (23)$$

$$\Delta_e S(3 \rightarrow 4) = \left[ C_p(\text{MH}_a^\alpha) + \left(\frac{1-a}{2}\right) C_p(\text{H}_2) \right] \ln \frac{T_f}{T_d} \quad (24)$$

$$\Delta_e S(4 \rightarrow 1) = (b-a) [\Delta_f H(T_f)] / T_f. \quad (25)$$

So that

$$\Delta_e S(\text{cycle}) = (b-a) \left( \frac{-\Delta_f H(T_d)}{T_d} + \frac{\Delta_f H(T_f)}{T_f} + \Delta_f C_p \ln \frac{T_d}{T_f} \right) = -\Delta_i S(\text{cycle}) \quad (26)$$

since

$$\Delta_i S(\text{cycle}) + \Delta_e S(\text{cycle}) = 0$$

and where

$$\Delta_f C_p = \left[ C_p(\text{MH}_b^\beta) - C_p(\text{MH}_a^\alpha) - \left(\frac{b-a}{2}\right) C_p(\text{H}_2) \right] / (b-a).$$

The irreversible entropy production in the solid-phase reaction is partially compensated for by the fact that the calorimetric enthalpies of formation and decomposition are exchanged at different temperatures, and partly because the distribution of  $\text{H}_2$  between gas and solid is different in the two reversible heating and cooling steps. Again it is important to remember that it is not possible to calculate the individual contributions  $\Delta_i S(2 \rightarrow 3)$  and  $\Delta_i S(4 \rightarrow 1)$  unless the equilibrium temperature is known. The above equations apply to a simple rectangular loop. A more general equation is

$$\Delta_i S(\text{cycle}) = \oint \frac{\Delta_f H}{T} dr \quad (27)$$

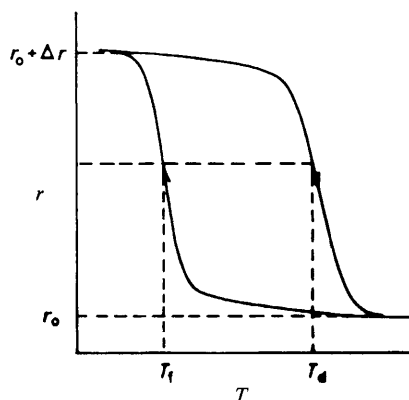


Fig. 6. General form of isobaric hysteresis loop for metal–hydrogen system showing diffuse transitions.

where  $\Delta_f H$  refers to the reaction in which 1 mol of  $\frac{1}{2}\text{H}_2(\text{g})$  is absorbed, and in some regions is a partial molar quantity reflecting the diffuseness of the transition (fig. 6). If  $\Delta_f C_p \approx 0$  so that  $\Delta_f H$  is constant this reduces to

$$\Delta_i S(\text{cycle}) = -\Delta_f H \int_{r_0}^{r_0+\Delta r} \Delta(1/T) \, dr \quad (28)$$

where  $\Delta(1/T)$  is the width of the loop, plotted as  $r$  against  $1/T$ , and  $r_0$  and  $r_0 + \Delta r$  are the limits of the loop. To relate this to the entropy production per unit amount of  $H$  involved in the cycle,  $\Delta_i S(\text{cycle})$  obtained using eqn (28) must be divided by  $\Delta r$ .

### Approximate Location of the Equilibrium State

It is not possible to demonstrate from thermodynamic arguments alone that the free-energy losses due to irreversibility should be equal for hydride formation and decomposition, and indeed they may not be generally equal. For the palladium–hydrogen case, however, it has been argued<sup>1</sup> that the hysteresis is related to the formation of dislocations in the crystal lattice and that similar dislocation densities are associated with both the  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \alpha$  transitions. Experimental support for this has been given.<sup>2</sup> On this basis one might then postulate that  $\Delta_i G(\alpha \rightarrow \beta) = \Delta_i G(\beta \rightarrow \alpha)$ . In this case it follows that for isothermal hysteresis:

