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Alan W. Searcy

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I. Introduction

The ceramist or metallurgist seeks for high temperature applications substances which are as resistant to all kinds of reactions as possible. He wishes, if possible, substances that are thermodynamically stable in their high temperature environment. If such materials are not available or are prohibitively expensive, he wishes substances whose reactions with chemicals in the environment are as slow and harmless as possible.

In two recent papers[1,2] the author has discussed the thermodynamic generalizations that can be formulated for high temperature reactions. The orientation of the present paper will be deliberately more practical. For amplification of the discussion of thermodynamics (Part II) and for many more specific examples and references, the reader may consult references 1 and 2.

In this paper we will briefly analyze factors that determine thermodynamic stability and factors that influence the kinetics of reaction of a solid. The reactivity of solid materials to two important high temperature reagents, oxygen and carbon, will then be outlined.

II. Thermodynamic Considerations

A reaction can occur at a given temperature and pressure only if the Gibbs free energy of reaction is negative. The thermodynamically stable products of reaction are those substances that can form with greatest decrease in the free energy of the system. Changes in chemical stabilities with increased temperature can always be traced to changes in the relative importance of the two terms that together determine the Gibbs free energy of the possible reactions. Always $\Delta F = \Delta H - T\Delta S$ where ΔF is the Gibbs free energy of reaction, ΔH is the heat of reaction, T is the absolute temperature, and ΔS is the entropy of reaction.

For qualitative discussions of changes in the free energy of reaction, both ΔH and ΔS can be considered to be independent of temperature so long as no reactant or product undergoes a change in state.[2] With this approximation, the free energy of reaction is a linear function of temperature. The key to understanding and predicting the changes with temperature in the thermodynamically stable substances in any particular system lies in evaluating the changes in bond energies and the changes in entropies in the possible reactions. At temperatures close to absolute zero the entropy term can make only a small contribution to determination of the free energy of reaction, but the importance of the entropy term increases with temperature, and the larger the absolute value of ΔS the more rapidly the free energy of reaction changes as a function of temperature. At low temperatures the thermodynamically stable chemical species in any system will be those of maximum total bond energy, but as the temperature rises, species that have lesser bonding energies but higher entropies become increasingly important.

Fortunately, entropy changes depend to a good first approximation only on what general kind of reaction occurs and only secondarily depend on the particular chemical substances involved. For example a familiar and useful rule is that the entropies of vaporization of many substances at their normal boiling points are about 22 cal/deg/mole of gas (Trouton's rule). Similarly, the entropies of fusion of most *metallic* elements are about 2.2 cal/deg/gram-atomic weight of the metal.[3]

Similar useful generalizations can readily be developed for various other classes of high temperature reactions. For example the entropies of reactions in which all reactants and products are ordered crystalline solids are about 0 ± 1 cal/deg/gram-atomic weight of reactant or product. As a result solid state reactions are almost always exothermic, i.e. take place with a net increase in the bonding energy which, by convention, means that they take place with a negative heat of reaction (but see references 1 or 2 for a discussion of the circumstances that give rise to endothermic solid state reactions). Furthermore, if an exothermic solid state reaction is found to occur at any temperature, the reaction can be expected to occur at any other temperature provided that the temperature is not lowered to temperatures at which the reaction rate becomes immeasurably slow and provided that the temperature is not raised high enough so that some reaction involving a change in state supervenes. This fact follows because new substances can become the stable reaction products as a result of a change in the temperature only if the difference between the contributions of the $T\Delta S$ term to the free energy of the competing reactions is comparable in magnitude to the difference between the heats of the competing reactions. For solid state reactions the $T\Delta S$ per gram-atomic weight of reactant is usually of the order of ±1 kcal and ΔH per gram atom is usually of the order of -10 kcal. The difference between two such small $T\Delta S$ terms will seldom be larger than the difference between the generally much larger heats of possibly competing reactions.

Illustrations may be helpful in demonstrating practical applications of the above arguments. To predict, for example, whether or not one solid element can displace another element from a solid compound to form solid reaction products, we need only know the heats of formation of the compounds of the two elements. Thus, to determine whether or not the reaction

$$W(s) + Al_2O_3(s) = WO_3(s) + 2Al(s)$$

can occur at any temperature below the melting point of a reactant or product we need only calculate the heat of the reaction. This heat is simply

$$\Delta H_f(WO_3) - \Delta H_f(Al_2O_3) = -201 + 400 = +199 \text{ kcal (at 25°C)}^4 .$$

Because the heat is positive, reaction would not be expected and, furthermore, since the free energy of such a displacement reaction is little changed by fusion of one or more of the reactants or products, reaction is not expected even above the melting point of both oxides, although here we must be cautious because some solution of a tungsten oxide in the molten alumina might occur. The possibility of solution cannot be evaluated from the above calculation.

Our chief danger in using a calculation such as that above to predict whether or not two substances may react when heated together lies not in the boldness of the assumption that only the heat of reaction need be calculated to enable us to reach a decision, but in the possibility that we have overlooked some other reaction that may occur instead of the reaction for which we have performed our calculation. Experiment confirms our prediction that tungsten will not react with aluminum oxide at or even above the melting point of alumina to yield condensed phase reaction products. But if tungsten and alumina are heated together in vacuo, they do react to yield a gaseous sub-oxide of aluminum plus tungsten trioxide gas. The partial pressures of these oxides are between 10^{-6} and 10^{-5} atmos at 2500°K so for some purposes for which tungsten and alumina might be used in contact, the gaseous products would cause no trouble. However, for other applications, in particular those that require tungsten and alumina to be held in contact for long periods, vaporization might remove significant quantities of material. A method for setting an upper limit to the rate of reactions that yield gaseous products is presented in section III-B of this paper.

