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Acid-Base Models as Conceptual Aids to the Development of Thermochemical Cycles for Water Splitting. 1. Consideration of Simple Cycles Involving Oxides[1]

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Simple thermochemical cycles—those in which only one element besides H, O, and sometimes Cl undergoes oxidation and reduction—can be treated conceptually as a series of acid-base reactions. For workable cycles involving oxides, the Lux-Flood acid-base model is used; the maximum temperature for a workable cycle is 1300 K. Simple oxide cycles are classified according to their chemistries as (A) cycles involving stable high-oxidation-state oxides, (B) cycles involving unstable high-oxidation-state oxides, and (C) cycles involving unstable low-oxidation-state oxides. In type A and type B cycles, bases drive steam oxidation reactions and acids drive reductive thermal decompositions. In type C cycles, bases drive reductions and acids drive oxidations. Salts are formed in all of these cycles; completion of the cycles requires thermochemical splitting of the salts to regenerate the acids and bases. It is postulated that the standard enthalpy of reaction between the strongest acid and the strongest base used in a cycle is a measure of the chemical energy provided to the cycle by acid-base reactions. It is also shown that—in workable cycles—this standard enthalpy value must lie between -210 and -400 kJ/mol of evolved H_2. The acid-base postulates are combined with oxide decomposition temperatures in a scheme that can serve as a guide for the experimental development of new thermochemical cycles.

Thermochemical cycles for water splitting[2] employ thermal energy to drive a series of chemical reactions whose sum is simply H_2O + thermal energy = $H_2 + {}^1/_2O_2$. While several thermochemical cycles have been proposed and tested,[3] the search for cycles which might be industrially feasible continues. This search is sometimes hampered by a lack of reliable thermodynamic data. The purpose of this paper is to show how donor-acceptor models can (1) systemize the search for new thermochemical cycles and (2) help to predict reactions which might be used in thermochemical cycles, even when certain thermodynamic data are unavailable.

I. Definitions

(a) A *workable thermochemical cycle* is defined as one in which all of the chemical reactions proceed at temperatures less than about 1300 K. This temperature was chosen because high-temperature gas-cooled nuclear reactors (HTGRs)—a commonly suggested source of thermal energy for thermochemical cycles—are designed to operate at 1300 K or less.[4] Other factors important to the practicality of cycles—separation of reaction products, cost of materials, engineering efficiencies, etc.—are not discussed in this paper, which concerns itself only with the *chemical* feasibility of thermochemical cycles.

(b) A *simple thermochemical cycle* is defined as one in which only one element besides oxygen, hydrogen, and sometimes chlorine undergoes oxidation and reduction.

(c) *Decomposition temperature* is the lowest temperature at which ΔG for the evolution of a gas from a compound is 40 kJ mol^{-1} or less.

(d) A *thermally stable compound* is defined as one that does not undergo reductive thermal decomposition at temperatures below 1300 K. Water and Cr_2O_3(c) are thermally stable compounds by this definition.

(e) A *thermally unstable compound* is defined as one that is stable at 298 K but which undergoes reductive thermal decomposition at temperatures less than 1300 K. The oxides MnO_2(c), SO_3(g), and HgO(c) are thermally unstable compounds by this definition.

(f) A *high oxidation state compound* is defined as a compound in which the element most capable of undergoing oxidation or reduction has a *formal* oxidation state greater than +II. Examples include Na_2SO_4(c) and Fe_3O_4(c).

(g) A *low oxidation state compound* is defined as a compound in which the element most capable of undergoing oxidation or reduction has a *formal* oxidation state less than or equal to +II. Examples include Cu_2O(c) and $CdAl_2O_4$(c).

(h) In accord with the terminology proposed by Flood[5] and Lux,[6] an *oxide ion donor* (OD) is defined as a substance that has a greater tendency than water to release the hypothetical oxide ion, O^{2-}(g). Table I lists several oxygen-containing compounds according to their tendencies to release O^{2-}(g), relative to H_2O(g); the data for this and subsequent tables and figures were taken from the sources listed in ref 7. Such oxide-releasing reactions do not actually occur. However, the calculated tendencies of these species to act as ODs correspond in large part to their tendencies to act as Lewis bases (Figure 1) and to their relative tendencies to drive redox reactions (see Section II). For these reasons, the data in Table I are quite relevant to the reactions that take place in simple thermochemical cycles involving oxides.

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(1) Research sponsored by the Chemical Sciences Section, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp.

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Table I. Comparison of Some Oxide Ion Releasing Reactions

reaction	relative[a] $\Delta H_R°$, kJ/mol	ref	reaction	relative[a] $\Delta H_R°$, kJ/mol	ref
$Cs_2O(c) = 2Cs^+(g) + O^{2-}(g)$	−2320	7a	$CaCl_2(c) + H_2O(g) = Ca^{2+}(g) + 2HCl(g) + O^{2-}(g)$	−535	7a,f
$Na_2O(c) = 2Na^+(g) + O^{2-}(g)$	−1680	7a	$CdO(c) = Cd^{2+}(g) + O^{2-}(g)$	−433	7c
$2NaOH(c) = 2Na^+(g) + H_2O(g) + O^{2-}(g)$	−1480	7a	$MnO(c) = Mn^{2+}(g) + O^{2-}(g)$	−410	7d
$Na_2CO_3(c) = 2Na^+(g) + CO_2(g) + O^{2-}(g)$	−1360	7a	$MgO(c) = Mg^{2+}(g) + O^{2-}(g)$	−364	7f
$Li_2O(c) = 2Li^+(g) + O^{2-}(g)$	−1340	7a	$HgO(c) = Hg^{2+}(g) + O^{2-}(g)$	−333	7d
$Ag_2O(c) = 2Ag^+(g) + O^{2-}(g)$	−1240	7d	$FeO(c) = Fe^{2+}(g) + O^{2-}(g)$	−290	7d
$BaO(c) = Ba^{2+}(g) + O^{2-}(g)$	−1100	7f	$MgCl_2(c) + H_2O(g) = Mg^{2+}(g) + 2HCl(g) + O^{2-}(g)$	−267	7a,f
$2LiCl(c) + H_2O(g) = 2Li^+(g) + 2HCl(g) + O^{2-}(g)$	−1070	7a	$CoO(c) = Co^{2+}(g) + O^{2-}(g)$	−235	7d
$CaO(c) = Ca^{2+}(g) + O^{2-}(g)$	−983	7f	$ZnO(c) = Zn^{2+}(g) + O^{2-}(g)$	−184	7c
$Cu_2O(c) = 2Cu^+(g) + O^{2-}(g)$	−966	7d	$NiO(c) = Ni^{2+}(g) + O^{2-}(g)$	−145	7d
$BaCO_3(c) = Ba^{2+}(g) + CO_2(g) + O^{2-}(g)$	−831	7a,f	$CuO(c) = Cu^{2+}(g) + O^{2-}(g)$	−103	7d
$BaCl_2(c) + H_2O(g) = Ba^{2+}(g) + 2HCl(g) + O^{2-}(g)$	−738	7a,f	$H_2O(g) = 2H^+(g) + O^{2-}(g)$	0.0	7a
$CaCO_3(c) = Ca^{2+}(g) + CO_2(g) + O^{2-}(g)$	−575	7a,f	$CO(g) = C^{2+}(g) + O^{2-}(g)$	946	7c
			$CO_2(g) = CO^{2+}(g) + O^{2-}(g)$	1040	7c
			$O_2(g) = O^{2+}(g) + O^{2-}(g)$	1650	7c

[a] Relative standard enthalpy of reaction in kJ mol^{-1}. Relative $\Delta H_R° = \Delta H_R° - \Delta H_R°$ for $H_2O(g)$, where $\Delta H_R°$ for $H_2O(g) = 2H^+(g) + O^{2-}(g)$ equals 4235 kJ mol^{-1} and $\Delta H_f°$ for $O^{2-}(g)$ equals 920 kJ mol^{-1}. This value was taken from ref 26, p 722.

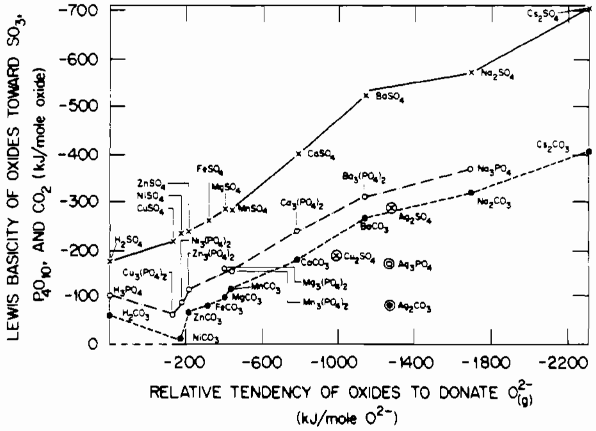

Figure 1. Lewis basicity of oxides toward $SO_3(g)$, $P_4O_{10}(c)$, and $CO_2(g)$ vs. relative tendencies of the oxides to donate $O^{2-}(g)$ (see Table I). Lewis basicity is the $\Delta H°$ for the reaction of 1 mol of MO or M_2O with the three acidic oxides to give the products shown on the graph. All products are in crystalline states.

Figure 1 illustrates the correspondence between the tendency of certain oxides to act as both ODs (abcissa) and Lewis bases toward $CO_2(g)$, $P_4O_{10}(c)$, and $SO_3(g)$ via reactions such as $B_mO + CO_2(g) = B_mCO_3$ (ordinate). This correlation can be explained thermodynamically: Consider the reaction between an oxide-containing Lewis base and a Lewis acid in terms of eq 1–3, in which B_mO represents a Lewis base, A_y a Lewis acid,

$$B_mO = B_m{}^{2+}(g) + O^{2-}(g) \quad \Delta H_1° \tag{1}$$

$$A_y + O^{2-}(g) = A_yO^{2-}(g) \quad \Delta H_2° \tag{2}$$

$$A_yO^{2-}(g) + B_m{}^{2+}(g) = B_mA_yO \quad \Delta H_3° \tag{3}$$

$$\begin{gathered} \text{sum} = B_mO + A_y = B_mA_yO \\ \Delta H_4° = \Delta H_1° + \Delta H_2° + \Delta H_3° \end{gathered} \tag{4}$$

A_yO^{2-} an oxyanion, and B_mA_yO the product of the acid–base reaction. For reactions of several Lewis bases with a single Lewis acid, $\Delta H_2°$ will be the same in every case. If the lattice enthalpies ($\Delta H_3°$) of the resulting salts are not very different, then the enthalpies of the overall reactions ($\Delta H_4°$) should very according to the differences in the oxide ion donating capabilities ($\Delta H_1°$) of the various Lewis bases. Deviations from the predicted trend are apparent in Figure 1. Accordingly, these deviations *must* be due to differences in the lattice enthalpies of the salts ($\Delta H_3°$). It is apparent that the factors which determine the Lewis basicity of an oxide are closely related to those which determine its tendency to donate $O^{2-}(g)$. These factors are discussed in detail elsewhere.[8,9]

The above-stated definition of an OD relates to the *general* tendency of a compound to donate $O^{2-}(g)$. The comparable reaction of $H_2O(g)$ is used as a reference because water is a reactant in all thermochemical cycles. It is conceivable that, in a particular chemical reaction, a strong OD will donate $O^{2-}(g)$ to a weaker OD. In this case, the weaker OD must be considered to be an oxide ion acceptor (see below), even though it has a greater tendency than water to donate oxide ion.