$$\ln(p_f/p_e) = \ln(p_e/p_d) \quad (29)$$

$$\text{or} \quad p_e = (p_f p_d)^{\frac{1}{2}} \quad (30)$$

while for isobaric hysteresis, assuming  $\Delta C_p = 0$  or  $(T_d - T_f)$  is small,

$$T_e = (T_d + T_f)/2. \quad (31)$$

For small temperature differences the arithmetic and geometric mean are approximately equal so that

$$T_e \approx (T_d T_f)^{\frac{1}{2}}. \quad (32)$$

On the other hand, if  $\Delta_i S$  is the same for both transitions the same answer is obtained for isothermal hysteresis, but for isobaric hysteresis a slightly different condition emerges:

$$\frac{T_d - T_e}{T_d} = \frac{T_e - T_f}{T_f} \quad (33)$$

which for  $T_d \approx T_f$  reduces to eqn (32).



It is now possible to rewrite eqn (20) and (21) in the following approximate and more useful forms:

$$\frac{\Delta_i S(\text{cycle})}{(b-a)} = -\frac{\Delta_f H(T_e) \Delta T}{T_d T_f} \quad (34)$$

$$\frac{\Delta_i G(\text{cycle})}{(b-a)} = \frac{\Delta_f H(T_e) \Delta T}{(T_d T_f)^{\frac{1}{2}}} \text{ where } \Delta T = T_d - T_f. \quad (35)$$

Alternatively, if one attempts to treat the problem in terms of a statistical theory which predicts the form of fig. 4 (or the equivalent pressure–composition diagram exhibiting a van der Waals type loop) one could again predict the location of  $p_e$ . In the isobaric case, the problem is rather more complicated, but is in principle soluble.

### Derivation of ‘Apparent’ Thermodynamic Quantities

It is a common practice to use values of  $p_f$  or  $p_d$  at different temperatures to derive apparent enthalpies of hydride formation [ $\Delta_f H(\text{app})$ ] or decomposition [ $\Delta_d H(\text{app})$ ] from the equations

$$\Delta_f H(\text{app}) = \frac{R}{2} \left( \frac{\partial \ln(p_f/p^\ominus)}{\partial (1/T)} \right)_r \quad (36)$$

$$\Delta_d H(\text{app}) = \frac{-R}{2} \left( \frac{\partial \ln(p_d/p^\ominus)}{\partial (1/T)} \right)_r \quad (37)$$

where  $\Delta_f H$  and  $\Delta_d H$  refer to the transfer of 1 mol of  $\frac{1}{2}\text{H}_2$ . Less commonly, the variations of the transition temperatures in isobaric measurements at a range of pressures have been used:

$$\Delta_f H(\text{app}) = \frac{R}{2} \left( \frac{\partial (1/T_f)}{\partial \ln(p/p^\ominus)} \right)_r^{-1} \quad (38)$$

$$\Delta_d H(\text{app}) = \frac{-R}{2} \left( \frac{\partial (1/T_d)}{\partial \ln(p/p^\ominus)} \right)_r^{-1}. \quad (39)$$

If the quantities derived from eqn (36) and (37) were true enthalpies then

$$\Delta H(\text{cycle}) = \oint \Delta H(\text{app}) \, dr = 0. \quad (40)$$

This criterion has been shown not to be satisfied for the  $\text{H}_2$ –Pd system,<sup>10</sup> while a similar discrepancy exists for adsorption–desorption hysteresis.<sup>11</sup> The problems arising in the use of the above equations were discussed tentatively by Everett and Whitton<sup>11</sup> and by La Mer.<sup>12</sup> This discussion can be extended in the following way.