The problem of selecting the reaction that is most likely to occur when a metal is heated with a metal carbide, a metal silicide, or a metal boride is particularly difficult because many of the transition metals form more than one compound with carbon, boron, or silicon. Often a metal may react with one of these compounds, not to displace the other metal as the free element, but to form a compound of the reacting metal and a new compound of the second metal. Furthermore the uncertainties in the heats of formation of metal carbides, borides and silicides are often so large that the calculated heats of displacement reactions involving these substances become highly uncertain. Under these circumstances, the wisest course is to resort to experimental test of whether or not a suspected reaction can take place. Because entropies of solid state reactions are small, we need only establish that a given reaction does or does not occur at one temperature to be nearly certain that the same reaction does or does not occur at all temperatures for which only solid state reactants and products are important. So, for example, to decide whether or not boron will displace silicon from its carbide, we need only heat boron with silicon carbide at a single temperature. If reaction to form boron carbide and silicon is found to occur, we have our answer for all practical temperatures, but if reaction is not found to occur, we should attempt the reverse reaction in order to be sure that a positive free energy rather than unfavorable kinetics prevented the first reaction.

The work of performing a solid state ternary reaction study such as that for the silicon-boron-carbon system just mentioned can be facilitated and the interpretation much simplified if any available reaction information is used to develop a simple isothermal ternary phase diagram. This approach is outline in previous papers.[5,2]

We have seen that when solid state reactions are under consideration, reaction products can be predicted usually from knowledge only of the heats of the possible reactions. However, when a reactant or product of reaction is a gas, the entropy of reaction has great influence in determining which substances will be stable at high temperatures. The most important class of gas-solid reactions is probably that in which a reactant or product is a diatomic molecule. Among substances stable as diatomic gas molecules over a wide range of pressures at high temperatures are oxygen, nitrogen, hydrogen, the halogens, the hydrogen halides, carbon monoxide, sulfur, selenium, and phosphorus. This list includes most of the gases that cause serious corrosion of materials at high temperatures. When a mole of one of these diatomic gases reacts with a solid to yield only solid reaction products, the entropy change is about -40 cal/deg. A better average entropy change for reactions of a particular diatomic gas can, of course, be obtained if only reactions of that gas are considered. For oxygen and nitrogen reactions treated as a separate class, a better average is -44 to -45 cal/deg/mole and for bromine gas reactions a better average is -36 cal/deg/mole.

These high negative entropies of reaction make a large positive contribution to the free energy of reaction. For the reaction $Co(s) + \frac{1}{2}O_2(g) = CoO(s)$, for example, $\Delta H^\circ_{298} = -57$ kcal, ΔS° is roughly -20 cal/deg., and the approximate contribution of the $-T\Delta S^\circ$ term to the free energy of reaction is about +20 kcal at 1000°K and +40 kcal at 2000°K. Because of their high negative entropies of formation from the metal and the diatomic gas, oxides, nitrides, hydrides, sulfides and halides have free energies of formation that become rapidly less negative with increasing temperatures. At sufficiently high temperatures some of such compounds decompose back to the elements. The decomposition and vaporization reactions of refractory compounds will be discussed in a subsequent section. At this point we need only cite two important examples of the effect of the high negative entropy of condensation of these diatomic gas molecules and the high positive entropy of their formation in influencing the course of reactions.

A familiar example is provided by the rapid increase in the effectiveness of carbon as a reducing agent with increasing temperature. Carbon monoxide, silicon monoxide, and germanium monoxide have more negative heats of formation than any other gaseous monoxides, but their heats of formation, all near -20 kcal, are very low compared to the heats of formation of most solid metallic oxides. The heats of formation of solid oxides range up to -150 kcal per gram-atomic weight of oxygen in the solid. As a consequence, at low temperatures, where the $T\Delta S$ contribution to a reaction such as $Fe_3O_4(s) + 4C(s) = 4\ CO(g) + 3\ Fe(s)$ is small, carbon will not reduce most metallic oxides, but at high temperatures, particularly if the carbon monoxide is continuously removed by pumping or by sweeping with a carrier gas, reaction can be carried to completion.

A somewhat less familiar example of the importance of entropy changes in influencing reaction equilibria is provided by the behavior of transition metal carbides, silicides or nitrides when heated in nitrogen. Such compounds are often attacked by nitrogen at relatively low temperatures, say around 1500°K, but are not attacked at <u>higher</u> temperatures, say 2000° to 2500°K. A displacement reaction such as $TiC(s) + \frac{1}{2}N_2(g) = TiN(s) + C(s)$ proceeds to the right at low temperatures because at low temperatures the more negative heat of formation of TiN (about -80 kcal per mole of TiN compared to about -45 kcal per mole of TiC) determines the reaction equilibrium, but at higher temperatures the negative entropy of reaction, -22 cal/deg, overbalances the difference in the heats of formation. It should be remarked, however, that the kinetics of reactions that involve nitrogen as a reactant or a product are sometimes much slower than reactions of other diatomic gases, and the thermodynamically predicted reactions involving nitrogen sometimes do not occur in the time of an experimental study.

More detailed discussions of the use of thermodynamic generalizations to predict or understand the course of high temperature reactions can be found in the earlier publications of the author[1,2] and in references 6 and 7. In applying these thermodynamic generalizations to studies of specific systems, compilations of thermodynamic data are an indispensible aid. Appendix I of this paper contains a list of such compilations that may be useful.

III. Kinetic Considerations

A. General Comments

While the final equilibrium that can be attained among reacting substances is purely a function of the chemical components present and of temperature and pressure, the path of the reaction and the rate of the reaction depend on a variety of additional variables, often in rather subtle ways. Among these variables are particle size, the extent of mixing, rate of diffusion, the presence or absence of inert gases, and even such physical properties of the solids or liquids concerned as strength, coefficient of thermal expansion, and viscosity.

An understanding of the mechanisms of solid state reactions can be of very practical value. A striking example of this fact is provided by the behavior of elemental germanium toward oxidation. The usual expectation is that the rate of oxidation of any metal will increase with increased oxygen pressure, but this expectation is sometimes wrong. Over a considerable temperature range the rate of oxidation of germanium actually decreases with increase in the oxygen pressure in the system. This peculiarity has been satisfactory explained by Bernstein and Cubicciotti.[8] They have shown that two competing processes occur on the surface of germanium in oxygen atmospheres. A condensed phase layer of germanium dioxide forms and gaseous GeO is evolved. At high oxygen pressures the formation of the condensed phase dioxide predominates and a thick protective layer is built up. At low oxygen pressures the layer remains thin and the diffusion process necessary for evolution of GeO goes at a more rapid rate. Perkins, Reidinger and Sokolsky[9] have shown that the rate of oxidation of molybdenum disilicide is also faster at reduced oxygen pressures than it is at one atmosphere oxygen pressure.