(i) An *oxide ion acceptor* (OA) is defined as a compound that has a greater tendency than $H_2O(g)$ to react with an oxide ion donor. It follows that, since ODs tend to act as Lewis bases, OAs should tend to act as Lewis acids in chemical reactions. Table II lists several substances according to their tendencies, relative to $H_2O(g)$, to react with the strong OD $Na_2O(c)$. However, it should be cautioned that, e.g., when either $MgO(c)$ or $CaO(c)$ replace $Na_2O(c)$ as the reference OD, the relative strengths of some OAs change, (Figure 2). For example, HCl is a stronger OA than P_4O_{10} with respect to Na_2O, but P_4O_{10} is the stronger OA with respect to MgO and CaO. A Born–Haber treatment similar to that of eq 1–4 again shows that lattice enthalpies are responsible for this reversal: For reactions of a single Lewis base with several Lewis acids, $\Delta H_1°$ will be the same in every case. For HCl, eq 2 can be written as $2HCl + O^{2-}(g) = H_2O(g) + 2Cl^-(g)$; for P_4O_{10}, eq 2 can be written as $^1/_6P_4O_{10} + O^{2-}(g) = {}^2/_3PO_4{}^{3-}(g)$. In both cases, $\Delta H_2°$ is independent of the OD being used as the reference. This means that $\Delta H_3°$ must be responsible for the observed changes in the relative strengths of OAs toward different ODs.

The foregoing discussions were presented to emphasize the difference between the thermodynamics of acid–base reactions

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Table II. Reactions of Some Oxide Ion Acceptors with $Na_2O(c)$

reaction[a]	relative[b] $\Delta H_R°$	ref	reaction[a]	relative[b] $\Delta H_R°$	ref
$Na_2O(c) + Cl_2O_7(g) = 2NaClO_4$	−432	7c,h	$Na_2O(c) + NaPO_3(c) = Na_3PO_4$	−106	7h
$+ SO_3(g) = Na_2SO_4$	−380	7a	$+ WO_3(c) = Na_2WO_4$	−91	7a
$+ 2HNO_3(g) = 2NaNO_3 + H_2O$	−296	7c,h	$+ {}^2/_3H_3PO_4(l) = {}^2/_3Na_3PO_4 + H_2O$	−69	7c,h
$+ 2HBr(g) = 2NaBr + H_2O$	−278	7a,h	$+ Na_4P_2O_7(c) = 2Na_3PO_4$	−55	7h
$+ 2HCl(g) = 2NaCl + H_2O$	−269	7a	$+ SiO_2(c) = Na_2SiO_3$	−40	7a
$+ 2ClO_2(g) = NaClO_2 + NaClO_3$	−261	7a,h	$+ H_2O(g) = 2NaOH$	0.0	7a
$+ 2HI(g) = 2NaI + H_2O$	−259	7a	$+ \alpha\text{-}Al_2O_3(c) = 2NaAlO_2$	1	7a
$+ 2HF(g) = 2NaF + H_2O$	−237	7a	$+ 2NaHCO_3(c) = 2Na_2CO_3 + H_2O$	3	7a,h
$+ H_2SO_4(l) = Na_2SO_4 + H_2O$	−204	7c,h	$+ TiO_2(c) = Na_2TiO_3$	4	7a,n
$+ SO_2(g) = Na_2SO_3$	−183	7a,h	$+ H_2S(g) = Na_2S + H_2O$	17	7a
$+ {}^1/_6P_4O_{10}(c) = {}^2/_3Na_3PO_4$	−182	7a,h	$+ \gamma\text{-}Al_2O_3(c) = 2NaAlO_2$	18	7a
$+ CrO_3(c) = Na_2CrO_4$	−128	7d,h	$+ SnO_2(c) = Na_2SnO_3$	37	7c,h
$+ CO_2(g) = Na_2CO_3$	−127	7a	$+ Fe_2O_3(c) = 2NaFeO_2$	38	7k
$+ Na_2Cr_2O_7(aq) = 2Na_2CrO_4$	−108	7h	$+ ZnO(c) = Na_2ZnO_2$	173	7c,h

[a] All reaction products except $H_2O(g)$ are in crystalline states. [b] Relative standard enthalpy of reaction in kJ (mol of $Na_2O(c))^{-1}$. Relative $\Delta H_R° = \Delta H_R° - \Delta H_R°$ for $H_2O(g)$, where $\Delta H_R°$ for $H_2O = -192.9$ kJ (mol of $Na_2O(c))^{-1}$.

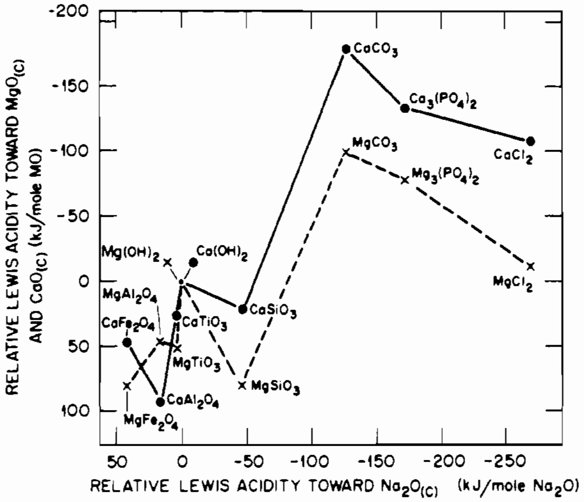

Figure 2. Relative Lewis acidity of crystalline Fe_2O_3, Al_2O_3, TiO_2, SiO_2, and P_4O_{10}, and gaseous H_2O, CO_2, and HCl toward MgO(c) and CaO(c) vs. the relative Lewis acidity of the same compounds toward $Na_2O(c)$. Relative Lewis acidity is defined as the $\Delta H°$ for the reaction of the acids with 1 mol of MgO, CaO, or Na_2O, minus $\Delta H°$ for the reaction of $H_2O(g)$ with those same bases.

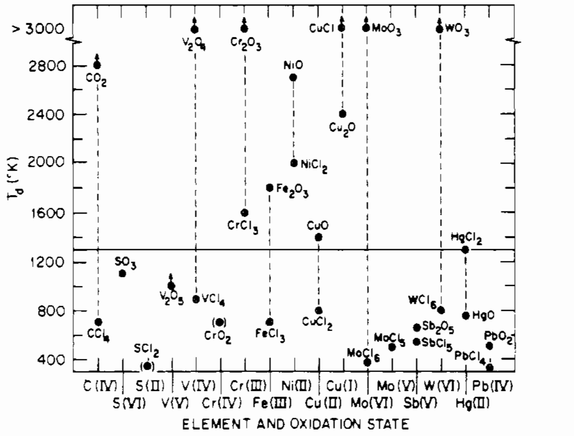

Figure 3. Decomposition temperatures for some oxides and chlorides. The ranking on the abcissa is arbitrary.

in aqueous solutions and OD–OA reactions between solids. In general, if the $[H^+(aq)]$ is known for dilute solutions of an acid and a base and if complexation reactions can be neglected, then the $\Delta H°$ for the reaction of the two solutions can be predicted with a reasonable degree of accuracy.[10] In reactions between solids, data on the relative thermodynamic tendencies of compounds to donate or accept $O^{2-}(g)$ are insufficient for predicting reaction enthalpies; accurate predictions can only be made if the lattice energies of the reaction products can be determined.

II. Preliminary Observations

Examples of compounds containing elements in their highest oxidation state always include fluorides or oxo compounds—oxides, salts of oxoanions, and oxohalides.[8] For highest oxidation states of +III or greater, fluorides and oxo compounds are usually more stable toward reductive thermal decomposition than are other compounds. Figure 3 provides some examples of this general trend: While the Fe(III) oxide is thermally stable, the iron(III) chloride tends to decompose at 700 K. (The mixed-valence oxide $Fe_3O_4(c)$ decomposes at 2700 K. $FeCl_3(g)$ dimerizes to form $Fe_2Cl_6(g)$ at 700 K; at this temperature, ΔG for the reaction $Fe_2Cl_6(g) = 2FeCl_2(c) + Cl_2(g)$ is 23 kJ, a value low enough to make the formation of $Cl_2(g)$ appreciable.) The chemistries of sulfur and iodine also illustrate this phenomenon:[12] sulfates, sulfur(VI) oxohalides, SO_3, and SF_6 are known, but the highest sulfur chloride is SCl_4, which decomposes at about 260 K.[7g] Similarly, periodates and IF_7 exist, but ICl_3 is the highest iodine chloride and IBr is the highest iodine bromide. Fundamental reasons for these general observations are discussed in ref 8 and 9.

For elements whose highest formal oxidation state is +II or less (i.e., for elements of groups 1 and 2), the chlorides, iodides, phosphates, etc. are often more stable toward thermal reduction than are the corresponding oxides. Figure 3 shows this for compounds of Cu(I) and Hg(II).

To date, no proposed thermochemical cycles are based upon the redox chemistry of fluorine. This is because it is extremely difficult to oxidize F^- chemically. Fluorine and fluorides will not be discussed further in this paper.