We consider first the simple case of a rectangular hysteresis loop. From eqn (6) we have

$$\begin{aligned} -\frac{d[\Delta_i G(2 \rightarrow 3)/T]}{d(1/T)} &= -\left( \Delta_i G(2 \rightarrow 3) + \frac{1}{T} \frac{d\Delta_i G(2 \rightarrow 3)}{d(1/T)} \right) = \frac{d\Delta_i S(2 \rightarrow 3)}{d(1/T)} \\ &= \left( \frac{b-a}{2} \right) R \left( \frac{d \ln(p_f/p^\ominus)}{d(1/T)} - \frac{d \ln(p_e/p^\ominus)}{d(1/T)} \right) \\ &= (b-a) [\Delta_f H(\text{app}) - \Delta_f H] \end{aligned} \quad (41)$$

where  $\Delta_f H$  is the true enthalpy of formation of the hydride. A similar set of equations relates to  $\Delta_f G(4 \rightarrow 1)$ . For a complete cycle it follows by summing the contributions from

steps (2 → 3) and (4 → 1) that

$$\begin{aligned}\Delta_i G(\text{cycle}) + \frac{1}{T} \left( \frac{d \Delta_i G(\text{cycle})}{d(1/T)} \right) &= - \frac{d \Delta_i S(\text{cycle})}{d(1/T)} \\ &= -(b-a) [\Delta_f H(\text{app}) + \Delta_d H(\text{app})] \\ &= -(b-a) \Delta H(\text{app, cycle}).\end{aligned}\quad (42)$$

Two extreme cases can be identified:

(i) If  $\Delta_i S(\text{cycle})$  is independent of  $T$  then

$$\Delta H(\text{app}) = \Delta H \text{ and } \Delta H(\text{app, cycle}) = 0. \quad (43)$$

(ii) If  $\Delta_i G(\text{cycle})$  is independent of  $T$ . In each step

$$\Delta H(\text{app}) = \Delta H - \frac{\Delta_i G}{b-a} = \Delta H + \frac{T \Delta_i S}{b-a} \quad (44)$$

$$\text{and} \quad \Delta H(\text{app, cycle}) = -\Delta_i G(\text{cycle})^2 = \frac{1}{2} RT \ln(p_f/p_d). \quad (45)$$

Case (ii) is that which Everett and Whitton postulated might apply to adsorption-desorption hysteresis.

In the more usual situation of diffuse transitions case (i) gives

$$\Delta H(\text{app, cycle}) = \oint \Delta H(\text{app}) dr = 0 \quad (46)$$

while for case (ii), eqn (45) becomes

$$\Delta H(\text{app, cycle}) = \Delta_i G(\text{cycle}) = \frac{1}{2} RT \int_{r_0}^{r_0+\Delta r} \ln(p_f/p_d) dr. \quad (47)$$

If we define an apparent standard entropy, corresponding to the change of gas at  $p^\ominus$  to the hydride phase at pressure  $p$ , by

$$\Delta S^\ominus(\text{app}) = \frac{\Delta H(\text{app})}{T} - \frac{R}{2} \ln(p/p^\ominus) \quad (48)$$

then case (ii) corresponds to<sup>11</sup>

$$\oint \Delta S^\ominus(\text{app}) dr = 0 \quad (49)$$

*i.e.*  $\Delta S^\ominus(\text{app})$  behaves as a function of state. It seems likely (see below) that the behaviour of real systems lies between these two extremes.

In the general case it also follows from eqn (47) that

$$\begin{aligned}\oint \Delta H(\text{app}) dr &= \int_{r_0}^{r_0+\Delta r} [\Delta_f H(\text{app}) + \Delta_d H(\text{app})] dr = \frac{R}{2} \frac{\partial}{\partial(1/T)} \int_{r_0}^{r_0+\Delta r} \ln \frac{p_f}{p_d} dr \\ &= \frac{\partial}{\partial(1/T)} [\Delta_i S(\text{cycle})].\end{aligned}\quad (50)$$

Eqn (50) constitutes a thermodynamic consistency test of the analysis of experimental data.