In this section of the chapter the author will present and illustrate some generalizations about reaction kinetics that may help the materials scientist or engineer to overcome chemical problems that he encounters in development of high temperature materials. The reader is warned that this is a greatly simplified treatment of a complex subject. For further reading in topics related to solid-state kinetics the author particularly recommends "Reactions in and on Solids", a recent translation of a text by Karl Hauffe.[10] Other helpful books include references 11, 12, 13, 14 and 15.

B. Reactions Limited by the Rates of Arrival of Gaseous Reactants or Departure of Gaseous Products

Although for reactions in general there is no practical connection between thermodynamics and kinetics, for sublimation reactions, condensation reactions, and gas-solid reactions useful upper limits to the rates can be calculated from combination of kinetic theory for gases with thermodynamic data. This method of calculation is very useful because for many high temperature applications the choice of materials is limited by the rate at which the materials sublime or react with gases in their environment, and an upper limit to the reaction rate often is all that is needed to establish that a substance will last in its environment for some specified design time.

Reaction cannot proceed at a rate faster than the rate with which reactants are supplied to the reaction surface or than the rate at which products leave the reaction surface, whichever rate is smaller. The rate at which a reactant gas is supplied to the surface can be calculated from the pressure of the reacting gas through the application of simple kinetic theory.[16] $Z = P/(2\pi MRT)^{\frac{1}{2}}$, where Z = moles of reactant that strike the surface per unit time per unit area, P = pressure of the reactant gas, M = the molecular weight of the gas, R = the gas constant, and T = the absolute temperature. With P in atm, T in degrees K, and Z in grams/cm^2/hr, this becomes $Z = 1.596 \times 10^5 P/(MT)^{\frac{1}{2}}$. The maximum rate at which product gases can leave the reaction surface can be calculated from the same equation (the Hertz-Langmuir equation) if the equilibrium pressure of the product gas and its molecular weight are substituted into the equation. The equilibrium pressure can be calculated from the equation $\Delta F^\circ = -RT\ln K$, where ΔF° is the standard free energy for the reaction and K is the equilibrium constant.

Application of the Langmuir equation to calculation of the maximum rate at which a solid will sublime can readily be illustrated by an example. According to Coughlin,[4] the free energy of formation of magnesium oxide is -76 kcal at 2000°K. Magnesium oxide is known to sublime by the reaction

$$MgO(s) = Mg(g) + \tfrac{1}{2}\,O_2(g)$$

and since both magnesium and oxygen are gases in their standard states at 2000°K, the free energy of formation of magnesium oxide tabulated by Coughlin is the negative of the free energy for the sublimation reaction (i.e., +76 kcal). The pressure of magnesium and of oxygen then are calculated from $\Delta F^\circ = -RT\ln P_{Mg} \cdot P_{O_2}^{\frac{1}{2}}$. For free surface evaporation under neutral conditions, the number of magnesium atoms that leave the surface must be equal to twice the number of oxygen molecules that leave the surface. Therefore, $Z_{Mg} = 2Z_{O_2}$, $P_{Mg} = 2P_{O_2}\sqrt{M_{Mg}/M_{O_2}}$, and $+76{,}000 = -2000 \times 1.987\ln(2P_{O_2}^{\frac{3}{2}}\sqrt{M_{Mg}/M_{O_2}})$ So $P_{O_2} = 1.55 \times 10^{-6}$ and $P_{Mg} = 3.82 \times 10^{-6}$, and the number of moles of Mg leaving the surface is $Z_{Mg} = 2.75 \times 10^{-3}$ moles/cm^2/hr.

In the reaction of a gas with a solid to produce a gaseous reaction product, the first step in establishing the minimum upper limit to the rate that can be set by the Langmuir equation is to determine whether the rate of arrival of the reactant or the rate of departure of the product should be the slower process. For example, suppose the reaction $W(s) + O_2(g) = WO_2(g)$ is under consideration. According to Ackermann and Thorn,[17] for this reaction at high temperature, $\Delta F° = 7{,}360 - 5.80\ T$ cal. At 2500°K, therefore,

$$\ln(P_{WO_2}/P_{O_2}) = +\ 7{,}140/2500 \times 1.987$$

and $P_{WO_2} = 4.21\ P_{O_2}$, or $Z_{WO_2}\sqrt{M_{WO_2}} = 4.21\ Z_{O_2}\sqrt{M_{O_2}}$, and $Z_{WO_2} = 1.6\ Z_{O_2}$ under equilibrium conditions.

Since the rate of departure of $WO_2(g)$ from the surface cannot exceed the rate at which oxygen is supplied to the surface, the rate of oxygen arrival sets the smaller upper limit to the rate of reaction at 2500°K.

Although the rate of sublimation calculated by the Langmuir equation must be looked on as an upper limit to the actual sublimation rate, experiment has established that for many kinds of substances the actual rate of sublimation will closely approximate that calculated from the Langmuir equation. Present evidence, for example, indicates that essentially all of the metallic elements sublime at rates that lie between 0.3 and 1.0 times the rate calculated by recourse to the Langmuir equation.[18] Most simple oxides and other salts appear to sublime at rates that are at least 0.01 times the rates predicted by the Langmuir equation.

In the event, however, that some surface reaction is necessary to produce the vaporizing species from those that are present in the crystal lattice, an activation energy barrier for this surface reaction may reduce the actual rate of sublimation to a value many orders of magnitude below the predictions of the Langmuir equation. Brewer and Kane[19] have pointed out that modifications of arsenic, phosphorous, and arsenous oxide, which contain as units in the crystal lattice those molecules which are the equilibrium vapor species, show approximately the rate of sublimation predicted by the Langmuir equation, while other modifications of the same substances which have different lattice units show rates of sublimation as little as 10^{-6} times the predictions of the Langmuir equation.