The above-described observations have important implications for the reactions in thermochemical cycles. First of all, since oxo compounds are usually more stable than other high-oxidation-state compounds, ODs should tend to enhance the oxidation of reduced compounds. Figure 4 shows how dramatic this enhancement can be. Oxidation of $SO_2(g)$ by

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Table III. Lattice-Independent $\Delta G_R°$ Values for Oxidations by OAs and ODs Considering the Born–Haber Treatment Given by Eq a–d

$$E = E(g) \quad (a)$$
$$E(g) = 2e^- + E^{2+}(g) \quad (b)$$
$$2e^- + 2HA = 2A^-(g) + H_2(g) \quad (c)$$
$$E^{2+}(g) + 2A^-(g) = EA_2 \quad (d)$$
$$\text{sum} = E + 2HA = EA_2 + H_2(g)$$

eq c	relative[a] $\Delta G_R°$
$2e^- + 2H_2O(g) = 2OH^-(g) + H_2(g)$	0.0
$2e^- + 2HF(g) = 2F^-(g) + H_2(g)$	−164
$2e^- + 2HCl(g) = 2Cl^-(g) + H_2(g)$	−469
$2e^- + 2NaOH(c) = 2NaO^-(g) + H_2(g)$	313
$2e^- + Na_2O(c) + H_2O(g) = 2NaO^-(g) + H_2(g)$	161

[a] Relative standard free energy of reaction in kJ mol^{-1}. Relative $\Delta G_R° = \Delta G_R° - \Delta G_R°$ for $H_2O(g)$, where $\Delta G_R°$ for $H_2O(g)$ equals 179.0 kJ (mol of $H_2(g))^{-1}$. All values were taken from ref 7a.

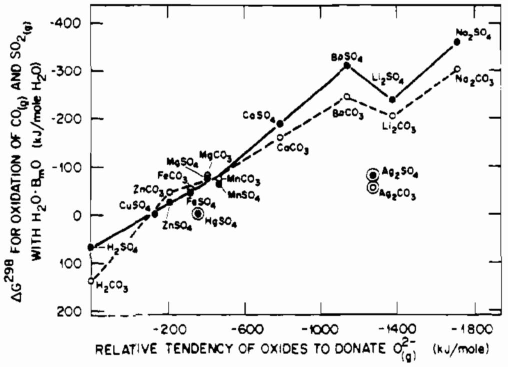

Figure 4. $\Delta G°$ for the steam oxidation of $SO_2(g)$ and $CO(g)$ in the presence of various ODs vs. the relative tendencies of those ODs to donate O^{2-} (see Table I). Free-energy values are for the oxidation of 1 mol of SO_2 or CO to the products shown on the graph. All products are in crystalline states.

$H_2O(g)$ under standard conditions is 427 kJ mol^{-1} more favorable in the presence of the strong OD $Na_2O(c)$ than in its absence. Furthermore, the degree of enhancement for this reaction by other ODs is proportional to their strengths. The figure shows a similar trend for the oxidation of CO(g) by $H_2O(g)$.

The importance of lattice energies in reactions involving solids is again demonstrated by the data presented in Figure 4 and Table III. The abbreviated Born–Haber treatment of $SO_2(g)$ oxidation in Table III shows that acids and H_2O undergo reduction coupled with the release of $H_2(g)$ more readily than do bases (cf. eq c in Table III). This trend is opposite to that shown in Figure 4. These facts show that, even though the reductive release of $H_2(g)$ from $Na_2O{\cdot}H_2O$, NaOH, and the other bases is less favorable than the release of $H_2(g)$ from $H_2O(g)$ alone, the bases (ODs) drive the oxidation of $SO_2(g)$ because the lattice energies (cf. eq d in Table III) of the resulting salts are greater than the "lattice energy" for $H_2SO_4(l)$.

There is a second implication of the above observations. Since oxo compounds of highly oxidized elements are usually more stable than same-oxidation-state compounds of that element with other ligands, replacement of O^{2-} by other ligands should make the element more susceptible to thermal reduction. Examples of this are shown in Table IV, which shows that conversion of $Fe_2O_3(c)$ or $Fe_3O_4(c)$ into $FeCl_3(c)$ (by treatment of the oxides with HCl, as in cycle 1 below) changes Fe(III) from a thermally stable form into a thermally unstable form. Additional examples are provided by reactions of compounds of V, As, and Ce (Table IV).

Finally, there is a third implication of the above observations. When the highest oxidation state compounds of an element with other anions are *more* stable than its same-oxidation-state oxides (e.g., for some compounds of group 1 and 2 metals), treatment of the nonoxides with ODs should make that element more susceptible to reductive thermal decomposition. Likewise, treatment of reduced forms of that element with OAs should make it more susceptible to oxidation than would treatment with ODs. The chemistry of mercury provides an example: the conversion of HgI_2 into HgO (via reaction of the iodide with K_2CO_3, as in cycle 5 below) changes Hg(II) from a thermally stable form into a thermally unstable form.

III. Outline of the OA–OD Model for Thermochemical Cycles

Simple thermochemical cycles involving oxides take advantage of the phenomena described in the previous section. In a given cycle, a stable compound of an element in a higher oxidation state is destabilized (step 1) by reaction with an OA (or OD). The resulting thermally unstable compound is then decomposed (step 2). The reduced product is then treated (step 3) with an OD (or OA), which makes it more susceptible to oxidation. Reoxidation (step 4) returns the element to its original higher oxidation state. In at least one of the OA- or OD-enhanced reactions, one of the products will be a salt. The

Table IV. Decomposition Temperatures for Some Oxides and Chlorides

reaction	T_d,[a] K	ref	reaction	T_d,[a] K	ref
$H_2O = H_2 + {}^1/_2O_2$	4400	7a	$2HCl = H_2 + Cl_2$	>6000	7a
$3TiO_2 = Ti_3O_5 + {}^1/_2O_2$	>3000	7a	$2TiCl_4 = 2TiCl_3 + Cl_2$	3300	7a
$V_2O_5 = V_2O_4 + {}^1/_2O_2$	2100	7b	$V_2O_5 + 10HCl = 2VCl_3 + 5H_2O + 2Cl_2$	450[b]	7a,b
${}^3/_2V_2O_5 = {}^1/_2V_6O_{13} + {}^1/_2O_2$	1000[d]	7b			
$V_2O_4 = V_2O_3 + {}^1/_2O_2$	>3000	7b	$2VCl_4 = 2VCl_3 + Cl_2$	900[b]	7a
$3Mn_2O_3 = 2Mn_3O_4 + {}^1/_2O_2$	1360	7b			
$Mn_3O_4 = 3MnO + {}^1/_2O_2$	1800	7b	$Mn_3O_4 + 8HCl = 3MnCl_2 + 4H_2O + Cl_2$	2400	7a,b,d
			$Mn_3O_4 + 6HCl = 3MnCl_2 + 3H_2O + {}^1/_2O_2$		7a,b,d
$3Fe_2O_3 = 2Fe_3O_4 + {}^1/_2O_2$	1800	7b	$2FeCl_3 = 2FeCl_2 + Cl_2$	700	7a
$Fe_3O_4 = 3Fe_{0.947}O + {}^1/_2O_2$	2700	7b	$Fe_3O_4 + 8HCl = 2FeCl_3 + FeCl_2 + 4H_2O$	500	11
${}^1/_2As_2O_5 = {}^1/_2As_2O_3 + {}^1/_2O_2$	1000	7b	$As_2O_5 + 10HCl = 2AsCl_3 + 5H_2O + 2Cl_2$	300[b]	7a,c
$As_2O_4 = As_2O_3 + {}^1/_2O_2$	1200[c]	7g			
$CdO = Cd + {}^1/_2O_2$	>1200[c]	7g,i	$CdCl_2 = Cd + Cl_2$	2500[b]	7c
$Sb_2O_5 = Sb_2O_4 + {}^1/_2O_2$	650[c]	7g	$SbCl_5 = SbCl_3 + Cl_2$	550[b]	7c
$Sb_2O_4 = Sb_2O_3 + {}^1/_2O_2$	1200[c]	7g			
$HgO = Hg + {}^1/_2O_2$	750	7a	$2HgCl_2 = Hg_2Cl_2 + Cl_2$	1300	7a
$2CeO_2 = Ce_2O_3 + {}^1/_2O_2$	2500	7b	$2CeO_2 + 8HCl = 2CeCl_3 + 4H_2O + Cl_2$	600	7a,b,l

[a] Unless otherwise indicated, T_d is the temperature at which ΔG for the written reaction is zero. [b] These values were calculated from 298 K data, assuming $(\partial Cp/\partial T) = 0$. [c] These temperatures are reported decomposition temperatures. The ΔG's for the written reactions are close to – but not necessarily equal to – zero at these temperatures. [d] $\Delta G = +25$ kJ.

splitting of this salt to reform the original OA and OD completes the thermochemical cycle (step 5).

The following sections will show that the formation of salts that are too stable makes it impossible to complete a cycle at temperatures below 1300 K. They will also show that several separate steps can be used to accomplish the salt-splitting reaction. In many cycles, two or more of steps 1–5 are combined into a single step.

IV. Statement and Illustration of the OA–OD Model

In this section, the OA–OD model is applied to simple thermochemical cycles in which oxides are involved. Such cycles are divided into three main types, and two examples of experimentally confirmed cycles are given for each type.

A. Cycles Involving Stable High-Oxidation-State Oxides. The reaction scheme presented in eq 5–9 generalizes cycles

$$\mathrm{EO}_n + \mathrm{H}_{2x}\mathrm{A}_y = \mathrm{EA}_y\mathrm{O}_{n-x} + x\mathrm{H_2O} \qquad (5)$$

$$\mathrm{EA}_y\mathrm{O}_{n-x} = \mathrm{EA}_y\mathrm{O}_{n-x-1} + {}^1/_2\mathrm{O_2(g)} \qquad (6)$$

$$\mathrm{EA}_y\mathrm{O}_{n-x-1} + \mathrm{B_mO}_x = \mathrm{EO}_{n-1} + \mathrm{B_mA}_y \qquad (7)$$

$$\mathrm{EO}_{n-1} + \mathrm{H_2O} = \mathrm{EO}_n + \mathrm{H_2(g)} \qquad (8)$$

$$\mathrm{B_mA}_y + x\mathrm{H_2O} = \mathrm{B_mO}_x + \mathrm{H}_{2x}\mathrm{A}_y \qquad (9)$$

involving thermally stable high-oxidation-state oxides. For simplicity, phase changes and separations are not included. Such cycles will arbitrarily be called "type A" or "stable high oxide" cycles. In the equations, E represents the element undergoing redox, $\mathrm{B_mO}_x$ is an OD, $\mathrm{H}_{2x}\mathrm{A}_y$ is an OA, and $\mathrm{B_mA}_y$ is a salt. In the first step (eq 5), a thermally stable oxide reacts with an OA. This makes E more susceptible to thermal reduction; no redox occurs in this step, but O^{2-} is replaced by some other ligand. After the decomposition of $\mathrm{EA}_y\mathrm{O}_{n-x}$ (eq 6), the reduced compound $\mathrm{EA}_y\mathrm{O}_{n-x-1}$ is reacted with an OD (eq 7). This step replaces the nonoxide anions with O^{2-}, yielding a salt and an oxidation-susceptible compound. Water oxidation of EO_{n-1} (eq 8) yields the original oxide and $\mathrm{H_2(g)}$. In the final step (eq 9), the salt is split to regenerate the OA and the OD.