Previous discussions of the thermodynamics of metal-hydrogen systems have derived so-called standard free energies and entropies.<sup>13</sup> It is important to stress that it is essential that the standard states be defined explicitly otherwise ambiguity and misunderstanding can arise. For example, the standard entropy of the equilibrium state with respect to

Table 1.

|                                       |                                     | $-\Delta_i G(\text{cycle})$                              | $\Delta_i S(\text{cycle})$                 | $d[\Delta_i S(\text{cycle})]/d(1/T)$ | $\Delta H(\text{app, cycle})$ |
|---------------------------------------|-------------------------------------|--|--|--------------------------------------|-------------------------------|
|                                       | $T/\text{K}$                        | $\text{J (mol H)}^{-1}$                                  | $\text{J K}^{-1} (\text{mol H})^{-1}$      | $\text{J (mol H)}^{-1}$              | $\text{J (mol H)}^{-1}$       |
|                                       |                                     | Flanagan <i>et al.</i> <sup>14</sup> : annealed Pd strip |  |                                      |                               |
| isothermal                            | 200                                 | 980  | 4.9  | 1160                                 | 1350                          |
|                                       | 273                                 | 865  | 3.2  |                                      |                               |
|                                       | 383                                 | 810  | 2.1  |                                      |                               |
|                                       |                                     | present research: another sample of Pd strip             |  |                                      |                               |
| isothermal<br>( $\Delta r = 0.0665$ ) | 300.2                               | (a)<br>690   | (b)<br>592                                 | (a)<br>2.30                          | (b)<br>1.97                   |
|                                       | isobaric<br>( $\Delta r = 0.0685$ ) | 289–300  | (c)<br>713                                 | (e)<br>661                           | (c)<br>2.44                   |
|                                       |                                     |  | Evans and Everett: <sup>10</sup> Pd sponge |                                      |                               |
| isothermal<br>( $\Delta r = 0.56$ )   | 353                                 | (b)<br>958   | (b)<br>2.71                                | 2070                                 | 1975                          |
|                                       | 373                                 | 909  | 2.42                                       |                                      |                               |
|                                       | 393                                 | 830  | 2.11                                       |                                      |                               |

<sup>a</sup> Calculated by approximate eqn (8). <sup>b</sup> Calculated by exact eqn (16). <sup>c</sup> Calculated by approximate eqn (35). <sup>d</sup> Calculated by exact eqn (28). <sup>e</sup> Calculated by exact eqn (28)+approximate eqn (53).

hydrogen at pressure  $p^\ominus$  (usually taken as atmospheric pressure) and pure metal is given by

$$\Delta_f S^\ominus(\text{E}) = \frac{\Delta_f H}{T} - \frac{R}{2} \ln(p_e/p^\ominus), \quad (51)$$

while for the system in state 3 (fig. 3), again starting from the same standard state, is

$$\Delta_f S^\ominus(3) = \frac{\Delta_f H}{T} - \frac{R}{2} \ln(p_t/p^\ominus). \quad (52)$$

Values of  $\Delta_f S^\ominus(\text{E})$  can only be calculated if  $p_e$  is known. Although this is not generally possible, it may in some circumstances be adequate to estimate  $p_e$  from eqn (30).

## Experimental and Results

The above discussion may be illustrated using the data of Kishimoto (unpublished) and Flanagan,<sup>14</sup> together with the work of Evans and Everett<sup>10</sup> and data from the present investigation.

In the former, thin, well annealed palladium strips were used in a conventional Sieverts apparatus. A series of measurements of plateau pressures were made in the temperature range 200–383 K and used to calculate  $\Delta_i G(\text{cycle})$  and  $\Delta_i S(\text{cycle})$  from eqn (8) (table 1). Since it was not possible to obtain complete hysteresis loops at lower temperatures, the alternative calculation through eqn (16) could not be applied to these data. Apparent enthalpies of formation and decomposition were calculated from the temperature dependence of the plateau pressures.