Among solids of high temperature interest, the nitrides and phosphides are classes of materials which can be expected to show lower rates of sublimation than predicted by the Langmuir equation. Gallium nitride has recently been shown to sublime at a rate that is approximately 10^{-6} times the predicted rate. The experimental data lend support to the conclusion that the slow step in the gallium nitride sublimation process is the formation of the N_2 molecule on the surface.[20]

Reactions between gases and solids to produce gaseous reaction products may also sometimes be controlled by the rate of a slow reaction on the surface of the solid. Reaction of oxygen with bare tungsten to produce gaseous tungsten oxides, for example, proceeds at high temperatures and low gas pressures at a rate that may be only 0.1 to 0.01 times the rate at which oxygen is supplied to the reaction surface even though equilibrium considerations predict that essentially all the arriving oxygen should be converted to gaseous tungsten oxides.[21] In fact, although the rate of reaction at a constant oxygen pressure increases with temperature in an apparently normal exponential manner over a wide temperature range, at very high temperatures the rate passes through a maximum and <u>decreases</u> with further increases in temperature. The temperature at which the maximum is reached is increased by increased oxygen pressures. For example, the maximum is at 2100°K when $P_{O_2} = 10^{-7}$ atm and 2250°K when $P_{O_2} = 10^{-6}$ atm.[22]

The maximum cannot be correlated with a decrease in stability of the gaseous reaction products. Apparently, the maximum occurs when the competing reaction of desorption of oxygen without reaction becomes more rapid than that of formation of the gaseous tungsten oxide.

Meyer and Gomer[23] demonstrated the interesting fact that when cold gases at low pressures impinge on a hot surface, the rate of reaction between the gas and the surface may sometimes be limited by the efficiency with which the cold gas is heated. They found, in particular, that methane gas at room temperature undergoes almost no cracking on a clean, graphite surface when the graphite is held at 2000°K, despite the fact that methane is highly unstable at that temperature relative to decomposition to carbon and hydrogen.

De Poorter and Searcy[24] found similar behavior when carbon dioxide at room temperature and 10^{-5} atm pressure impinged on a hot tungsten surface. At 1800°K there is no measurable reaction to form carbon monoxide and tungsten dioxide although thermodynamic calculations predict that some reaction should take place. At 2100°K a small amount of reaction becomes observable. Of the carbon dioxide molecules that strike the surface only one in 7000 reacts, however, compared to the prediction of the thermodynamic data that one in two should react.

Oxygen shows an entirely different behavior with hot tungsten. Apparently, oxygen molecules interact much more strongly with a tungsten surface than do carbon dioxide molecules during the time of a single collision and can become heated at the surface to a temperature sufficient for reaction to take place. The chemical factors which give rise to this striking difference in behavior between oxygen and carbon dioxide are under investigation.

One important conclusion to be drawn from the results of Meyer and Gomer and of De Poorter and Searcy is that experiments intended to demonstrate the chemical interactions between hot gases, such as might be formed for example in a rocket exhaust stream, with materials at high temperatures cannot necessarily be satisfactorily duplicated in apparatus in which the gas is introduced cold against a hot surface.

Obviously, a static inert atmosphere can reduce the rate of sublimation or of a reaction between a gas and a solid below the value calculated by means of the Langmuir equation. It seems probable, however, that in a stream of swiftly flowing gas the observed rate would approach the value predicted by the equation.

The rate of reaction of a gas with a solid may be reduced by even a monolayer of adsorbed impurity. For example, the rate of oxidation of graphite or carbons by carbon dioxide is reportedly reduced by a factor of 7 at 1100°C in the presence of phosphorous oxychloride.[25] Darken and Gurry[26] report that the rate of solution of nitrogen in molten iron is reduced by a very significant extent by such small quantities of oxygen that we must presume that the oxygen is present as a surface layer which inhibits the adsorption and subsequent solution of the nitrogen molecules. Solution of hydrogen in zirconium metal goes rapidly at 150°C, but if oxygen or water vapor is present the rate of solution is greatly reduced.[27]

The rate at which a substance vaporizes or sublimes can similarly be reduced by adsorbed films. Monomolecular films of fatty acids and long-chain alcohols have been demonstrated to reduce the rate of evaporation of water by factors as much as 10^4.[28] The use of such films is being actively considered for conservation of water stored in open reservoirs.[29]

C. Reactions Whose Rates May be Controlled by Solid State Diffusion

For preferential sublimation of one component of a solid solution (e.g., Ag from a Ag-Pd alloy) or for reaction of a gas with a solid to form a solid solution (e.g., the reaction of silver vapor with palladium to form a silver-palladium solid solution), the rate may be limited by a slow rate of diffusion in the solid rather than by the sublimation step. Similarly, in a reaction between a gas and a solid phase to produce a new solid phase (e.g., $2Cu(s) + \frac{1}{2} O_2 (g) = Cu_2O(s)$) or in the decomposition of a solid on heating to yield a second solid plus a vapor (e.g., $SiC(s) = C(s) + Si(g)$), a solid state diffusion step may limit the rate. In order to understand these gas-solid reactions, as well as solid-solid reactions and many liquid-solid reactions, we need to analyze the factors that control solid state diffusion.

For gas-solid and liquid-solid reactions or for decomposition of solids to produce a second solid plus a gas or liquid, the ratio of the volume of the solid produced by the reaction to the volume of that quantity of solid which has reacted is important in determining the mechanism and, therefore, the rate of reaction.

Clearly, unless the solid reaction product is removed by some means, reaction can only proceed by transfer of the gaseous reactant or of the escaping gas through or past the condensed phase reaction product. Pilling and Bedworth[30] first noted that for such reactions, when the volume occupied by the solid reaction product is greater than that occupied by the solid reactant, reaction can only proceed by diffusion of a reactant, or of a reaction product, through a protective layer of the solid reaction product. Reaction then is relatively slow and the quantity of material reacted usually varies in direct proportion to the square of the time of reaction. On the other hand, if the ratio of the volume of reaction product to reactant is less than unity, the reaction rate is usually relatively rapid and the quantity of material that reacts is directly proportional to the time of reaction.