Cycles 1 and 2 are examples of type A cycles. [Note: The reaction temperatures in these and all other cycles in the paper are quoted from the references in which the cycles are reported. A question mark (?) is used to indicate values about which doubt has been expressed.] In Cycle 1,[11] the stable oxide $\mathrm{Fe_3O_4}$

Cycle 1

$$\mathrm{Fe_3O_4 + 8HCl = 2FeCl_3 + FeCl_2 + 4H_2O} \qquad T_\mathrm{R} \simeq 500\ \mathrm{K}$$

$$\mathrm{2FeCl_3 = 2FeCl_2 + Cl_2} \qquad 700\ \mathrm{K}$$

$$\mathrm{Cl_2 + H_2O = 2HCl + {}^1/_2O_2} \qquad 1300\ \mathrm{K}$$

$$\mathrm{3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2} \qquad 1200\ \mathrm{K}$$

is treated with the OA HCl (cf. eq 5). This produces thermally unstable $\mathrm{FeCl_3}$ (or, at 700 K, $\mathrm{Fe_2Cl_6(g)}$[11]), which yields reduced $\mathrm{FeCl_2}$ and $\mathrm{Cl_2}$ (cf. eq 6); $\mathrm{Cl_2}$ is then used to obtain $\mathrm{O_2}$ from water via the reverse Deacon reaction.[13] The fourth step can be treated as the sum of

$$\mathrm{3FeCl_2 + 3H_2O = 3FeO + 6HCl} \qquad \text{(cf. eq 7 + eq 9)}$$

$$\mathrm{3FeO + H_2O = Fe_3O_4 + H_2} \qquad \text{(cf. eq 8)}$$

Cycle 2[14] provides another example of a type A cycle. In

Cycle 2

$$\mathrm{2CeO_2 + 3Na_4P_2O_7 = 2Na_3Ce(PO_4)_2 + 2Na_3PO_4 + {}^1/_2O_2} \qquad T_\mathrm{R} \simeq 1100\ \mathrm{K}$$

$$\mathrm{2Na_3Ce(PO_4)_2 + 3Na_2CO_3 + H_2O = 2CeO_2 + 4Na_3PO_4 + 3CO_2 + H_2} \qquad 1100\ \mathrm{K}$$

$$\mathrm{6Na_3PO_4 + 6CO_2 + 6H_2O = 6Na_2HPO_4 + 6NaHCO_3} \qquad 300\ \mathrm{K}$$

$$\mathrm{6NaHCO_3 = 3Na_2CO_3 + 3CO_2 + 3H_2O} \qquad 600\ \mathrm{K}$$

$$\mathrm{6Na_2HPO_4 = 3Na_4P_2O_7 + 3H_2O} \qquad 600\ \mathrm{K}$$

this process, $\mathrm{CeO_2}$ is treated with the OA $\mathrm{Na_4P_2O_7}$ (cf. eq 5 + eq 6). The OD $\mathrm{Na_2CO_3}$ drives the water oxidation of Ce(III). This step can be treated as the sum of

$$\mathrm{2Na_3Ce(PO_4)_2 + 3Na_2CO_3 = Ce_2O_3 + 4Na_3PO_4 + 3CO_2} \qquad \text{(cf. eq 7)}$$

$$\mathrm{Ce_2O_3 + H_2O = 2CeO_2 + H_2} \qquad \text{(cf. eq 8)}$$

The last three steps in the cycle are acid–base reactions that effect the reformation of the original OA and OD (cf. eq 9).

Other examples of stable high oxide cycles can be found in ref 2 and 3.

B. Cycles Involving Unstable High-Oxidation-State Oxides. It is not absolutely necessary to separate cycles of this type from stable high oxide cycles, but this separation makes the prediction of thermochemical cycles much simpler (see section V).

Equations 10–14 describe "type B" or "unstable high oxide"

$$\mathrm{EO}_n = \mathrm{EO}_{n-1} + {}^1/_2\mathrm{O_2(g)} \qquad (10)$$

$$\mathrm{EO}_{n-1} + \mathrm{B_mO}_x = \mathrm{B_mEO}_{n-1+x} \qquad (11)$$

$$\mathrm{B_mEO}_{n-1+x} + \mathrm{H_2O} = \mathrm{B_mEO}_{n+x} + \mathrm{H_2(g)} \qquad (12)$$

$$\mathrm{B_mEO}_{n+x} + \mathrm{H}_{2x}\mathrm{A}_y = \mathrm{EO}_n + \mathrm{B_mA}_y + x\mathrm{H_2O} \qquad (13)$$

$$\mathrm{B_mA}_y + x\mathrm{H_2O} = \mathrm{B_mO}_x + \mathrm{H}_{2x}\mathrm{A}_y \quad \text{(cf. eq 9)} \qquad (14)$$

cycles in a generalized form. The designations E, $\mathrm{B_mO}_x$, $\mathrm{H}_{2x}\mathrm{A}_y$, and $\mathrm{B_mA}_y$ have the same meanings as they did in eq 5–9. The first reaction (eq $\mathrm{H}_{2x}\mathrm{A}_y$, is simply the thermal decomposition of an oxide. The resulting lower oxide is then treated with an OD (eq 11), which makes E more susceptible to oxidation by water (eq 12). The product of this oxidation is a thermally stable compound, $\mathrm{B_mEO}_{n+x}$. Its treatment with an OA (eq 13) yields a salt and the thermally unstable oxide. As in type A cycles, splitting the salt, $\mathrm{B_mA}_y$, to regenerate the original OA and OD completes the thermochemical cycle (eq 14).

In Cycle 3,[15] the unstable oxide $\mathrm{Mn_2O_3}$ is thermally de-

Cycle 3

$$\mathrm{3Mn_2O_3 = 2Mn_3O_4 + {}^1/_2O_2} \qquad T_\mathrm{R} \simeq 1300\ \mathrm{K}$$

$$\mathrm{2Mn_3O_4 + 6NaOH = 6NaMnO_2 + 2H_2O + H_2} \qquad 700\ \mathrm{K}$$

$$\mathrm{6NaMnO_2 + 3H_2O = 3Mn_2O_3 + 6NaOH} \qquad 350\ \mathrm{K}$$

composed (cf. eq 10). The resulting reduced oxide, $\mathrm{Mn_3O_4}$, is oxidized either by NaOH or by $\mathrm{H_2O}$ in the presence of $\mathrm{Na_2O}$ (cf. eq 11 + eq 12). Treatment of $\mathrm{NaMnO_2}$ with the weak OA $\mathrm{H_2O}$ regenerates $\mathrm{Mn_2O_3}$ (cf. eq 13). The "salt" NaOH cannot easily be split into $\mathrm{Na_2O}$ and $\mathrm{H_2O}$ (cf. eq 14),

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(13) Chlorine is one of very few substances which (1) is the product of reductive thermal decompositions and (2) is capable of oxidizing $\mathrm{H_2O}$ to $\mathrm{O_2}$. Therefore, for the sake of simplicity, the high-temperature evolution of $\mathrm{Cl_2}$ from chlorides is considered equivalent to the production of $\mathrm{O_2}$ in this paper.

(14) C. E. Bamberger and P. R. Robinson, *Inorg. Chim. Acta*, **42**, 133 (1980).

(15) M. G. Bowman, Los Alamos Scientific Laboratory Quarterly Report LA-5731-PR, April–June, 1974.

so this reaction is coupled to the oxidation of Mn_3O_4 in the second step of the cycle.

In Cycle 4,[16] $CdSO_4$ is thermally decomposed. This first step is equivalent to the sum of the two equations

Cycle 4

$$CdSO_4 = CdO + SO_2 + {}^1/_2O_2 \qquad T_R \simeq 1300\ K$$

$$SO_2 + H_2O + CdO = CdSO_4 + H_2 \qquad 300\ K$$

$$CdSO_4 = CdO + SO_3 \quad (\text{cf. eq 13 + eq 14, where } x = 0 \text{ and } B_m = CdO)$$

$$SO_3 = SO_2 + {}^1/_2O_2 \quad (\text{cf. eq 10})$$

The second step in the cycle can be treated as the sum of

$$CdO + SO_2 = CdSO_3 \quad (\text{cf. eq 11})$$

$$CdSO_3 + H_2O = CdSO_4 + H_2 \quad (\text{cf. eq 12})$$

Other examples of unstable high oxide cycles can be found in ref 2 and 3.

C. Cycles Involving Unstable Low-Oxidation-State Oxides. Thermochemical cycles involving oxidation and reduction of some group 1 and 2 metals can be described in terms of the general equations (15)–(18). The major difference between these "type C" or "unstable low oxide" cycles and the type A and B cycles involves reaction with water. In type C cycles, H_2O that serves as the eventual source of H_2 and O_2 is introduced into the cycles in the salt-splitting reaction (eq 18). In the previous two types, it acted directly, as an oxidant (eq 8 and 12).

$$EA_yO_n + B_mO = EO_{n+1} + B_mA_y \tag{15}$$

$$EO_{n+1} = EO_n + {}^1/_2O_2(g) \tag{16}$$

$$EO_n + H_2A_y = EA_yO_n + H_2(g) \tag{17}$$

$$B_mA_y + H_2O = B_mO + H_2A_y \quad (\text{cf. eq 9 and 14}) \tag{18}$$

Cycles 5 and 6 are examples of unstable low oxide cycles. In Cycle 5,[17] the OD K_2CO_3 converts HgI_2 into the decomposable oxide HgO, which then undergoes thermal reduction. Accordingly, the first step in this cycle is actually the sum of

Cycle 5

$$HgI_2 + K_2CO_3 = Hg + 2KI + CO_2 + {}^1/_2O_2 \quad T_R \simeq 1000\ K$$

$$Hg^0 + 2NH_4I = HgI_2 + 2NH_3 + H_2 \qquad 600\ K$$

$$2NH_3 + 2KI + 2CO_2 + H_2O = 2NH_4I + 2KHCO_3 \quad 300\ K$$

$$2KHCO_3 = K_2CO_3 + CO_2 + H_2O \qquad 475\ K$$

$$HgI_2 + K_2CO_3 = HgO + 2KI + CO_2 \quad (\text{cf. eq 15})$$

$$HgO = Hg + {}^1/_2O_2 \quad (\text{cf. eq 16})$$

The second step can be treated as the sum of

$$2NH_4I = 2NH_3 + 2HI \quad (\text{cf. part of eq 18})$$

$$Hg + 2HI = HgI_2 + H_2 \quad (\text{cf. eq 17})$$

NH_4I (or HI) acts as a Lewis acid toward Hg; it does not accept oxide in this cycle and can only be called an OA on the basis of its chemical behavior in other reactions (e.g., $Na_2O + 2NH_4I = 2NaI + 2NH_3 + H_2O$). The third and fourth steps in Cycle 5 are equivalent to eq 18.

