A thermodynamic model of hysteresis in phase transitions and its application to rare earth oxide systems


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A thermodynamic model of hysteresis in phase reactions based on regular solution theory is developed by invoking metastabilities. The effect of enthalpy and entropy change, pressure, temperature, and interaction energy on the hysteresis curve term is explored. The influence of a variation of the interaction term with temperature and composition is also studied. Observed hysteresis for the phase reactions $\text{Tb}_2O_7 + \text{Pr}_2O_3 + 3/4\text{O}_2$ and $\text{Pr}_2\text{O}_3 + 9/7\text{Pr}_2\text{O}_3 + 2/7\text{O}_2$ is discussed and the theory is applied to each case. The experimental details of data acquisition and the observed hysteresis in the praseodymium oxide reaction are given.

INTRODUCTION

Hysteresis was first reported by Ewing in his work on magnetic systems and later by van Bemmelen in the adsorption of water on silica gel. Early attempts to establish a general thermodynamic theory of hysteresis were made by Brillouin and Duhem, with limited success owing to the small amount of experimental data available. Since then the phenomena of hysteresis have been well established, for example, in ferromagnetic materials, melting and crystallization of salts, adsorption-desorption processes, configurational changes in macromolecules, etc. Less numerous, however, are attempts to analyze these nonequilibrium phenomena and to elucidate the molecular origin of the underlying metastabilities.

For a definition of hysteresis consider a system defined by a set of independent external variables $(x_1, x_2, x_3, \ldots)$. If the system is taken from a state $A$ to a state $B$ along a given path, the dependent variable will pass through a certain set of values. Now, if the system is returned from state $B$ to state $A$ along the same path, then the process is called a reversible or equilibrium process. If, however, the path taken by the dependent variable during the change from $A$ to $B$ is different from that during the change from $B$ to $A$, and if all points on both paths correspond to stable, reproducible values of the dependent variables, then the change $A=B$ is said to exhibit hysteresis.

Hysteresis can be demonstrated graphically by plotting the external independent variable $x$ (e.g., temperature, pressure, pH values, etc.) against the internal dependent variable $y$ (e.g., volume, mole fraction, absorbance, etc.). A system showing hysteresis does not exhibit a unique relationship between the external independent variable $x$ and an internal dependent variable $y$. The internal variable can have values corresponding to any point within an area in the $xy$ plane, called the hysteresis loop. This hysteresis region is bounded by two curves, one which represents the states through which the system passes when the hysteresis region is approached from small values of $x$, and $x$ is increased until the hysteresis region is passed; the other boundary curve corresponds to decreasing values of $x$. Any point within the hysteresis loop can be reached by a suitable alteration of increasing and decreasing increments in $x$. This process is called scanning. The curves produced by the action of scanning are called scanning curves. This is also characteristic of hysteresis phenomena, and like the main branches of the hysteresis loop, they are also stable and reproducible.

As in the case of equilibrium or reversible phase transitions, systems exhibiting hysteresis have the property that for all values of the independent variable $x$ up to the transition value $x(A-B)$ the probability of transition is very small but as this value is approached the probability increases to unity over a small range of $x$ values. In equilibrium phase transitions the change occurs at a unique value of $x$, whereas in hysteresis the transition normally takes place over a small range of $x$. The study of hysteresis has two main aspects which are essential to a satisfactory understanding of the phenomena. One is a statistical mechanical interpretation in terms of molecular behavior, and the second is phenomenological thermodynamic correlation of the various experimental measurements which can be made on a system.

An early statistical model of hysteresis which should be mentioned, since it has the same general features as the model investigated in this communication, was developed by Lacher. This model was developed for the absorption-desorption of hydrogen in metals particularly palladium. Additional contributions to Lacher's model were made by Everett et al.