The criterion of Pilling and Bedworth for prediction of whether a reaction will be slow and will have a rate that decreases with time, or whether it will be relatively rapid with a linear dependence on time has proved extremely useful as a guide in predicting and understanding whether attack of oxygen or other gaseous reagents on a solid will produce a protective or a nonprotective coating. A satisfactory volume ratio does not always result in a protective coating, however, as recognized by Pilling and Bedworth themselves. A coating which occupies greater volume than the substrate may fail to yield protection for several reasons: the strains set up by volume mismatch may cause the coating to crack; differences in the coefficients of thermal expansion may cause the coating to crack during thermal cycling; mechanical forces in the environment may abrade or shatter the coating.

On the other hand, instances are known in which a pore-free protective coating has been produced even though the reaction product occupies a smaller volume than the reactant. For example, the iron produced by reduction of wüstite by hydrogen at 680°C forms a protective layer over the iron oxide.[31] Metallic niobium produced by the reaction $Nb_5Ge(s) = 5Nb(s) + Ge(g)$ forms a pore-free protective film over the niobium germanide phase and greatly reduces the rate of the decomposition reaction.[32]

In both of these examples the formation of the protective coating is observed at temperatures in excess of the sintering temperature of the metal. It seems probable that whenever the temperature is high enough so that the product phase may sinter, similar protection can be produced. In any reaction in which a new solid phase is formed there may be an induction period before reaction becomes observable. This period is the time necessary for nuclei of the product phase to form and grow to observable dimensions. Until the product layer becomes relatively thick, say of the order of 100 to 1000 Å, the reaction rate may be controlled by the electrostatic forces across the phase boundary or limited by the rates of the phase boundary processes.

For layers of greater thickness diffusion usually becomes rate determining and the quantity of material reacting varies with the square root of the time of reaction, unless, or until, the product layer becomes stressed to the point that cracking or spalling occurs, in which case sudden increases in the rate of reaction may be observable and subsequent reaction may be linear with time.

Because the initial stages of reaction may be markedly influenced by small concentrations of surface impurities, by particle shape, and even by previous mechanical treatment, experiments in which the relative degree of protection provided by different coatings is determined from the extent of reaction that occurs in fixed short-time periods may be misleading. For example, a protective coating of oxide forms on $MoSi_2$ more quickly than on Mo_5Si_3, and after a heating period of 30 minutes at 1500°C in O_2 at 8 mm pressure the disilicide has been considerably less attacked than has Mo_5Si_3. Within a period of 90 minutes, however, a sound protective coating of oxide on Mo_5Si_3 has normally formed, and the Mo_5Si_3 may show longer life at high temperatures than does an $MoSi_2$ sample.[33]

The rates of diffusion-controlled reactions characteristically can be expressed by equations of the form

$$\text{Rate} = A \exp(-\Delta H^{\ddagger}/RT)$$

i.e., the rates of such reactions increase exponentially with temperature. The smaller the value of $\Delta H^{\ddagger}$, the activation energy for the diffusion process, the more rapidly will diffusion take place at any given temperature. For classes of compounds of generally similar bonding types, values of the activation energy for self diffusion vary roughly in proportion to the heats of fusion or to the heats of sublimation <u>per gram-atom</u> of the compound. Thus, for any given temperature diffusion in, for example, a group of oxides will often be slowest in that oxide which has the greatest thermodynamic stability. The Tammann temperature is the approximate temperature at which bulk diffusion through solids and diffusion-controlled solid-state reactions become observable for given classes of materials. For metals and for inorganic solids the Tammann temperature is approximately 0.5 of the absolute melting temperature.

There are some dramatic deviations from predictions based on thermodynamic stabilities or melting points, however. For example, uranium dioxide is one of the most stable oxides and has a melting point of at least 2700°K, but reaction of oxygen with uranium oxide to produce a phase of excess oxygen content over the stoichiometric UO_2 value can be observed below 500°K.

Although there is far from universal agreement among experts upon the mechanisms of diffusion in solids, it can be concluded that most bulk solid-state diffusion is dependent upon either movement of atoms through interstices of the regular lattice sites or upon exchange of atoms with vacancies. In the event that the vacancy concentration in the lattice is low, the activation energy for diffusion is frequently the sum of the activation energy of vacancy formation and the activation energy for vacancy movement. Diffusion on grain boundaries is more rapid than diffusion inside the crystal because of the high concentration of vacancies in the boundaries and because of the lower thermodynamic stability and resultant lower activation energy for atom movement at the boundaries.

Rates of diffusion at temperatures low relative to the absolute melting point of a solid are highly structure-sensitive. That is, they depend strongly on the concentration of impurities, vacancies, dislocations, grain boundaries and other imperfections that have been introduced by previous treatment. Mechanical working, of course, introduces vacancies and dislocations, whose presence reduces the activation energy for diffusion.

The activation energy for grain boundary diffusion is apparently always lower than the activation energy for bulk diffusion. As a result, grain boundary diffusion becomes significant at temperatures below those at which bulk diffusion is observed. In fine-grained materials, grain boundary diffusion may account for very significant amounts of material transfer over a considerable temperature range. At high temperatures relative to the melting temperature, however, the introduction of impurities is almost always accompanied by a significant change in the concentration of vacancies or interstitial atoms or ions. Introduction into a salt of ions of different charge from that of the major ion of the same sign, e.g., addition of +2 ions into the salt of a +1 metal, is particularly effective in changing the rate of diffusion. Thus, for example, solution of divalent cations in alkali halide salts increases the concentration of cation vacancies. Because of the increased concentration of vacancies the rate of cation diffusion at low temperatures is increased (but shows a lesser temperature dependence than does diffusion at high temperatures).[34]

On the other hand, if diffusion of a metal proceeds by movement of metal ions on interstitial sites of a semiconductor, addition of metal ions of higher valence may significantly <u>reduce</u> the rate of diffusion.[35] For example, Al_2O_3 additions reduce the rate of diffusion of zinc in zinc oxide while addition of lithium oxide increases the diffusion rate.[36] The reasons are understood but cannot be discussed here.