The steps in Cycle 6[18] correspond directly to eq 15–18. In the first step, the OD $Ca(OH)_2$ converts Cu(II) into the thermally unstable CuO (cf. eq 15). CuO is then decomposed (cf. eq 16). The resulting Cu_2O is oxidized by HBr (cf. eq 17), and the $CaBr_2$ from step 1 is split to regenerate HBr and $Ca(OH)_2$ (cf. eq 18).

Cycle 6

$$2CuBr_2 + 2Ca(OH)_2 = 2CuO + 2CaBr_2 + 2H_2O \quad T_R \simeq 300\ K\ (?)$$

$$2CuO = Cu_2O + {}^1/_2O_2 \qquad 1400\ K$$

$$Cu_2O + 4HBr = 2CuBr_2 + H_2O + H_2 \qquad 300\ K$$

$$2CaBr_2 + 4H_2O = 2Ca(OH)_2 + 4HBr \qquad 1200\ K$$

Additional examples of unstable low oxide cycles are presented in ref 2 and 3.

D. Energetics of Salt-Splitting Reactions. The relative strengths of the OAs and ODs used in Cycles 1–6 were not discussed in sections A–C. This important topic is treated in this section.

Inspection of Cycles 1–6 shows the following: (1) when a *strong* OA is used to drive one of the redox reactions in a thermochemical cycle, a *weak* OD is used to drive the other (cf. Cycles 1, 4, and 6); (2) when a *weak* OA is used to drive one redox reaction, a *strong* OD is used to drive the other (cf. Cycle 3); (3) when an *OA of moderate strength* is used to drive one redox reaction, an *OD of moderate strength* is used for the other (cf. Cycles 2 and 5).

Table V presents enthalpy data for reactions between the strongest OA or Lewis acid and the strongest OD or Lewis base used in each of the example cycles (Cycles 1–6). The indicated states are those used in cycles. Data for other acid–base reactions, and for compounds in other states, are presented for comparison. It is difficult to assign unambiguously the enthalpies of reaction between HCl or NaOH and water (reactions 1a and 3a, Table V), because they are so dependent upon the relative amount of water used (compare 1a to 1b, Table V). The values shown in the table were chosen to be consistent with those for the other example cycles.

It is interesting to note that each reaction a in Table V has a standard enthalpy which is between −214 and −303 kJ/mol of $H_2(g)$ evolved in the corresponding cycle. When one notes that the enthalpy of formation of $H_2O(g)$ is −242 kJ/mol at 298 K (−239 kJ/mol at 1300 K),[7a] the data for reactions a in Table V imply that (1) *the redox-driving OA–OD reactions in a workable thermochemical cycle supply an amount of energy which is nearly equivalent to—or greater than—the enthalpy of formation of water* [about −240 kJ/mol evolved $H_2(g)$]. In other words, the OA–OD reactions can be thought of as providing the chemical energy that is needed to split water in a thermochemical cycle. Furthermore, (2) *the standard enthalpy of the reaction between the strongest OA and the strongest OD used in a thermochemical cycle serves as an approximate measure of the chemical energy that a particular OA–OD or acid–base pair can supply to the cycle.*

Similar data for Cycles 7–10 (see below) are presented in Table VI, where the most negative enthalpy for the OA–OD reaction in a workable cycle is −344 kJ/mol of evolved $H_2(g)$ (Cycle 9 with M = Sr). These data suggest that there must be an upper limit on the (negative) enthalpy of reaction between the strongest OA and OD. This suggestion is consistent with the nature of thermochemical cycles. If any single reaction is too energetically favorable, some other reaction in

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[16] H. Barnert and R. Schulten, U.S. Patent 3995012, Nov 30, 1976.

[17] E. H. Appelman, F. Schreiner, and B. M. Abraham, in "Proceedings of the 2nd World Hydrogen Energy Conference", Zurich, Switzerland, 1978, T. N. Veziroglu and W. Seifritz, Eds., Pergamon Press, New York, 1978, p 851.

[18] "Hydrogen Production from Water Using Nuclear Heat", EURATOM Progress Report 3, EUR 5059e, 1974, available from the EURATOM Ispra Establishment, Ispra (Varese), Italy.

Table V. Data for OAs and ODs from Cycles 1-6

cycle and label	OA[a]	OD[a]	reaction[b]	$\Delta H_R°$, kJ[b]	ref
1a	$HCl(g)$	H_2O	$8HCl(g) = 8HCl \cdot H_2O(aq)$	−234	7c
1b			$8HCl(g)$ + excess $H_2O = 8HCl(aq)$ (1.0 *m*)	−599	7c
2a	$CO_2(g)$	$Na_3PO_4(c)$	$3CO_2(g) + 6Na_3PO_4(c) = 3Na_2CO_3(c) + 3Na_4P_2O_7(c)$	−214	7c,h
2b	$Na_4P_2O_7(c)$	$H_2O(g)$	$3Na_4P_2O_7(c) + 3H_2O(g) = 6Na_2HPO_4(c)$	−203	7c,h
2c			$3Na_4P_2O_7(c) + 3H_2O(l) = 6Na_2HPO_4(c)$	−171	7c,h
2d	$CO_2(g)$	$Na_2CO_3(c)$	$3CO_2(g) + 3Na_2CO_3(c) + 3H_2O(g) = 6NaHCO_3(c)$	−287	7c,h
2e			$3CO_2(g) + 3Na_2CO_3(c) + 3H_2O(l) = 6NaHCO_3(c)$	−255	7c,h
3a	$H_2O(l)$	$NaOH(c)$	$6NaOH(c)$ + excess $H_2O = 6NaOH(aq)$ (1.0 *m*)	−257	7h
3b		$Na_2O(c)$	$3Na_2O(c) + 3H_2O(l) = 6NaOH(c)$	−455	7c,h
3c			$3Na_2O(c) + 3H_2O(g) = 6NaOH(c)$	−487	7c,h
4a	$SO_3(g)$	$CdO(c)$	$SO_3(g) + CdO(c) = CdSO_4(c)$	−279	7a,c
5a	$CO_2(g)$	$NH_3(g)$	$2CO_2(g) + NH_3(g) + 2KI(c) + 2H_2O(g) = 2KHCO_3(c) + 2NH_4I(c)$	−303	7a,c,h
5b			$CO_2(g) + 2NH_3(g) + H_2O(l) = 2(NH_4)_2CO_3(aq)$	−170	7a,h
5c		$K_2CO_3(c)$	$CO_2(g) + K_2CO_3(c) + H_2O(g) = 2KHCO_3(c)$	−137	7a,h
6a	$HBr(g)$	$Ca(OH)_2(c)$	$4HBr(g) + 2Ca(OH)_2(c) = 2CaBr_2(c) + 4H_2O(g)$	−215	7c,f
6b	$HBr(aq)$	$Ca(OH)_2(aq)$	$4HBr(aq) + 2Ca(OH)_2(aq) = 2CaBr_2(aq) + 4H_2O(l)$	−223	7c,f

[a] OAs and ODs for reactions a are in the state in which they are used in the cycle. Other reactions are listed for comparison in (b)-(e). [b] Stoichiometries and standard enthalpies of reaction for the number of moles of OA and/or OD needed to produce 1 mol of $H_2(g)$ in the cycles.

Table VI. Data for OAs and ODs from Cycles 2 and 7-10

cycle and label	OA[a]	OD[a]	reaction[b]	$\Delta H_R°$, kJ[b]	ref
2	$CO_2(g)$	$Na_3PO_4(c)$	$3CO_2(g) + 6Na_3PO_4(c) = 3Na_4P_2O_7(c) + 3Na_2CO_3(c)$	−214	7c,h
7	$HCl(g)$	$H_2O(l)$	$4HCl(g)$ + excess $H_2O = 4HCl(aq)$	−300	7c
8	$HCl(g)$	$Li_3PO_4(c)$	$6HCl(g) + 2Li_3PO_4(c) = 2H_3PO_4(l) + 6LiCl(c)$	−225	7a,c,m
c		$Na_3PO_4(c)$	$6HCl(g) + 2Na_3PO_4(c) = 2H_3PO_4(l) + 6NaCl(c)$	−597[d]	7a,c
c	$H_3PO_4(l)$	$NaOH(c)$	$2H_3PO_4(l) + 6NaOH(c) = 2Na_3PO_4(c) + 6H_2O(l)$	−470[d]	7a,c,h
9	$HCl(g)$	$Ca_3(PO_4)_2(c)$	$6HCl(g) + Ca_3(PO_4)_2(c) = 2H_3PO_4(l) + 3CaCl_2(c)$	−247	7c,f
		$Sr_3(PO_4)_2(c)$	$6HCl(g) + Sr_3(PO_4)_2(c) = 2H_3PO_4(l) + 3SrCl_2(c)$	−344	7c,f
c		$Mg_3(PO_4)_2(c)$	$6HCl(g) + Mg_3(PO_4)_2(c) = 2H_3PO_4(l) + 3MgCl_2(c)$	−123[d]	7c,f
c		$Ba_3(PO_4)_2(c)$	$6HCl(g) + Ba_3(PO_4)_2(c) = 2H_3PO_4(l) + 3BaCl_2(c)$	−464[d]	7c,f
e	$H_3PO_4(l)$	$H_2O(l)$	$2H_3PO_4(l)$ + excess $H_2O = 2H_3PO_4(aq)$ (1.0 *m*)	−43	7c
10	$H_2O(l)$	$NaOH(c)$	$6NaOH(c)$ + excess $H_2O = 6NaOH(aq)$	−257	7c,h
	$CO_2(g)$	$Na_2TiO_3(c)$	$3CO_2(g) + 3Na_2TiO_3(c) = 3Na_2CO_3(c) + 3TiO_2(c)$	−391	7a,h,n

[a] See note *a* in Table V. [b] See note *b* in Table V. [c] Designates reactions which are similar to those used in Cycles 2 and 7-10, which *cannot* be used in analogous "workable" thermochemical cycles. [d] Values outside the range 200–400 kJ (mol of evolved $H_2(g))^{-1}$. [e] This reaction shows the enthalpy difference between reactions with $H_3PO_4(l)$ and $H_3PO_4(aq)$ in Cycles 8 and 9.

the cycle will be impossible to achieve.[19] As a third general rule, then, it can be stated that (3) *a thermochemical cycle will be impossible to complete if the standard enthalpy for the reaction between the strongest OA and the strongest OD used in the cycle is much more negative than −400 kJ/mol of $H_2(g)$ evolved in the cycle.*