In the present work another sample of palladium was used in an isothermal experiment at 300.2 K, and an isobaric experiment at  $p = 7.65$  Torr (1.02 kPa). The results are presented in fig. 7 and 8. The hysteresis loops were not taken to complete conversion, but both the isobaric and isothermal experiments spanned approximately the same range of  $r$  (0.03–0.10). Table 1 includes values of  $\Delta_i G(\text{cycle})$  and  $\Delta_i S(\text{cycle})$  calculated for the

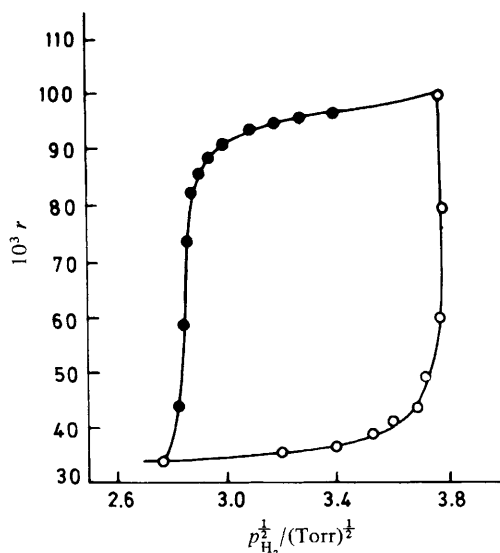


Fig. 7. Isothermal hysteresis loop at 300.2 K for palladium-hydrogen:  $r$  is shown as a function of  $p_{\text{H}_2}^{1/2}/\text{Torr}^{1/2}$  (this work).

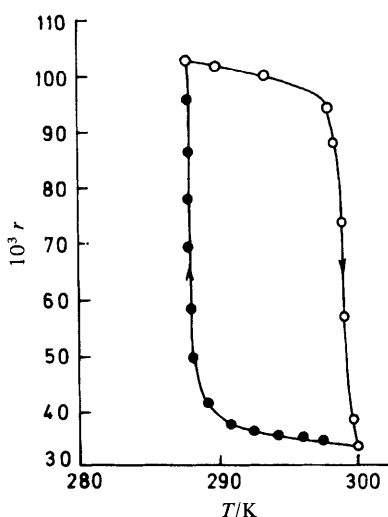


Fig. 8. Isobaric hysteresis loop at 7.65 Torr for palladium-hydrogen:  $r$  is shown as a function of  $T$  (this work).

isothermal experiment using eqn (8) and (16) and for the isobaric experiment using eqn (35), (28) and (53). In each case the approximate eqn (8) and (35) gave larger absolute values of both  $\Delta_1 G(\text{cycle})$  and  $\Delta_1 S(\text{cycle})$  than the exact equations, which take account of the diffuseness of the transitions.

Evans and Everett, using the apparatus and Pd sponge sample described by Everett and Nordon,<sup>3</sup> reported hysteresis loops between complete conversion and recovery of the  $\alpha$ -phase, *i.e.*  $r$  in the range 0.03–0.59, at temperatures in the range 353–393 K. Values

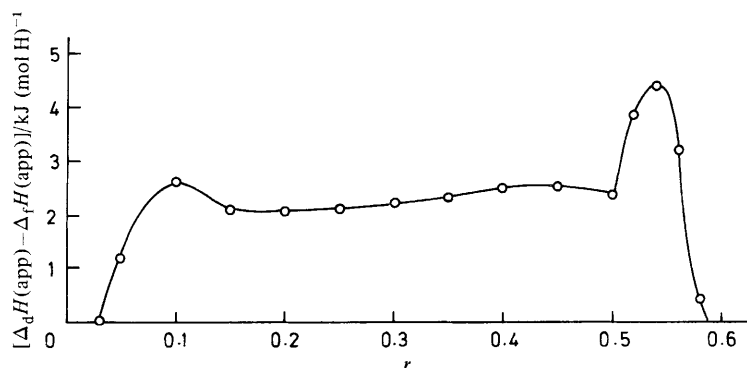


Fig. 9.  $[\Delta_d H(\text{app}) - \Delta_f H(\text{app})]/\text{kJ (mol H)}^{-1}$  as a function of  $r$  for the hydrogen–palladium system at 400 K (Evans and Everett<sup>10</sup>).

of  $\Delta_i G(\text{cycle})$  and  $\Delta_i S(\text{cycle})$  obtained in this work and calculated using eqn (16) are given in table 1, while  $[\Delta_f H(\text{app}) - \Delta_d H(\text{app})]$  calculated from their data is shown as a function of  $r$  in fig. 9.