Diffusion at temperatures near the melting point is insensitive to impurities and to mechanical working because the equilibrium concentration of vacancies produced by high thermal excitations of the lattice becomes large in comparison to the concentration of vacancies associated with the introduction of the impurity atoms, and above the annealing temperature of the material mechanically introduced imperfections are, of course, annealed out.

D. Relative Diffusion Rates and the Mechanisms of Diffusion Controlled Reactions

For a variety of reasons it is helpful to know the relative rates of diffusion of the ions, atoms, and electrons in that solid phase for which diffusion determines the rate of some chemical reaction. One reason which might not be immediately apparent is that the physical form and dimension of objects made by solid state diffusion of one substance into another are determined by the relative diffusion rates. For example, if tantalum carbide is made by thermal decomposition of a hydrocarbon on the surface of a heated tantalum rod, the end product of the process is a rod of tantalum carbide. If, on the other hand, tantalum carbide is made by thermal decomposition of a tantalum halide vapor on a graphite rod, the final product is a tube of tantalum carbide which has an inner diameter that approximates the initial diameter of the graphite rod from which the tube was formed. This difference in behavior in these two systems with the same chemical end product provides a graphic illustration of the fact that carbon diffuses in tantalum carbides much more rapidly than does tantalum.

In ionic substances such as the compounds formed by metals in their +1 or +2 oxidation states with the halogens or oxygen family elements, the metal ions normally diffuse more rapidly than do the nonmetal ions. The rates of diffusion of the slower ions, however, usually increase more rapidly with increased temperature and may become comparable with the rates of the faster ions at temperatures close to the melting point.

For ions of a given charge, rates of diffusion appear to be faster for the smaller ions. Thus, sodium can be expected to diffuse more rapidly in salts than does potassium or heavier alkali metals. The charge of the ion, however, is probably usually more important in determining its diffusion rate than is the size, and the higher the charge of the ion the more slowly it can be expected to diffuse.

Knowledge of the relative rates of diffusion of atoms or ions through a product phase can help the investigator in finding means to control the rate of reaction. We have already seen that altervalent ions may be used to change the rate of ionic diffusion very significantly. Similarly, the reaction of tantalum with carbon replacement of some of the carbon by nitrogen could conceivably have a marked influence on the rate of diffusion of the remaining carbon.

The rates of diffusion of the nonmetallic components in those carbides, nitrides, and borides that show metallic conductivity are orders of magnitude faster than the rate of diffusion of the metallic components. In solid iron, the rates of diffusion of interstitial elements vary in the order $H > C > N > Si$ at any given temperature. The same relative order probably would be found in other interstitial solids. The rates of diffusion of the slower atoms normally increase with temperature more rapidly than do the rates of the faster atoms.[37] In general, the difference in rates of diffusivity will be least at the melting point and greatest at the minimum temperature at which diffusion can be measured.

In interstitial carbide, silicide, boride and nitride solutions the rate of diffusion of the nonmetal appears often to be strongly dependent upon the concentration of the nonmetal in the solid. Characteristically, for metal-nonmetal systems in which more than one intermediate phase is stable, different phases form on the surface of the metal in layers in the order of increasing nonmetal content. Usually the layers of phases of low nonmetal content are very thin relative to the layers of the phase of highest nonmetal content for each system.

There is some evidence that for any class of interstitial solids, say the carbides, rate of diffusion of the nonmetal in the solids is highest in the phases that have the lowest heats of formation. Thus, a layer of molybdenum carbides, which are of relatively low stability compared to tantalum or niobium carbides, forms more rapidly at a given temperature than does a layer of tantalum or niobium carbides.

Qualitative data suggest that rhenium is a less effective barrier to carbon diffusion than is molybdenum or tungsten despite the fact that rhenium does not react with carbon to form a rhenium carbide phase. Carbon dissolves to a small extent in rhenium metal and because it is only weakly bound, diffuses through the metal rapidly.

In the transition metal carbides, silicides, nitrides, and borides, the non-metals diffuse as atoms. The rate of reaction depends only upon the rate of diffusion of the non-metals, which are the most rapidly diffusing components of the product phases. For some reactions, however, the rate may depend on diffusion of the second fastest kind of particle. This point can be illustrated by contrasting the mechanism of a reaction of a gas with a metal to form a semiconductor and the mechanism of reaction of a gas with a metal to form a salt that has no electronic conductivity.

In formation of silver sulfide, which is a semiconductor, the rate of reaction is controlled by the rate at which silver ions diffuse outward to react with the gas at the exterior surface of the product layer. Electroneutrality is maintained by the rapid transfer of electrons as well as the silver ions outward through the sulfide layer.

In formation of an electronically insulating alkaline earth halide from the metal and the halogen, reaction can only proceed through the movement of counter currents of positive and negative ions. The reaction product must remain electrically neutral and reaction proceeds at a rate limited by the movement of the second fastest of the two ions that pass through the product layer.

Diffusion controlled reactions that yield gaseous products have another limitation. The rates of such reactions must normally be limited by the rate at which the solid reactant is transferred outward through the protective coating, no matter whether the solid or the gaseous reactant diffuses more rapidly through the coating material. For example, in the reaction $2Ge(s) + O_2(g) = 2GeO(g)$, the rate will be limited by the transfer of germanium out through the germanium dioxide layer. This statement is based on the premise that the gaseous reaction product if formed anywhere other than on the outer surface would be unable to escape except by formation of bubbles which have sufficient pressure to fracture the coating. No such boiling phenomenon was mentioned in an experimental study.[8] At high temperatures this process may in fact become important; its occurrence should be signalled by obvious bubble formation under, or in, the oxide phase.

E. Corrosion by or through Liquids

Diffusion through liquids is very much faster than diffusion through solids. Sometimes an oxidation reaction that initially follows a slow, parabolic rate law has been observed to undergo a sudden transition to a rapid, linear reaction which can be associated with simultaneous fusion of the oxide surface film.[38] The presence of oxides that are low melting or that will contribute to formation of low-temperature eutectics, e.g., MoO_3, V_2O_3, PbO, or Bi_2O_3, is therefore often undesirable when oxidation resistance is sought.