These three approximations are best illustrated by considering possible modifications of the example cycles: If H_2O were replaced in the last step of Cycle 1 by a stronger OD—NaOH(c), for example—the oxidation of $FeCl_2(c)$ would proceed much more facilely, as in the alternative reactions in eq 19–21. However, it would be extremely difficult to regenerate NaOH(c) and HCl(g) from the resulting salt, NaCl(c), by means of thermochemical reactions, even at 1300 K (eq 22). For NaOH and HCl, the reaction that is analogous to eq 1a in Table V is given by eq 23; note that −549 kJ is a great deal more negative than the suggested limit of −400 kJ for such reactions.

$$2FeCl_2(c) + 4NaOH(c) = Fe_2O_3(c) + 4NaCl(c) + H_2O(g) + H_2 \qquad \Delta G_R° = -383\ \mathrm{kJ}^{7a} \tag{19}$$

$$2FeCl_2(c) + 4NaOH(c) + 2H_2O(l) = 2Fe(OH)_3(c) + 4NaCl(c) + H_2 \qquad \Delta G_R° = -347\ \mathrm{kJ}^{7a,c} \tag{20}$$

$$2FeCl_2(c) + 6NaOH(c) = 2NaFeO_2(c) + 4NaCl(c) + 3H_2O(g) + H_2 \qquad \Delta G_R° = -615\ \mathrm{kJ}^{7a,k} \tag{21}$$

$$NaCl(l) + H_2O(g) = NaOH(l) + HCl(g) \qquad \Delta G_R^{1300} = 125\ \mathrm{kJ}^{7a} \tag{22}$$

$$4NaOH(c) + 4HCl(g) = 4NaCl(c) + 4H_2O(g) \qquad \Delta H_R° = -549\ \mathrm{kJ}^{7a} \tag{23}$$

Cycle 3 provides a similar illustration. If H_2O were replaced in the last step by a stronger OA—HCl(g) or HCl(aq), for example—the reduction of the Mn(III) in $NaMnO_2(c)$ would occur at a temperature much lower than that for the decomposition of $Mn_2O_3(c)$; in fact, 3 N HCl(aq) reduces $NaMnO_2(c)$ and $Mn_2O_3(c)$ to $MnCl_2(aq)$ within 30 min at 70 °C.[20] However, as was the case with the preceeding example, the too stable salt NaCl is formed.

Recent experimental data on thermochemical cycles involving Ce(IV)/Ce(III)[14,21,22] and Mn(III)/Mn(II)[23] provide instructive illustrations of how these rules about OA–OD

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(19) J. Funk, *Int. J. Hydrogen Energy*, **1**, 33 (1976).

(20) P. R. Robinson, unpublished results.

(21) C. E. Bamberger and P. R. Robinson, *Inorg. Chem.*, **19**, 2181 (1980).

(22) P. R. Robinson and C. E. Bamberger in "Proceedings of the 2nd Miami International Conference on Alternative Energy Sources", T. N. Veziroglu, Ed., Hemisphere, Washington, D.C., 1980, p 3349.

(23) P. R. Robinson, J. Kilyk, Jr., and C. E. Bamberger, to be submitted for publication.

reactions can be used to devise new thermochemical cycles. Cycle 2 and Cycles 7–10 are examples of Ce(IV)/Ce(III)

Cycle 7[24]

$$2CeO_2 + 8HCl = 2CeCl_3 + 4H_2O + Cl_2 \quad T_R \simeq 600\ K$$

$$2CeCl_3 + 4H_2O = 2CeO_2 + 6HCl + H_2 \quad 1300\ K$$

$$Cl_2 + H_2O = 2HCl + {}^1/_2O_2 \quad 1300\ K$$

Cycle 8[21]

$$2CeO_2 + H_4P_2O_7 = 2CePO_4 + 2H_2O + {}^1/_2O_2 \quad T_R \simeq 980\ K$$

$$2CePO_4 + 6LiX + 4H_2O = 2CeO_2 + 2Li_3PO_4 + 6HX + H_2 \quad 1200\ K$$

$$6HX + 2Li_3PO_4 = 2H_3PO_4 + 6LiX \quad 300\ K$$

$$2H_3PO_4 = H_4P_2O_7 + H_2O \quad 490\ K$$

$$(X = Cl, Br, I)$$

Cycle 9[22]

$$2CeO_2 + H_4P_2O_7 = 2CePO_4 + 2H_2O + {}^1/_2O_2 \quad T_R \simeq 980\ K$$

$$2CePO_4 + 3MCl_2 + 4H_2O = 2CeO_2 + M_3(PO_4)_2 + 6HCl + H_2 \quad 1100\text{–}1300\ K$$

$$6HCl + M_3(PO_4)_2 = 2H_3PO_4 + 3MCl_2 \quad 300\ K$$

$$2H_3PO_4 = H_4P_2O_7 + H_2O \quad 490\ K$$

$$(M = Ca, Sr)$$

Cycle 10[25a]

$$2CeO_2 + 3TiO_2 + Na_2TiO_3 = 2NaCeTi_2O_6 + {}^1/_2O_2 \quad T_R \simeq 1400\ K$$

$$2NaCeTi_2O_6 + 6NaOH = 2CeO_2 + 4Na_2TiO_3 + 2H_2O + H_2 \quad 800\ K$$

$$4Na_2TiO_3 + 3H_2O = 6NaOH + 3TiO_2 + Na_2TiO_3 \quad 300\ K$$

thermochemical cycles of type A (stable high oxide). [Note: Pyrophosphoric acid, $H_4P_2O_7$, can lose water to form other condensed species such as $H_3P_3O_9$ or P_4O_{10} at temperatures above 490 K.] Data for the OAs and ODs used in these cycles are shown in Table VI, along with data for OA–OD pairs which cannot be used to drive similar workable cycles. Experiments have shown that $MgCl_2$ cannot drive the second step in Cycle 9. This result was expected, on the basis of the relatively low enthalpy of reaction between HCl and $Mg_3(PO_4)_2$ (−123 kJ) (cf. Table VI). This value implies that the formation of $Mg_3(PO_4)_2$ cannot drive the removal of PO_4^{3-} ion from $CePO_4$ (see Cycle 2). Also, $MgCl_2$ is known to react readily with steam at 850 K to form MgO and HCl(g).[27] The resulting MgO is also apparently too weak an OD to displace PO_4^{3-} from $CePO_4$, since the reaction of MgO and steam with $CePO_4$ yields no $H_2(g)$ or CeO_2.[22]

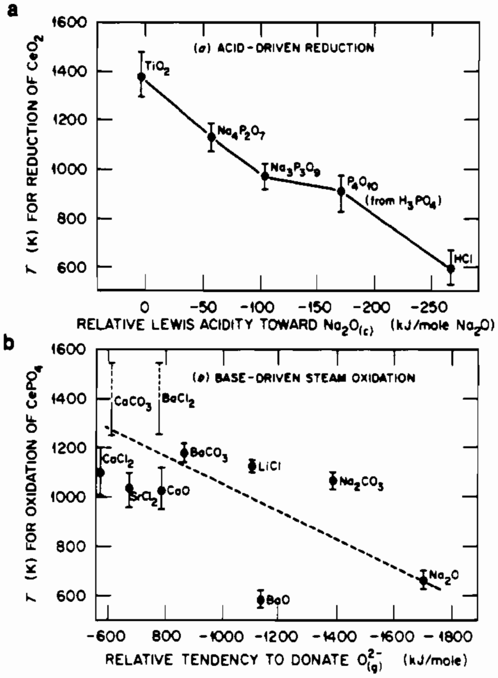

Figure 5. (a) Temperatures at which the partial pressure of $O_2(g)$ evolved from CeO_2 reaches a maximum vs. the relative Lewis acidity of the OAs used to drive the reactions. Bars indicate the range of temperatures through which P_{O_2} is 10^4 Pa or greater (for experiments performed in a stream of Ar(g) flowing at 0.1 L min^{-1}, in which 5–50 mmol of CeO_2(c) was heated at a rate of 5 K min^{-1}). (b) Temperatures at which the partial pressure of $H_2(g)$ evolved during the steam oxidation of $CePO_4$ reaches a maximum vs. the relative tendencies to donate $O^{2-}(g)$ of the ODs used to drive the reactions. Bars indicate the range of temperatures through which P_{H_2} is 10^4 Pa or greater under the reaction conditions described immediately above. In every case, the flow rate of $H_2O(g)$ corresponded to ~2 mL of $H_2O(l)$ at STP.

At the other extreme, the reaction of $BaCl_2$ and steam with $CePO_4$ yields $H_2(g)$ and CeO_2, but only at a slow rate at 1450 K.[22] A cycle analogous to Cycle 9 with M = Ba is therefore not a workable thermochemical cycle. This result was also expected, since the enthalpy of reaction between HCl and $Ba_3(PO_4)_2$ is −464 kJ (Table VI), a value which is more negative than the suggested limit of −400 kJ. Treatment of $CePO_4$ with NaCl and steam yielded no reaction at temperatures up to 1500 K.[21] This is consistent with the enthalpy of −597 kJ for the treatment of Na_3PO_4 with HCl. In other words, it seems that the formation of $MgCl_2$ provides too little energy to drive a thermochemical cycle similar to Cycle 9 and that both $BaCl_2$ and NaCl are too stable to be used in workable cycles similar to Cycles 9 and 8.

The OD Na_2CO_3 can drive the steam oxidation of $NaCeTi_2O_6$ in a manner analogous to the second step in Cycle 10[25] at 1000 K.[25b] The $\Delta H_R°$ of −391 kJ for the reaction of CO_2 with Na_2TiO_3 fits this observation.

E. Double Oxide Formation. The first step in every Ce(IV)/Ce(III) cycle (Cycles 2, 7–10) is equivalent to the simultaneous occurrence of eq 5 and 6. It is instructive to view the reduction of Ce(IV) in Cycles 2 and 8–10 as the sum of

$$2CeO_2 = Ce_2O_3 + {}^1/_2O_2(g)$$

$$Ce_2O_3 + A_y = Ce_2O_3 \cdot A_y$$

The enthalpy of the first step will be the same for every reaction of CeO_2 with an acid. The enthalpy of the second step—the formation of a double oxide salt—should be pro-

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(24) M. G. Bowman, in "Proceedings of the ERDA Contractors Review Meeting on Chemical Energy Storage and Hydrogen Energy Systems", ERDA-CONF-761134, 1976, p 102.

(25) (a) C. E. Bamberger and D. H. Nichols, *Int. J. Hydrogen Energy*, **4**, 513 (1979); (b) C. E. Bamberger in "Proceedings of the 15th Intersociety Energy Conversion/Engineering Conference, Seattle, Washington, 1980", American Institute of Aeronautics and Astronautics, Washington, D.C., p 2293.