A more general model, with a range of applicability to all hysteresis problems, was proposed by Everett et al., and extended by Enderby. In this model Everett assumes that a system exhibiting hysteresis can be treated as an assembly of independent domains, with the characteristics of a given domain being independent of the states of its neighbors. Here, domain is used to mean a group of molecules, or some element of the system, which can exist in one of two states. The conversion from one state to the other is brought about by a change in the external variable $x$. If state $A$ is stable at small values of $x$, then on increasing $x$ a change to state $B$ occurs at $x(A-B)$, while reversion to $A$ on lowering $x$ takes place at a value $x(B-A)$, smaller than $x(A-B)$. At least one of these changes must occur irreversibly. The values of $x(A-B)$ and $x(B-A)$ differ from domain to
FIG. 1. A van der Waals type curve representing the phase transformation between states A and B. On the abscissa the internal parameter (e.g., volume or extent of reaction, in this case mole fraction) is plotted against the external parameter (e.g., temperature or pH). $\Delta H^\ominus = 0.7$ and $\Delta S = 1.7$ in Eq. (1.8).

state develops metastability. For example, hysteresis would occur if the transition from state A to B occurred at equilibrium [$x = x(B)$] and the transition from B back to A occurred at $x(B-A)$. In this case, state A would never be metastable, whereas state B would be metastable in Region D.

The object of the present work is to describe hysteresis quantitatively using a macroscopic thermodynamic model of the van der Waals type. Hysteresis in this model is derived from an interaction term $\Gamma$, which describes the net interaction energy between systems of states $A$ and $B$ in the phase transition and from invoking metastable states. This model is designed to reproduce the hysteresis loop from measurable thermodynamic quantities.

Another purpose of this paper is to report the experimental results of the isobaric measurements of the phase reaction $\text{PrO}_1.74 + 0.032\text{O}_3 = \text{PrO}_1.78$ and to apply the thermodynamic model of hysteresis studied in this paper to the experimental data on hysteresis for the phase reactions in the systems $\text{PrO}_1.74 - \text{PrO}_1.78$ and $\text{ThO}_1.900 - \text{ThO}_1.714$.

Section I provides a general discussion on how hysteresis is arrived at using Eq. (1.2). The free energy curves in the hysteresis region and the relationships between $\Gamma$, $\Delta H^\ominus$, and $\Delta S$ needed to insure metastabilities are also examined. Finally in this section the temperature dependence of $\Gamma$ is discussed for the purpose of correlating the experimental data. In Sec. II the isobaric measurement for the phase reaction in the system $\text{PrO}_1.74 - \text{PrO}_1.78$ is given and the application of the theoretical model to the hysteresis of $\text{PrO}_1.74 - \text{PrO}_1.78$ and $\text{ThO}_1.900 - \text{ThO}_1.714$ is presented.

I. GENERAL CONSIDERATIONS OF THE MODEL

Consider the phase transformation

$$A = B,$$

(1.1)

where $A$ and $B$ represent two solid phases whose transformation exhibits hysteresis. For the transformation $A = B$ as the phase transition point is approached, some $B$ systems will begin to appear in the $A$ matrix at the expense of $A$ systems. An analogous transformation occurs in the reverse direction $B - A$. Thus in this case near the transition point the Gibbs free energy of the total system can be written as

$$G = N_A \mu_A + N_B \mu_B + \frac{N_A N_B}{N_A + N_B} \Gamma$$

$$+ (N_A + N_B) kT \left[ x_B \ln x_B + (1 - x_B) \ln(1 - x_B)\right],$$

(1.2)

where $x_B$ is the mole fraction of $B$; $\Gamma$ represents the net interaction energy between $A$ and $B$; and $N_A$ and $N_B$ represent the number of elementary units (e.g., atoms, or molecules) of $A$ and $B$, respectively. The model given by Eq. (1.2) is well known in the area of liquid and solid mixtures and magnetic systems. Here we apply this model to phase changes that exhibit hysteresis.

When the system is at equilibrium, $G$ is a minimum. To minimize $G$, the Lagrange multiplier method is
FIG. 2. Gibbs free energy curves where the free energy $G^*$ is plotted against mole fraction $x_B$ for different temperatures. The values $\Delta H^* = 0.7$ and $\Delta S = 1.7$ are used in Eq. (1.9).

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![Diagram of Gibbs free energy curves](image)

FIG. 3. The free energy values at the local minima in Fig. 2 are plotted against temperature.

An understanding of the nature of the metastabilities can be achieved through a consideration of the free energy function Eq. (1.2) at constant temperatures in the region of the van der Waals type phenomena. Using Eqs. (1.4), (1.5), and (1.7), Eq. (1.2) becomes

$$G^* = (\Delta H^* - T^* \Delta S) x_B + x_B (1-x_B) + T^* [x_B \ln x_B + (1-x_B) \ln (1-x_B)],$$

(1.9)

where $G^* = G / (N_A + N_B) - \mu_A / \Gamma$. Figure 2 shows a series of isotherms constructed from Eq. (1.9) with $x_B$ being plotted against $G^*$ with the same constant $\Delta H^*$ and $\Delta S$ as used for Fig. 1.