Often a liquid phase may seriously corrode a solid even though the solid has a very low solubility in the liquid. This corrosion occurs when a slight temperature gradient exists in the liquid so that the solid can be dissolved at the higher temperature and be precipitated at the lower temperature where the solubility limit is exceeded. Whenever a liquid is used as a heat transfer medium, the possibility that mass transfer in the temperature gradient will cause corrosion must be seriously considered. This problem as well as other possible sources of metal corrosion are discussed, with illustrations, in a valuable short review article by Cubicciotti.[38]

IV. Stability of Solids in Two High-Temperature Environments

A. Stability toward Oxygen

As examples of the analysis of the problem of finding suitable materials for high temperature use we may consider the reactions of various materials with two important high-temperature reagents: oxygen and carbon. These substances, important in themselves, serve as prototypes of behavior of other gaseous and solid non-metals. The arguments leading to the statements made, and the sources of the data given, are cited in recent review articles by the author and will not be repeated here.[1,2]

Very few materials (other than oxides) that have high melting points are thermodynamically stable toward oxygen attack. Although essentially all metal fluorides are thermodynamically stable to attack by oxygen, no fluorides have melting points above 1200-1500°C. Furthermore, the fluorides are slowly attacked by water vapor with formation of hydrogen fluoride and of metal oxides if heated in undried air. Salts of the other halogen elements are less stable than fluorides and have even lower melting points. They do not deserve serious consideration for high-temperature applications, except perhaps as heat-transfer fluids.

Most of the familiar solid oxides are, of course, stable toward oxygen attack, but a few exceptions are worth noting. Uranium dioxide reacts at only a few hundred degrees to absorb additional oxygen. Ignition in air at ordinary burner temperatures produces U_3O_8. Above about 1350°C, UO_2 becomes stable toward oxygen attack because at such temperatures the dissociation pressures of higher uranium oxides exceed 1 atmosphere. Similar oxidation reactions are undergone by Ce_2O_3 and several other rare earth oxides. Normal barium oxide (BaO) and strontium oxide (SrO) can be oxidized at relatively low temperatures to the super-oxides BaO_2 and SrO_2.

None of the high-melting sulfides, nitrides, phosphides, carbides, silicides, or borides are thermodynamically stable in oxygen atmospheres. Some of these compounds show moderate to good oxidation resistance, however, because of formation of a protective coating of a metal oxide. Apparently the greatest oxidation resistance yet achieved for compounds of this class is shown by silicon carbide and molybdenum disilicide (see section III-C). These two substances can be used for many hours in oxygen or air atmospheres at temperatures up to 1600 or 1700°C. Above this temperature diffusion becomes rapid through the silica coating that provides protection to both of these substances. Of the solid elements only gold, silver, platinum, palladium, iridium, and rhodium are thermodynamically stable toward oxygen at high temperatures. Of these, rhodium and iridium are the highest melting. The prospects of obtaining solids, other than oxides, that are thermodynamically stable toward attack by oxygen at normal pressures above the melting point of iridium (2454°C) can be completely discounted. The probabilities of success in developing effective protective oxide coatings for use above this temperature are perhaps small, but must be explored vigorously.

B. Stability toward Carbon

When carbon is heated with a stable metal oxide, the usual reaction is one that produces carbon monoxide gas plus the metal carbide. The extent to which such reactions proceed at any given temperature may depend to some degree on the rate of transport of reactants through the carbide layer. Beryllium oxide is said to be the oxide that is most resistant to carbon attack.[39] Though it is by no means certain that this conclusion is rigorously correct, the relatively negative heat of formation of BeO and the fairly low stability of Be_2C make BeO thermodynamically less vulnerable to carbon attack than almost any other oxide.

All the oxides react with carbon at high temperatures unless the carbon monoxide pressure is maintained higher than the equilibrium carbon monoxide pressure for the oxide-carbon reaction. The effect of the CO pressure on the effectiveness of carbon as a reducing agent is discussed in reference 2.

The stabilities of borides, silicides, and nitrides toward carbon are best described in terms of simplified ternary phase diagrams as discussed in a previous review.[2] The important compounds of these classes for materials applications are those of the transition metals of groups IV, V, and VI. Commonly the most stable boride of a given transition metal is stable to reaction with carbon, whereas its borides of higher or lower non-metal content are unstable. For example, ZrB_2 is stable toward reaction with carbon, while ZrB and ZrB_{12} are not.[40] Transition metal nitrides are usually stable toward carbon at low temperatures but become unstable above some characteristic temperature for a given nitrogen pressure. For 1 atm. N_2 pressure, the characteristic temperatures lie from 1200-2200°C depending on the transition metal. For a specific nitride this temperature can be estimated from the equation

$$T = \frac{\Delta H^\circ_{298} - \Delta F^\circ_{298}}{\Delta S^\circ_{298}}$$

where ΔH°_{298}, ΔF°_{298}, and ΔS°_{298} are the heat, the free energy, and the entropy change at 25°C for the reaction $M_xN(s) = x\,M(s) + \frac{1}{2}N_2(g)$. The entropy change for this reaction is always about 22±2 cal $deg.^{-1}$ Storms has recently reviewed the properties of high-melging nitrides.[41]

Of the high-melting metals, all of the six platinum metals and rhenium are stable to attack by carbon at temperatures below 2000°C. Above that temperature some of these metals have been demonstrated to form carbides.[42]