(26) J. C. Bailar, Jr., H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson, "Comprehensive Inorganic Chemistry", Vol. 2, Pergamon Press, New York, 1973, pp 485–490.

(27) B. Lecart, M. Devalette, J. P. Manaud, G. Meunier, and P. Hagenmuller, *Int. J. Hydrogen Energy*, **4**, 7 (1979).

portional to the strength of the OA (Lewis acid) being used. The products of the reactions under consideration can be described as complex oxides—$Ce_2O_3 \cdot 2P_2O_5 \cdot 3Na_2O$, $Ce_2O_3 \cdot P_2O_5$, and $Ce_2O_3 \cdot 4TiO_2 \cdot Na_2O$—where Na_2O and Ce_2O_3 are basic oxides and P_2O_5 and TiO_2 are acidic oxides.

Figure 5a shows the correspondence between the strengths of the OAs (relative to Na_2O(c)) used to drive CeO_2 reduction and the temperatures at which the maximum pressure of evolved O_2(g) or Cl_2(g) occurs. The temperatures at which steam oxidizes $CePO_4$ in the presence of some ODs are shown in Figure 5b. Figure 5 shows that (a) stronger OAs generally drive the reduction of Ce(IV) at lower temperatures and (b) stronger ODs usually drive the reoxidation of Ce(III) at lower temperatures. Similar results have been obtained for several thermochemical cycles based upon the Mn(III)/Mn(II) redox couple.[23] These observations are consistent with the three general rules which were presented earlier in this section. The experimental results for Ce- and Mn-based cycles give rise to two additional general approximations for simple thermochemical cycles involving oxides: (4) *If a strong OA is needed to drive one redox reaction in a thermochemical cycle, a weak OD should suffice to drive the other, and visa versa.* (5) *The temperature at which a redox reaction occurs is inversely proportional to the strength of the OA or OD being used to drive that redox reaction.* Rule 4 is a qualitative restatement of rules 1 and 2. In practice, it has proved to be a useful guide to the development of thermochemical cycles when thermodynamic data for some acid–base (OA–OD) reactions were not available.[23] Rule 5 can be explained thermodynamically: The redox reactions in thermochemical cycles involve evolution of H_2(g) or O_2(g); in Cycles 2 and 7–10, other gases are also evolved. Therefore, $\Delta S°$ for these high-temperature redox reactions is usually positive.[1] A reasonably good approximation can be added to this: $[\partial(\mathrm{Cp})/\partial T] \simeq 0$, which implies that $[\Delta(\Delta G)/\Delta T]_p \simeq -\Delta S°$, where $\Delta S° \simeq 146$ J K^{-1}/mol of evolved gas.[28] Therefore, for two different reactions that evolve equal amounts of the same gases, $\Delta S_1°$ and $\Delta S_2°$ will be approximately the same. This means that at temperatures T_1 and T_2 where $\Delta G_1° = \Delta G_2° = 0$ for the two reactions, we have eq 24 and 25. Equation 25 shows that, if $\Delta H_1° > \Delta H_2°$,

$$\Delta H_1° - T_1 \Delta S° \simeq \Delta H_2° - T_2 \Delta S° \tag{24}$$

$$\Delta H_1° - \Delta H_2° \simeq \Delta S°(T_1 - T_2) \tag{25}$$

then $T_1 > T_2$. Reactions of a base (OD) with strong acids (OAs) are less endothermic than reactions of that base with weak acids (OAs). Equation 25 implies that the temperatures for reaction of a base (OD) with strong acids (OAs) will be less than the temperatures for its reactions with weak acids (OAs); this implication is an alternative way of stating rule 5.

Because it was assumed in the above derivation that the reactions evolved equal amounts of the same gases, rule 5 applies most accurately to very similar reactions such as the second step in Cycle 9 when Ca is replaced by Sr. However, as Figure 5 shows, it applies to some extent to reactions which are less similar.

In Figure 5b, the BaO point is the most obvious deviation from the overall trend. The low temperature at which it drives the steam oxidation of $CePO_4$ undoubtedly reflects the large absolute entropy of $Ba_3(PO_4)_2$—for $Ba_3(PO_4)_2$(c), $S° = 356$ J mol^{-1} K^{-1}, vs. 241 J mol^{-1} K^{-1} for $Ca_3(PO_4)_2$(c), 293 J mol^{-1} K^{-1} for $Sr_3(PO_4)_2$(c), and 195 J mol^{-1} K^{-1} for Na_3PO_4(c).[7m] This implies that the formation of highly stable $Ba_3(PO_4)_2$(c) enables BaO to drive the oxidation of $CePO_4$ at lower-than-predicted temperatures.

The temperatures for $CePO_4$ oxidation in the presence of $CaCl_2$(c) and $SrCl_2$(c) appear to be lower than expected. This can be explained in part by the fact that $CaCl_2$(c) melts at 1045 K[7a] and $SrCl_2$(c) melts at 1146 K.[7g] Therefore, their tendencies to donate O^{2-}(g) should be based upon the reaction

$$MCl_2(l) + H_2O(g) = M^{2+}(g) + 2HCl(g) + O^{2-}(g)$$

The relative tendency of $CaCl_2$(l) and steam to donate O^{2-}(g) is −557 kJ[7a] (compare to −535 kJ for $CaCl_2$(c)); the tendency for $SrCl_2$(l) should be greater than that for $SrCl_2$(c) by a similar amount. However, $BaCl_2$(c) melts at 1236 K,[7g] so this same argument cannot be used to explain why it appears to react at higher-than-expected temperatures. In this respect, the OA–OD model is too simple. Because it neglects entropic differences and phase changes, the numerical accuracy of its predictions is limited.

F. Summary. Simple thermochemical cycles in which oxides undergo oxidation or reduction can be divided into three classes: (A) stable high oxide, (B) unstable high oxide, and (C) unstable low oxide cycles. Chemical energy is provided to all of these cycles by acid–base (OA–OD) reactions. The acid–base reactions must provide at least 210–250 kJ—but no more than about 400 kJ—for the splitting of 1 mol of water. In certain instances, there is an approximately inverse correlation between the strengths of the acids (OAs) or bases (ODs) which drive a reaction and the temperature at which that reaction occurs. Five general rules were presented as guides to the consideration of the energetics of the acid–base reactions in cycles of the three types A–C.

V. Modification and Prediction of Thermochemical Cycles

This section describes how the information presented in section IV can be combined with information about the decomposition temperatures of oxides to modify existing thermochemical cycles and to predict new ones.

A. Use of the Model to Modify Existing Cycles. The first applications of acid–base concepts to thermochemical cycles gave rise to Cycles 2, 8, and 9. In the case of Cycle 2, it was known that $Na_3P_3O_9$ drove the reduction of CeO_2 to $CePO_4$ and that NaOH drove the oxidation of $CePO_4$ to CeO_2. However, the difficulty of thermochemically regenerating NaOH and $Na_3P_3O_9$ from Na_3PO_4 prevented these reactions from being used together in a workable thermochemical cycle. The subsequent use of Na_2CO_3, an OD weaker than NaOH, to drive the oxidation of $CePO_4$ gave rise to Cycle 2.

It was also found that ODs even weaker than Na_2CO_3—LiCl, LiBr, and LiI—could drive the steam oxidation of $CePO_4$. According to the model, this meant that OAs which were stronger than $Na_4P_2O_7$ or $Na_3P_3O_9$ should be able to drive the reduction of CeO_2. This led to the use of H_3PO_4 in Cycles 8 and 9.

Similar reasoning led to the development of the Mn(III)/Mn(II) cycles described in ref 23. All of these cycles were derived from the modification of Cycle 3. A series of OAs were selected from Table II and used to drive the reduction of Mn(III) compounds. Steam oxidations of the resulting Mn(II) compounds were driven by a series of ODs that were chosen in accord with the principles described in section IV.

The results of current studies aimed at the modification of cycles based upon Fe(III)/Fe(II) and Cr(V)/Cr(III) redox couples will be reported in subsequent papers.

B. The Model as a Guide to the Development of New Cycles. Figures 6–8 show decomposition temperatures for oxides of several elements. [Cost, abundance, and toxicity of elements—all of which are vitally important to the practicality of thermochemical cycles—will not be considered here (cf. section Ia)]. This section describes how these data can be combined with the principles presented in section IV to form

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[28] F. T. Wall, "Chemical Thermodynamics", 2nd ed., W. H. Freeman, San Francisco, Calif., 1965, p 255.

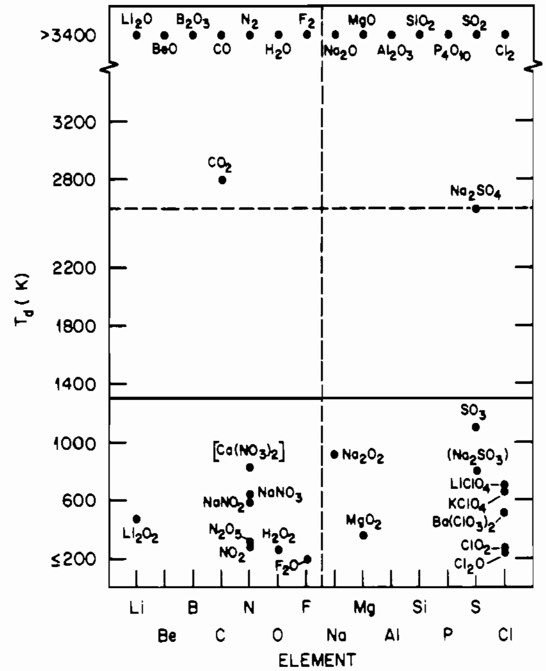

Figure 6. Decomposition temperatures for selected oxo compounds of some second and third period elements. The solid horizontal line delineates 1300 K. The dotted line indicates 2600 K. Upward pointing arrows show that decomposition occurs above the indicated temperature.

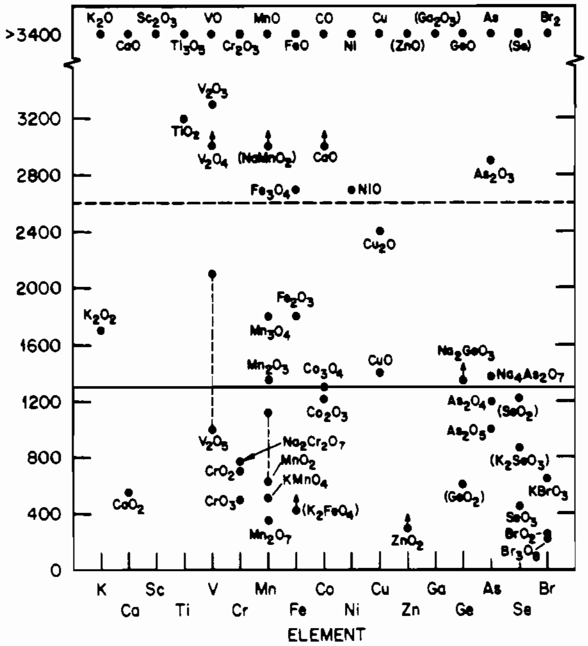

Figure 7. Decomposition temperatures for selected oxo compounds of some fourth period elements. Upward pointing arrows show that decomposition occurs above the indicated temperature. Vertical dotted lines indicate that ΔG is nearly zero throughout the included temperature range.