### Discussion

It has been postulated from earlier work<sup>1,2</sup> that in isothermal hysteresis  $\Delta_i G(\alpha \rightarrow \beta) = \Delta_i G(\beta \rightarrow \alpha)$  and a similar postulate for isobaric hysteresis is that  $\Delta_i G(\beta \rightarrow \alpha)$  at  $T_d = \Delta_i G(\alpha \rightarrow \beta)$  at  $T_r$ , in which case  $p_e$  and  $T_e$  can be calculated from eqn (30) and (32). This would imply that  $\Delta_i G(\text{cycle})$  in isothermal hysteresis should be independent of temperature *i.e.* that the hysteresis phenomena conform to case (ii) above.

The data presented in table 1 show, however, that both  $\Delta_i G(\text{cycle})$  and  $\Delta_i S(\text{cycle})$  depend on temperature, so that the systems fall into a class intermediate between (i) and (ii). The magnitudes of these quantities for one of the samples used by Flanagan *et al.* are broadly similar to those obtained from the work of Evans and Everett, although the temperature coefficients are very different. The other sample of Flanagan *et al.* leads to rather smaller values of both quantities, but this may not be significant because the measurements were made on different samples and over a much smaller range of  $r$ .

Eqn (50) indicates a thermodynamic link between the temperature dependence of  $\Delta_i S(\text{cycle})$  and  $\Delta H(\text{app, cycle})$ . The data of Evans and Everett give  $d[\Delta_i S(\text{cycle})]/d(1/T) = 2070 \text{ J (mol H)}^{-1}$  while, from fig. 9,  $\Delta H(\text{app, cycle}) = 1975 \text{ J (mol H)}^{-1}$ , thus checking the internal consistency and the reliability of their calculations of the apparent enthalpy. A second check on the applicability of case (ii) is to compare  $\Delta H(\text{app, cycle})$  with  $-\Delta_i G(\text{cycle})$ : they should be equal. At 373 K  $-\Delta_i G(\text{cycle}) = 909 \text{ J (mol H)}^{-1}$ , which is less than one half of  $\Delta H(\text{app, cycle})$ .

The work of Flanagan *et al.* gives  $d[\Delta_i S(\text{cycle})]/d(1/T) = 1150 \text{ J (mol H)}^{-1}$ , while the apparent enthalpies calculated from their data lead to  $\Delta H(\text{app, cycle}) = 1350 \text{ J (mol H)}^{-1}$ . Although this differs from the value derived from  $\Delta_i S(\text{cycle})$ , it is probable that it is within the experimental uncertainty of the enthalpy calculation which was based on approximating the hysteresis loop by a rectangular loop. Again both quantities differ significantly from  $\Delta_i G(\text{cycle}) = 865 \text{ J (mol H)}^{-1}$  at 273 K, thus illustrating the inadequacy of case (ii).

A direct comparison between isothermal and isobaric hysteresis follows from fig. 7 and 8.  $-\Delta_i G(\text{cycle})$  at 300.2 K calculated from the approximate formula (8),  $690 \text{ J (mol H)}^{-1}$ , is higher than that,  $592 \text{ J (mol H)}^{-1}$ , obtained by integration [eqn (16)].