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APPENDIX I

Sources of High Temperature Thermodynamic Data

Source	Title or Description	Date
Kelley, Bull. U.S. Bur. Min., 350, 394, 434 and 477	Entropies of inorganic substances	1932-1950
Kelley, Bull. U.S. Bur. Min., 371 and 476	High temperature heat contents and entropies of inorganic substances	1934-1949
Bichowsky and Rossini, Reinhold, New York	*The Thermochemistry of the Chemical Substances*	1936
Kelley, Bull, U.S. Bur. Min., 407	Properties of carbides and nitrides	1937
Rossini, et al, Circ. U.S. Bur. Stand., 461	Organic molecules to 1500°K	1947
Rossini, et al, Circ. U.S. Bur. Stand., Series III compilation	Inorganic substances to 5000°K (issued in sections)	1947-date
NBS-NACA 'Tables of Thermal Properties of Gases', Circ. U.S. Bur. Stand., 564 (1955)	O, O_2, N, N_2, H, H_2, He, Hg, CO_2, CO, NO, and A to 5000°K	1949-1951
Brewer, Bromley, Gilles and Lofgren, National Nuclear Energy Series, Vol. IV-19B, ed. Quill, McGraw-Hill, N.Y.	Elements and inorganic substances including nitrides, carbides, sulfides, silicides, phosphides, halides, and common gases	1950
Latimer, MDDC-1462 (rev)	Diatomic gases to 5000°K	1952
Latimer, Prentice-Hall, N.Y.	The Oxidation States of the Elements, 2nd edition	1952
Ribaud, French Air Ministry Pub. No. 266	Gases at high temperatures	1952

Source	Title or Description	Date
Rossini, et al, Circ. U.S. Bur. Stand., 500	Selected Values of Chemical Thermodynamic Properties, Series I and II	1952
Brewer, Chem. Rev., 52, 1 (1953)	Properties of oxides and their vaporization processes	1953
Rossini, Amer. Petrol. Inst. Project 44 Rep., Carnegie Press	Organic molecules to 1500°K	1953
Coughlin, Bull. U.S. Bur. Min., 542	Heats and free energies of formation of inorganic oxides	1954
Zeise, S. Hirzel, Leipzig	Thermodynamik auf den Grundlagen der Quantentheorie, Quantenstatistik und Spektroskopie. Bd. III, Ergebnisse in tabellarische und graphische Form	1954-1957
Fickett and Cowan, J. Chem. Phys., 23, 1349 (1955); Los Alamos Rep. LA-1727	Properties of H_2, CO, N_2, NO, O_2, C_2, CO_2, H_2O and graphite to 12,000°K	1955
Hultgren, Orr, et al, Minerals Res. Lab., Univ. Calif., Berk.	Properties of metals and alloys (issued in sections)	1955-date
Katz and Margrave, J. Chem. Phys. 23, 983 (1955)	Free energy functions for gaseous atoms from H to Nb	1955
General Electric, McGraw-Hill, N.Y.	Properties of Combustion Gases, Vol. I, Thermodynamic Properties. Vol. II, Chemical Composition of Equilibrium Mixtures	1956

Source	Title or Description	Date
Kolsky, Gilmer and Gilles, J. Chem. Phys., 27, 494 (1957); Los Alamos Rep. LA-2110	Properties of 54 Elements considered as ideal monatomic gases	1956
Kubaschewski & Catterall, Pergamon, London	*Thermochemical Data of Alloys*	1956
Roginskii, A.E.C. translation No. AEC-tr-2873 (1956); Nuclear Sci. Abs., 11, 10488 (1957).	Thermodynamic functions for isotope molecules	1956
Stull and Sinke, Amer. Chem. Soc. Adv. in Chem. Series, No. 18	Properties of the elements to 3000°K	1956
Glassner, Argonne Nat. Lab. Rep. ANL5750	Properties of oxides, fluorides and chlorides to 2500°K	1957
Kubaschewski & Evans, Pergamon, London	*Metallurgical Thermochemistry*, 3rd edition	1958
Bockris, White & MacKenzie *Physico-Chemical Measurements at High Temperatures*, Butterworths, London	Free energy functions, heat of formation for gaseous atoms, some common gases, condensed phase binary and ternary oxides, carbides, hydroxides, and sulfides. Free energy functions for condensed phase elements.	1959
Brewer & Chandrasekharaiah UCRL-8713	Free energy functions for gaseous monoxides	1959
Dow Chemical, JANAF Interim Thermochemical Tables	Complete thermodynamic data over extended temperature ranges for substances of rocket propellant interest.	1960

Source	Title or Description	Date
Kelley, Bull. U.S. Bur. Min., 584	High temperature heat content, heat capacity and entropy data for elements and inorganic compounds	1960
Rand & Kubaschewski, A.E.R.E.-R3487	Thermochemical properties of uranium compounds	1960
Ackermann & Thorn, Prog. in Ceram. Sci., 1, 39-88 ed. J. E. Burke	Vaporization properties of oxides	1961
Brewer & Brackett, Chem. Rev., 61, 425-32	Free energy functions for condensed and gaseous diatomic alkali halides. Enthalpies of sublimation and dissociation.	1961
Brewer, U.C.R.L. - 9952	Enthalpies of formation of condensed and gaseous diatomic alkali halides	1961
Brewer & Rosenblatt, Chem. Rev., 61, 257-63	Dissociation energies of gaseous metal dioxides	1961
Brewer & Pitzer, Thermodynamics, McGraw-Hill, N.Y.	Free energy functions and heats of formation for gaseous elements; solid, liquid, and gaseous halides; solid and gaseous oxides; carbon compounds and related compounds. Free energy functions for solid and liquid elements	
Kelley & King, Bull. U.S. Bur. Min., 592	Entropies of the elements and inorganic compounds	1961

Source	Title or Description	Date
Haar, Friedman, & Beckett Nat. Bur. of Stand. Monograph #20	Thermodynamic functions (up to 5000°K) of gaseous binary hydrides, deuterides and tritides	1961
Freeman, Oklahoma State Univ., Res. Foundation Rept. #60	Heats of formation of binary sulfides; solid, liquid and gaseous	1962
Kelley, Bull. U.S. Bur. Min. 601 [A reprint of Bulletins 383 (1935), 384 (1935), 393 (1936), and 406 (1937)]	Free energies of vaporization and vapor pressures of inorganic substances. Correlations and applications of the thermodynamic properties of metal carbonates. Heats of fusion of inorganic substances. Thermodynamic properties of sulfur and its inorganic compounds.	1962
Searcy & Finnie, J. Am. Ceram. Soc., 45, 268-73	Heats of formation of metal silicides	1962
Storms, L.A.M.S.-2674 (I)	Thermodynamic properties of group 4a, -5a, and -6a carbides	1962
Storms, L.A.M.S.-2674 (II)	Thermodynamic properties of group 4a, -5a, and -6a nitrides	1962

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