When Eq. (1.9) is plotted in three dimensions with $T^*$ as the other variable, these curves form a surface with two free-energy valleys separated by a ridge. The two valleys represent states of stability, while the ridge is an energy barrier which prevents the system from moving from one valley to the other. If the system is not at the equilibrium transition temperature, one valley will be energetically more stable than the other. But the system may be in the less stable state (metastable state) owing to the energy barrier preventing the system from moving to the more stable state. This will lead to hysteresis.

In the following discussion the idea of free energy curves will be used to show how hysteresis can arise (note Figs. 1, 2, and 3). If one starts, at a tempera-
ture near zero, the system will follow a path of minimum free energy represented in Figs. 1–3 by $I\rightarrow E$.

As $T^*$ increases, the system reaches $E$, where two possibilities arise since the minima $E$ and $G$ correspond to the same free energy. If the system can cross the energy barrier $F$ (Fig. 2) as in the case of an equilibrium process, the system would attain an equilibrium distribution between the two states. On the other hand, if the system cannot cross the barrier $F$, then in order to reach Region $B$, the temperature must be increased until at point $II$ the energy barrier no longer exists and the system can move to III in Region $B$, which is now the only thermodynamically stable state. Under these conditions the system will follow the path from states $A$ to $B$, $I\rightarrow E\rightarrow II\rightarrow III$. In a similar way, the path followed from states $B$ to $A$ with decreasing temperatures will be $III\rightarrow G\rightarrow IV\rightarrow I$.

In comparing Figs. 1, 2, and 3, the following should be noted. In Fig. 1 the curves $IEE$ and $IIIIV$ correspond to the local minima in Fig. 2, states $A$ and $B$, respectively, and the curve $IIFIV$ corresponds to the local maximum in Fig. 2. The equilibrium point $x(E)$ does not coincide with the center of the hysteresis loop in the model (Fig. 1). Rather, $x(E)$ marks the point where both the free energy minima have the same value of $G^*$ (note Fig. 2 at $T^*=0.412$). The line segments $EF$ and $FG$ in Fig. 1 are equal in length. In Fig. 3 the equilibrium point corresponds to the point where the curves representing systems $A$ and $B$ cross. Figure 3 can be very useful in finding the equilibrium point in hysteresis-type phenomena.

In a similar way other thermodynamic properties of the system, in the hysteresis region, could be calculated from the free energy.

Since $\Delta H^*$ and $\Delta S$ are experimentally determined quantities, $\Gamma$ is the only parameter in Eq. (1.8) to be adjusted in fitting the experimental data. Thus, for a particular phase transformation, $\Gamma$ must be determined so that the experimental and theoretical curves can be compared.

In Sec. II the data are interpreted by varying $\Gamma$ with respect to temperature. It will therefore be desirable to let $\Gamma$ vary linearly with temperature and compare the hysteresis loops so calculated with those found with constant $\Gamma$.

Since thermodynamically the transition behavior of cooperative systems with metastabilities can be described by state functions of the van der Waals type, Eq. (1.8) will be examined to find under what conditions of $\Gamma$, $\Delta H^*$, and $\Delta S$ a van der Waals type behavior will be exhibited.

In the discussion that follows, positive values of $\Delta H^*$ will be used. The theoretical results for negative $\Delta H^*$, which correspond to most experimental phase transformations, can be obtained from the positive results by a change in sign of $\Delta H^*$ and $\Delta S$ and a reflection along the vertical line corresponding to $x_B=0.5$.

To get a van der Waals type equation from Eq. (1.8), we plot the external independent parameter $T^*$ against the internal dependent parameter $x_B$. Since $x_B$ ranges from zero to one, two cases must be considered. In the first case the numerator can become zero as $x_B$ varies. This corresponds to values of $\Delta H^*$ between zero and one and will be called Case I. Case II will be when $\Delta H^*$ is greater than or equal to one.