To apply eqn (35) to the isobaric experiment it is necessary to know  $\Delta_f H$ . Reported calorimetric values are  $-19.2$ ,<sup>15</sup>  $-19.2$ <sup>16</sup> and  $-20.1$ <sup>17</sup> kJ (mol H)<sup>-1</sup>. From fig. 8,  $\Delta T = 10.9$  K,  $T_e \approx (T_f T_d)^{\frac{1}{2}} = 293.4$  K. Taking a value of  $-19.2$  kJ (mol H)<sup>-1</sup> for  $\Delta_f H$  gives  $-\Delta_i G(\text{cycle}) = 713$  J (mol H)<sup>-1</sup> at the mean temperature of 293.4 K. If the integration indicated by eqn (28) is used, together with the approximation

$$-\Delta_i G(\text{cycle}) = (T_f T_d)^{\frac{1}{2}} \Delta_i S(\text{cycle}) \quad (53)$$

a lower figure [661 J (mol H)<sup>-1</sup>] results.

Thus values of  $\Delta_i G(\text{cycle})$  and  $\Delta_i S(\text{cycle})$  calculated from isothermal and isobaric hysteresis are in reasonably close agreement. This is to be expected since the isobaric loop covers a range of only 11 K, over which  $\Delta_i G(\text{cycle})$  will not vary appreciably (*cf.* table 1):  $\Delta_i G(\alpha \rightarrow \beta)$  and  $\Delta_i G(\beta \rightarrow \alpha)$  will be essentially the same in both types of experiment. It follows that because of this small temperature range these data cannot be used to distinguish between cases (i) and (ii). For this to be possible it would be necessary to seek conditions under which the isobaric loop covers a much wider range of temperature.

It is of considerable practical importance to observe that, provided  $\Delta T$  is not too large,  $\Delta_i G(\text{cycle})$  calculated from isobaric hysteresis is a reasonable approximation to  $\Delta_i G(\text{cycle})$  derived from isothermal hysteresis at the mean temperature. For many systems isobaric but not isothermal data are available, so that if  $\Delta H$  for the change is known, the extent of isothermal hysteresis can be estimated; conversely  $\Delta T$  for isobaric hysteresis can be calculated from a knowledge of the isothermal behaviour.

### Hysteresis in Metal Oxide Systems

Data for metal oxide systems are less extensive and are probably of lower precision than those for the palladium–hydrogen system. Here we make use of the work of Eyring and his coworkers who have measured both isothermal and isobaric hysteresis loops for a series of terbium and praseodymium oxides.<sup>18–20</sup> The isothermal data have been analysed by Porter<sup>21</sup> to obtain values of  $\Delta_i G(\text{cycle})$  (which he denotes by  $Q$ ). He used a different method of analysis in terms of the first equality of eqn (16), which is equivalent to that using the last equality, and expressed the results in terms of the conversion of one mole of metal. The values of  $\Delta_i G(\text{cycle})$  were found to vary erratically with temperature: no temperature dependence can be discerned. Recalculation to correspond to the reaction of one mole of  $\frac{1}{2}\text{O}_2(\text{g})$  leads to the mean values given in table 2. In three of the four systems analysed by Porter  $\Delta_i G(\text{cycle})$  is close to 2.5 kJ (mol O)<sup>-1</sup>; the fourth gives a much higher but more uncertain value which is, however, not inconsistent with that for the other systems. Eyring's data for  $\text{Pr}_7\text{O}_{12}/\text{Pr}_9\text{O}_{16}$  which were not included by Porter lead to a value of 0.5 kJ (mol O)<sup>-1</sup>, although the results of a later study by Inaba and Naito<sup>22</sup> give 1.21 kJ (mol O)<sup>-1</sup>.

Comparison of isothermal and isobaric measurements is possible for two systems (see table 2). In both instances, in the absence of calorimetric data, it has been necessary to use values of  $\Delta H(\text{app})$  in the calculations. In view of the other uncertainties it is unlikely that this approximation will lead to serious errors. In the case of  $\text{Tb}_2\text{O}_3$ – $\text{Tb}_7\text{O}_{12}$  the value of  $\Delta_i G(\text{cycle})$  calculated from isobaric measurements is some 2.80 times higher than that from the isotherms. For  $\text{Pr}_7\text{O}_{12}$ – $\text{Pr}_9\text{O}_{16}$  a similarly large discrepancy is found if one adopts the value from isothermal data of Eyring *et al.*, although the value of Inaba and Naito is close to the isobaric value.