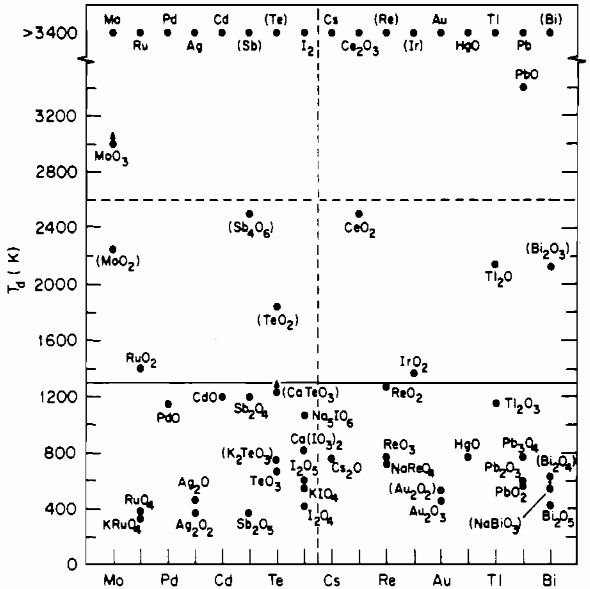

Figure 8. Decomposition temperatures for selected oxo compounds of some fifth and sixth period elements. Upward pointing arrows show the decomposition occurs above the indicated temperature.

a guide to the development of new thermochemical cycles.

The chemistry of many elements prevents them from serving as the basis for simple cycles involving oxides. Of the elements in Figures 6–8, Be, B, Al, Si, P, Sc, Ti, and Ga are such elements because all of their higher oxides are thermally stable, and they cannot be converted chemically into thermally unstable compounds at temperatures below 1300 K. It is interesting to note that the higher oxides of these elements all decompose at temperatures higher than 2600–2800 K. Other elements—Li, Na, Mg, K, Ca, Zn—form thermally unstable peroxides, but only by reactions of their stable oxides with O_2 or other peroxides. The products of their thermal decomposition are incapable of acting as reducing agents in thermochemical water-splitting cycles. One other element from Figures 6–8—F—was eliminated from consideration in section II.

Three types of elements remain: (1) those not in groups 1B or 2B whose oxides are thermally unstable, (2) those not in groups 1B or 2B whose oxides are thermally stable, and (3) those in groups 1B or 2B whose oxides are thermally unstable.

According to section IVB, elements in the first category—N, S, Cl, V, Cr, Mn, Co, Ge, As, Se, Br, Ru, Pd, Sb, Te, I, Re, Tl, Pb, and Bi—might be chemically capable of serving as the basis for unstable high oxide (type B) cycles. References 2 and 3 include cycles in which N, S, Cr, Mn, Co, Se, and I are used in this way. The elements V, S, Ge, As, Se, Sb, Te, I, and Bi have been used in other types of cycles; these simple chloride cycles and complex cycles are briefly discussed in section VI. It should be possible to devise type B cycles with these other elements. In the case of As, for example, the existence of thermally stable Na_3AsO_4 and $Na_4As_2O_7$ ($T_d \simeq 1370$ K) implies that the oxidation of As_2O_3 to As(V) can be driven by ODs such as NaOH or Na_2CO_3. Treatment of the resulting As(V) salt with OAs such as CO_2 or SiO_2 should remove, e.g., Na_2O from Na_3AsO_4, making the As(V) more susceptible to thermal reduction. In cases where a high oxide is extremely unstable (e.g., Sb_2O_5, $T_d \simeq 370$ K) only very strong bases should be capable of stabilizing the high oxidation state; weak acids should suffice to drive the subsequent reduction. When an unstable high oxide decomposes at temperatures close to 1300 K (e.g., ReO_2, $T_d \simeq 1260$ K), weak bases should suffice to stabilize the element in the high oxidation state; strong acids should be needed to drive the reduction of the resulting compound.

Of the elements in the second category listed above—C, Fe, Ce, and Ir—all but Ir have been used in stable high oxide (type A) cycles.[2,3] All of these elements form oxides which decompose between 1300 and 2600–2800 K. While there may be certain exceptions, it appears that *factors which make oxides so stable that they decompose above 2600–2800 K also make it impossible to chemically convert those oxides into thermally unstable compounds at temperatures below 1300 K.* Some other elements in Figures 6–8—Mo, Ru, Sb, Te, Re, Tl, Bi—form lower oxides that decompose between 1300 and 2600 K, which means that they might be capable of serving as the basis for type A cycles in which one of their lower oxidation state compounds is the most oxidized species in the cycle. In the case of Mo, for example, it should be possible to convert MoO_2 into a thermally unstable compound by reacting it with an acid such as HCl or H_3PO_4. Treatment of reduced MoOCl, $MoCl_3$, or $MoPO_4$ with weak ODs should make them susceptible to steam oxidation; strong ODs might very well drive their oxidation all the way to Mo(VI), in which case it would be extremely difficult to complete the thermochemical cycle.

Of the elements in the third category listed above—Cu, Ag, Cd, Au, and Hg—all but Au have been used in unstable low oxide (type C) cycles.[2,3] The model correctly predicts that treatment of AuCl or $AuCl_3$ with an OD such as H_2O yields a thermally unstable oxide. It incorrectly predicts that the reduced product—gold metal—should be susceptible to oxidation by strong OAs such as HCl or H_2SO_4. This and other limitations of the model are discussed in the next section.

This section can be summarized as follows: Knowledge of decomposition temperatures of the oxides of a given element enables an experimentor to decide whether an element can be used in a simple thermochemical cycle involving oxides. To some extent, this knowledge enables one to decide which of the three general types of simple oxide cycles best fit the element in question. Finally, by applying the principles described in section IV, one can select OA–OD pairs which should be capable of driving the redox reactions of thermochemical cycles for which that element serves as the basis.

VI. Limitations of the OA–OD Model

A. Lattice Energy Effects. Lattice energies are not generally available, and the calculation of lattice energies is nontrivial. This limits the practical application of the OA–OD model, since it therefore cannot be used to predict exact energies of high-temperature reactions. Section II gives the basis for this limitation, and section IVE illustrates it. Therefore, the model is best used as a guide to the selection of experiments. It can limit the choice of OAs or ODs that might be reacted with a given compound in attempts to drive its oxidation or reduction.

B. Reaction Rates. Since the model is thermodynamical, it says nothing about reaction rates. For example, it predicts that treatment of $NaClO_4$ or $KMnO_4$ with OAs will make these compounds more susceptible to thermal reduction; it does not predict that explosions may result.

C. Separations. Quite often, a cycle is made unworkable because the products of one of its reactions cannot be separated. Sections IVD and IVE were concerned only with the thermodynamics of salt-splitting reactions, not with their practical aspects. An example of problems which might arise deals with attempts to replace Na_2CO_3 with $BaCO_3$ in the second step of Cycle 2. $BaCO_3$ drove the steam oxidation of $CePO_4$, and CO_2 at 5 atm over H_2O partially converted $Ba_3(PO_4)_2$ into $BaHPO_4$ and $BaCO_3$. However, $BaHPO_4$ and $BaCO_3$ could not be separated due to their similar insolubilities.

D. Other Types of Cycles. The OA–OD model is limited by definition to simple thermochemical cycles involving oxides. There are three other types of cycles for which the model has limited applicability: (D) simple chloride cycles, (E) complex cycles, and (F) electrochemical (hybrid) cycles.

Simple chloride (type D) cycles involve a small number of elements that form chlorides or oxochlorides which are thermally unstable and which can be re-formed by treatment of the reduced product with HCl. These cycles all use the reverse Deacon reaction (step 3 in Cycle 1) for the production of oxygen from chlorine. Because Br_2 and I_2 cannot thermochemically oxidize water, Br and I cannot replace Cl in cycles of this type. (The electrochemical reduction of aqueous Br_2 to HBr is considered in the context of type F cycles.) Elements which can be used as the basis for type D cycles include V, Cu, Eu, Ta, and Bi.[2,3]

Complex (type E) cycles are those in which more than one element—besides H, O, and sometimes Cl—undergoes oxidation and reduction. In many of these, SO_3 is decomposed to form SO_2, which is then used to reduce compounds of other elements. These in turn are used to reduce other species, eventually leading to the reduction of H_2O. Cycle 11 is one example of a complex cycle. In this process, it is difficult to attribute the water splitting to energy provided by acid–base reactions. In other complex cycles, however, the OA–OD model can be used to interpret—and perhaps to modify—one or more of the steps.

Cycle 11[29]

$$SO_3 = SO_2 + {}^1/_2O_2 \qquad T_R \simeq 1100\ \text{K}$$

$$SO_2 + I_2 + H_2O = 2HI + SO_3 \qquad 300\ \text{K}$$

$$2HI = I_2 + H_2 \qquad 600\ \text{K}$$

Electrochemical (type F) thermochemical cycles can be described as those in which electrons are the acid that drives a particular redox reaction. The nonelectrolysis steps in these cycles are usually amenable to treatment by the OA–OD model, since they usually involve the oxidation or reduction of oxides.

VII. Conclusions

The foregoing discussions showed that acid–base concepts can be used to classify and to analyze the energetics of simple thermochemical cycles involving oxides. With certain limitations, they can also be used as a guide to the modification of thermochemical cycles of this type and to the development of new thermochemical cycles. Acid–base models can also be applied to other types of cycles, but with limited success.

Acknowledgment. The author wishes to thank Dr. J. Brynestad for his extremely helpful criticism. The comments and suggestions of Drs. H. F. Bittner, G. P. Smith, J. Braunstein, and O. L. Keller are also gratefully acknowledged.

Registry No. H_2O, 7732-18-5; H_2, 1333-74-0.

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(29) J. L. Russell, Jr., K. H. McCorkle, J. H. Norman, J. T. Porter III, T. S. Roemer, J. R. Schuster, and R. S. Sharp, in "Proceedings of the 1st World Hydrogen Energy Conference, Miami Beach, Florida, 1976", T. N. Veziroglu, Ed., Pergamon Press, New York, 1976, pp 1A–105.