In Case I both the numerator and denominator can become zero as $x_B$ varies. In this case the numerator will become zero either before or after the denominator as $x_B$ increases. If the numerator becomes zero before the denominator, van der Waals type curve will not be obtained (note Fig. 4). In the other case the denominator will reach zero first and a van der Waals type curve can be obtained, which means hysteresis can occur. Thus, with a fixed $\Delta H^*$, the range of values of $\Delta S$ which ensure a van der Waals type curve can be obtained by setting the denominator and numerator equal to zero and solving for $\Delta S$ in Eq. (1.8). The result is

$$\Delta S<\ln\frac{1+\Delta H^*}{1-\Delta H^*};$$

(1.10)

A lower limit on $\Delta S$ can be obtained by taking the derivative of Eq. (1.8) with respect to $x_B$ and setting this equal to zero. The result is

$$\Delta S=\frac{(1+\Delta H^*)}{x_B(1-x_B)}-\ln\frac{1-x_B}{x_B}.$$

(1.11)

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Examination of Eq. (1.11) shows a maximum and a minimum characteristic of the van der Waals type curves will occur only if \( \Delta S > 2 \Delta H^* \). Combining this result with Eq. (1.10), we find that hysteresis can occur only if

\[
2 \Delta H^* < \Delta S < \ln \frac{1 + \Delta H^*}{1 - \Delta H^*},
\]

where again \( \Delta H^* \) is between zero and unity. This case is illustrated in Fig. 4.

Case II is much simpler since the numerator never becomes zero. Thus, from Eq. (1.12), \( \Delta S \) has a lower boundary \( \Delta S > 2 \Delta H^* \) with no upper boundary. The result of this case is illustrated in Fig. 5.

Next consider \( \Gamma \) a function of temperature. Expanding \( \Gamma' \) in a power series of temperature and truncating the series after the second term yields a linear function:

\[
\Gamma'(T) = \Gamma_0 + \Gamma_1 T.
\]

Substituting Eq. (1.13) for \( \Gamma' \) in Eq. (1.2) and minimizing \( G \) as before yields

\[
T^* = \frac{1 - 2x_B + \Delta H^*}{\ln[(1 - x_B)/x_B] + \Delta S - \Gamma_1(1 - 2x_B)},
\]

where \( \Gamma_1 \) is in units of \( k \) (the Boltzmann constant), \( T^* = T/\Gamma_0 \) and \( \Delta H^* = \Delta H^0/\Gamma_0 \). The behavior of Eq. (1.14) at different values of \( \Gamma_1 \) is illustrated in Fig. 6. As \( \Gamma_1 \) decreases, the van der Waals curve becomes longer and wider until the value of \( x_B \) which makes the denominator zero exceeds the value of \( x_B \) which makes the numerator zero. In this case a van der Waals type curve will no longer be observed. The numerator will become zero at a fixed value of \( x_B \) while the denominator will become zero depending upon the value of \( \Gamma_1 \). This means the hysteresis loop will have a maximum length greater than the length at \( \Gamma_1 = 0 \) (i.e., constant \( \Gamma \)). Noticing also that the equilibrium temperature remains constant with varying values of \( \Gamma_1 \).

Linear variations of \( \Gamma \) with composition and with composition–temperature have also been considered. The hysteresis loops obtained from considering the composition dependence of \( \Gamma \) cannot be made longer than those obtained with \( \Gamma \) constant. The hysteresis loops can be made only narrow and short with an upward shift. Considering \( \Gamma \) to depend on both temperature and composition gave results comparable to those already investigated. Since the data to be presented later are to be fit using only a temperature dependent \( \Gamma \) the derivation and graphical description of the composition and composition–temperature dependence are not included. It was disappointing that the length and width of the loops could not be modified by changing \( \Gamma \) alone. Such changes require the variation of either \( \Delta H^* \) or \( \Delta S \).