On the basis of the available evidence, therefore, one cannot draw any firm conclusions concerning the applicability of the equations developed in this paper to oxide systems. Because of the known sensitivity of the results to the pretreatment of the sample it is important that isothermal and isobaric experiments be carried out on the same sample and that the recoverability of the system be confirmed experimentally. It is not clear to what extent this condition was satisfied in the work on the metal–oxygen systems.

Table 2.

| reaction<br>[for<br>addition of<br>$\frac{1}{2}(\text{O}_2)$ ]  | $T$ or $T$<br>range | ref.    | isothermal:<br>$-\Delta_i G(\text{cycle})$<br>kJ (mol O) $^{-1}$ | $\Delta T$<br>K  | $(T_i T_d)^{\frac{1}{2}}$<br>K | isobaric                         |   |
|---|---------------------|---------|--|------------------|--------------------------------|----------------------------------|---|
|   |                     |         |  |                  |                                | $\Delta H$<br>kJ (mol O) $^{-1}$ | $-\Delta_i G(\text{cycle})$<br>kJ (mol O) $^{-1}$ |
| $\frac{7}{8}\text{Tb}_2\text{O}_3/\frac{3}{8}\text{Tb}_7\text{O}_{12}$<br>( $\text{TbO}_{1.50}/\text{TbO}_{1.71}$ )       | 981–1079            | 19, 21  | $2.51 \pm 0.38$  | 78.3             | 1205.8                         | 108                              | 7.01  |
| $\frac{1}{8}\text{Tb}_7\text{O}_{12}/\frac{7}{8}\text{Tb}_{11}\text{O}_{20}$<br>( $\text{TbO}_{1.71}/\text{TbO}_{1.82}$ ) | 760–804             | 21      | $3.56 \pm 1.15$  |                  |                                |                                  |   |
| $\frac{9}{8}\text{Pr}_7\text{O}_{12}/\frac{7}{8}\text{Pr}_9\text{O}_{16}$<br>( $\text{PrO}_{1.71}/\text{PrO}_{1.78}$ )    | 973<br>838          | —<br>22 | 0.5<br>1.21  | 9.3 <sup>a</sup> | 854.7 <sup>a</sup>             | 118.6 <sup>a</sup>               | 1.29 <sup>a</sup>                                 |
| $5\text{Pr}_9\text{O}_{16}/9\text{Pr}_5\text{O}_9$<br>( $\text{PrO}_{1.78}/\text{PrO}_{1.80}$ )                           | 737–776             | 21      | $2.48 \pm 0.31$  |                  |                                |                                  |   |
| $6\text{Pr}_5\text{O}_9/5\text{Pr}_6\text{O}_{11}$<br>( $\text{PrO}_{1.80}/\text{PrO}_{1.83}$ )                           | 708–753             | 21      | $2.20 \pm 0.30$  |                  |                                |                                  |   |

<sup>a</sup> Ref. (18)

## Conclusions

The analysis presented in this paper leads to both approximate and exact equations for the calculation of the loss of free energy and the production of entropy in cycles both at constant temperature and constant pressure. Provided that the temperature range involved in isobaric hysteresis is not too large and the enthalpy of reaction is known, the quantities calculated from such data are in good agreement ( $\pm 6\%$ ) for palladium–hydrogen with those obtained from isothermal measurements. The status of apparent enthalpies derived from the temperature dependence of isothermal measurements is examined. Two extreme cases are identified in which (i) the entropy production is independent of temperature, when the apparent enthalpies are measures of the true enthalpies; (ii) the loss in free energy is independent of temperature, when the apparent enthalpy, integrated round the cycle, is equal to the loss in free energy. The behaviour of the palladium hydrogen system appears to fall between these two limits. Available evidence for rare-earth metal–oxygen systems is inconclusive.

T. B. F. and his coworkers at the University of Vermont acknowledge financial support by the N.S.F.

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Paper 5/1814; Received 18th October, 1985