II. APPLICATIONS

The higher oxides \( (RO_2) \), \( 0 \leq \delta \leq 0.5 \) of cerium, praseodymium, and terbium are a complex set of fluorite-related phases. They include a compositional homologous series \( R_0Zn-2 \), \( 4 \leq n \leq \infty \) of a known structural homologous series where \( 7 \leq n \leq 12 \), as well as two phases of wide composition range; \( 0 \leq \delta \leq 0.28 \), \( \alpha \) phase, and \( 0.30 \leq \delta \leq 0.50 \), \( \sigma \) phase.\(^{16}\)

Most transformations to and from the widely nonstoichiometric phases \( \sigma \) and \( \alpha \) in the praseodymium oxide system and between the ordered intermediate phases of \( R_0Zn-2 \) of quite narrow composition range in either the praseodymium or terbium oxide system are accompanied by a demonstrated intrinsic hysteresis. Within each single phase region, including the grossly nonstoichiometric ones, the temperature–composition path is reversible. A significant point which will be dis-

![FIG. 5](image_url)

**FIG. 5.** Representative curves for \( \Delta H^* > 1 \) with constant \( \Gamma \), \( \Delta H^* \leq 1 \), and \( \Delta S \) takes values 0.5, 2.0, and 3.5 with hysteresis occurring for \( \Delta S > 2 \).

![FIG. 6](image_url)

**FIG. 6.** Representative curves for \( \Gamma \) as a function of temperature \( (\Gamma^* = \Gamma_1 + \Gamma_2 T) \). \( \Delta H^* = 0.7 \), \( \Delta S = 1.7 \), and \( \Gamma_1 = 0.15 \), 0.0, and –0.15.
cussed later is that in the intrinsic isobaric curves there are no regions where transformation between phases occurs at a fixed temperature but rather occurs over a range of temperatures. That is, if the temperature is increased by a small amount in the middle of a phase transformation, the metastable equilibrium point will be shifted but the system will not go to stable equilibrium.

Structurally the fluorite-related homologous series $R_2O_3$ is divided between the odd-$n$ members which have a relatively small triclinic unit cell and the even members whose primitive triclinic cells are twinned or quadrupled at the unit cell level to give larger monoclinic unit cells. The odd members have [135] fluorite planes in common, differing only in the spacing whereas the even members have [110] fluorite planes in common with distinctive spacing. The end member of the compositional series ($R_2O_3$) has a fluorite-related structure also but does not have a plane common to either the odd or other even members of the series.

It would not be surprising if the nature of transitions between odd and even members were different from odd and even members and if both were different yet from transitions between odd members and the sesquioxide. Hysteresis, which ultimately has a structural basis, should be qualitatively different for each type of transition.

A study is under way wherein the technique of high-resolution electron microscopy is applied to materials undergoing hysteresis. This technique affords imaging of the specimens at a resolution of about 3.5 Å to reveal, if not atoms themselves, small clusters of atoms and their arrangements during reaction.

Extant data from studies of Kordis and Eyring on the odd member-sesquioxide phase reaction

$$\text{Tb}_2\text{O}_3 = \frac{7}{2}\text{Tb}_2\text{O}_3 + \frac{3}{4}\text{O}_2$$  \hspace{1cm} (2.1)

will be treated theoretically according to the discussion in Sec. 1, and new measurements on the odd-odd phase reaction

$$\text{Pr}_2\text{O}_3 = \frac{9}{7}\text{Pr}_2\text{O}_3 + \frac{2}{7}\text{O}_2$$  \hspace{1cm} (2.2)

are to be reported here and treated theoretically.

A. Experimental part

1. Tensimetric experiments

Isobaric runs of the phase reaction shown in Eq. (2.2) were made on an Ainsworth-RV thermogravimetric balance with an accuracy of ± 20 µg. The mass of the sample was such that the change in composition between $\text{Pr}_2\text{O}_3$ and $\text{Pr}_2\text{O}_3$ corresponded to about 30 mg weight change. Temperatures were obtained to within ±2 °C by means of a calibrated Pt–Pt, 10% Rh thermocouple located 0.5 cm from the sample bucket. A large ballast system was used to reduce the oxygen pressure variation during reaction. The pressure variation due to the combined effects of the temperature cycling of the sample, the room temperature fluctuation, and the liberation and/or absorption of O₂ by the phase reaction amounted to ±0.3 Torr during any one run. The run at 0.90 Torr is an exception in that the constant oxygen pressure was maintained by two step pressure controls (one by manual and the other by an automatic controller) to within ±0.02 Torr for the entire run. The oxygen pressures were continuously monitored by means of a Datametrics capacitance manometer, type 1014A. The praseodymium oxide of purity 99.999% was supplied by Research Chemicals, Division of Nucor Corporation, and was used without further purification. Detailed experimental procedures (sample condition, data acquisition, etc.) have been previously described by Hyde et al. ¹⁸

Each hysteresis loop was traced between 520 and 700 °C at a given oxygen pressure and at the two extreme temperatures the specimen was annealed for several hours to ensure a well-ordered single phase for the reverse reaction. In manual runs, the temperature after each increment was held constant until no further changes in composition were observed.

B. Experimental results

1. Tensimetric measurements

Figure 7(a) shows isobars at two pressures (10.5 and 4.6 Torr) with various heating and cooling rates. As the rate of the programmed temperature changes be-
comes slower, the hysteresis loops approach the intrinsic one (i.e., time independent) and below a certain rate the loops coincide with the one that was traced manually. In monophasic regions the weight changes follow closely upon the temperature changes indicating rapid equilibration. However, in diphasic regions it takes about 2 h [Fig. 7(b)] to reach the new equilibrium position after each temperature increment. Once the metastable equilibrium is attained, the system remains fixed within the experimental time frame (it has been tested for weeks) unless the temperature and/or the pressure is altered. The existence of the equilibrium of the metastable state and thus the stability of the hysteresis loop form the basis of treating the directional process with equilibrium thermodynamics.8

The isobars recorded in Fig. 8 are the intrinsic hysteresis loops traced manually except for Run 0.90 (the run numbers are the nominal experimental oxygen pressures), where the rate of continuous temperature change is as indicated. The slope of the isobars was the same for all pressures. The widths of the hysteresis loops at the midpoint of the phase reaction appear constant within experimental error for the three greatest pressures. The width of the loop of Run 0.90 appears to be wider by about 4° than those at higher pressures. This trend to wider loops at lower pressures (and temperatures) is predicted by the theory and is even more pronounced in the case represented by Eq. (2.1). The loops also lengthen as expected.

Assuming classical phase transition behavior and taking the equilibrium temperatures at the middle of the width of the hysteresis loop the $\Delta H$ value calculated from these data is $-2.1$ kcal/Pr, which compares with $\Delta H = -1.8$ kcal/Pr.18

### 2. High-resolution microscopy

As a preliminary to a detailed high-resolution microscopic study of the reaction products during hysteresis, crystals of Pr$_6$O$_{12}$ have been reduced to Pr$_4$O$_9$ in the vacuum of the microscope. Invariably, under these conditions the material has transformed by disordering across the $\{135\}$ fluorite planes, giving uneven spacing (streaking in the diffraction pattern) in the images corresponding to planar intergrowths of the $n = 9$, 8, and 7 phases sometimes only one unit cell wide but extending along $\{135\}$ indefinitely.

In contrast, Pr$_4$O$_9$ or Pr$_9$O$_{12}$ has been observed to decompose directly to Pr$_4$O$_9$ only by the formation of more or less classical domains which appear to result from the growth of nuclei initiated at random in the parent material. Thus the electron microscopy suggests that a quite different type of phase reaction occurs in the two regions.

### C. Theoretical applications

The theoretical results will now be applied to hysteresis in phase transformations in the rare earth oxide systems. These can be represented in the following form:

$$\text{MO}_a + \frac{1}{2}b\text{O}_2 \rightarrow \text{MO}_{a+b}.$$  \hfill (2.3)

When we let $\text{MO}_a = A$ and $\text{MO}_{a+b} = B$ the Gibbs free energy equation analogous to Eq. (1.2) for this system is

$$G = N_A \mu_A + N_B \mu_B + \left[\frac{N_A N_B}{N_A + N_B}\right] \Gamma + \left(N_A + N_B\right) kT \left[\ln y_A + (1 - y_B) \ln(1 - y_B)\right].$$  \hfill (2.4)

Minimization of $G$ in this case is achieved by holding the total number of metal atoms ($N_A + N_B$) and oxygen atoms $[2N_A + aN_B + (a + b)N_B]$ constant. The result is Eq. (1.8), where

$$\Delta S = \Delta S^\circ + b/2 \ln P_O_2.$$  \hfill (2.5)

The activities of the metal oxide phases have been taken equal to unity.

It is necessary now to define some temperatures. First, the equilibrium temperature $T_w$ can be defined from Eq. (1.8) by $T_w \Delta S = \Delta H^\circ$, and secondly, the critical temperature $T_i$ is defined by $\Gamma = 2kT_i$.16 According to the thermodynamic model, at temperatures greater than or equal to $T_i$ the hysteresis phenomenon should no longer be observed. And as the temperature approaches $T_w$ from below, the hysteresis loop becomes narrower.

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It was pointed out by Neumann\(^8\) that from the hysteresis loop one can determine the entropy change due to irreversible changes. In nonequilibrium thermodynamics,\(^9\) the entropy change of a reaction can be divided as

\[
\frac{dS}{dT} = d_S + d_i S. \tag{2.6}
\]

The term \(d_S\) gives the contribution to the entropy which can be exchanged as heat with the environment, \(d_S = d_i Q/T\). This is the entropy contribution used in the above results. The second term, \(d_i S\), represents the irreversible contribution created internally within the system. This entropy change is related to the chemical contribution \(Ad\xi\) by

\[
Td_i S = Ad\xi, \tag{2.7}
\]

where

\[
A = - \sum_i \nu_i \mu_i, \quad \text{and} \quad d\xi = \nu_i d n_i.
\]

\(\mu_i\) denotes the chemical potential, \(\nu_i\) the stoichiometric coefficient, and \(n_i\) is the number of moles of component \(i\).

It can be shown that for the isobaric process of Eq. (1.1), \(\Delta S\) can be expressed as

\[
\Delta S = - T \int_{T_0}^{T} \frac{\Delta \mu}{\nu_i} d\xi.
\]

By expanding \(\Delta \mu\) in a power series of \(T - T_\text{eq}\), Eq. (2.9) becomes

\[
\Delta_i S = \frac{\Delta T^2}{2T} \left(\frac{1}{2} \Delta C_P - \Delta S\right)_\text{eq}. \tag{2.10}
\]

The values of \(\Delta_i S\) for the \(\text{PrO}_x\) and \(\text{TbO}_x\) systems as calculated from Eq. (2.10) are shown in Table 1 (\(\Delta C_P\) assumed zero). Notice that \(\Delta_i S\) represents a measure of the intrinsic irreversibility and that \(\Delta_i S\) for the Tb-O system is larger than for the Pr-O system.

In the Pr-O system it is possible to pick \(\Delta S\) values which will yield reasonably good theoretical fits of the

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<tr>
<td>3.33</td>
<td>1003</td>
<td>110.8</td>
</tr>
</tbody>
</table>

\(\Delta S(\text{PrO}_x) = -1.038; \Delta S'(\text{TbO}_x) = -2.34\), \(\Delta_i S\) and \(\Delta S\) are in units of \(R\), the gas law constant.

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experimental loops. A case where $\Delta S$ and $\Delta H$ are chosen in such a way as to improve the fit is illustrated in Fig. 10.

III. FURTHER DISCUSSION AND CONCLUSIONS

In view of the generality and simplicity of the macroscopic model of the van der Waals type developed and examined here, it is impressive to find reproduction of the experimental results on the rare earth oxides to the degree shown in the previous section.

It should be noted, however (see Figs. 8 and 9) that the present model can never account for the fact that constant temperature (or constant pressure) regions are never observed in hysteresis loops associated with rare earth oxide systems and that scanning loops are observed in these systems as well. In other words, the model can only provide the gross features of the main hysteresis loop between two phases.

One way of extending this treatment to account for the types of hysteresis characteristics mentioned above will be to introduce the domain effect into the present theoretical model and to associate with each set of domains a free energy function given by Eq. (1.2). Then from Everett’s work\(^{10,11}\) on the domain model of hysteresis, the two characteristics of hysteresis which cannot be explained by the present van der Waals type model can be accounted for easily. The work in progress is to investigate quantitatively such a synthesis.

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\(^{3}\) M. Brilliouin, C. R. Acad. Sci. 106, 416, 482, 537, 589 (1888); J. Phys. 8, 169 (1889).

\(^{4}\) P. Duhem, Mém. Acad. Belg. cn 4º, Mém. I, II, III, 54 (1896); Mém. IV, V, 56 (1896); Mém. IV, VI, 62 (1902).

\(^{5}\) J. A. Baldwin, J. Appl. Phys. 12, 555 (1941).


\(^{17}\) L. Prigogine, Étude Thermodynamique des Processus Irreversibles (Desour, Liège, 1947).


