

Synthetic Concepts

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“First comes the synthesis,” a quote attributed to John Corbett, is a logical paradigm of solid-state chemistry because every material used for examining basic scientific questions or for developing technological applications is the outcome of a chemical process. Therefore, synthesis is a necessary path towards discovery in solid state chemistry. In this section, we examine strategies, philosophies, and techniques for preparing solid-state compounds. These concepts rely on thermodynamics and kinetics, and understanding heterogeneous equilibria is especially important.

READING: A.K. Cheetham and P. Day, Eds., *Solid-State Chemistry: Techniques*, pp. 1-38.

A.R. West, *Solid State Chemistry and Its Applications*, 1984, Chapters 1, 11.

Some Basic Considerations about Forming Solids

(1) Stability: Thermodynamic vs. kinetic stability is always an issue to consider during the formation of reaction products.¹ The solid-state chemist should always ask, “did the synthetic procedure allow thermodynamic equilibrium to be established or not?” For any chemical system, *actual* or *thermodynamic* stability is defined by the global minimum of the system’s Gibbs free energy $G(T, p, N_i)$ surface and corresponds to its equilibrium state. However, solids can be apparently stable when any process towards the true equilibrium state is immeasurably slow. This situation describes *apparent* or *kinetic* stability, which is associated with a local minimum of the Gibbs free energy surface. The system seems to be stable because the time required to transform into the true equilibrium state is enormous. Two examples of kinetically stable solids are diamond and the anatase form of TiO₂. Graphite is the thermodynamically stable form of carbon at ambient temperature (~300 K) and pressure (~1 atm), but diamond also exists at these conditions and does not transform into graphite.² If graphite is subjected to sufficiently high pressures and temperatures, it can change spontaneously into diamond, but the reverse process, converting diamond to graphite, does not occur rapidly at ambient conditions. Anatase is a kinetically stable form of TiO₂ that, on heating in air to ~1000° C, transforms into rutile, which is the thermodynamically stable form of TiO₂.³ Therefore, stability is a *relative* term, although it is often used as an *absolute* description of a substance. Many chemists frequently refer to compounds that can be prepared, isolated, characterized, and stored as *stable*, but this distinction must always be qualified by the phrase, “stable *with respect to* ...”. Completing this phrase also includes specifying the external conditions of temperature, pressure, and other environmental parameters, such as “in (moist) air”, “under vacuum”, etc.

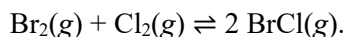
Thermodynamic stability occurs for any chemical reaction when chemical equilibrium is established. Let’s examine this principle using two examples:

- (a) *Homogeneous System:* All chemical species occur in the same mixture, such as a gas-phase or solution-phase reaction. Consider a mixture of 1.00 mole Br₂(g) and 1.00 mole Cl₂(g) added to a closed container and allowed to achieve the following equilibrium at 500 K and 1 atm pressure:

¹ For a perspective, see D.C. Johnson, *Science* **2008**, 454, 174-175.

² I.V. Popov, A.L. Görne, A.L. Tchougréeff, R. Dronskowski, *Phys. Chem. Chem. Phys.* **2019**, 21, 10961-10969.

³ D.A.H. Hanaor, C.C. Sorell, *J. Mater. Sci.* **2011**, 46, 855-874.



Accordingly, n moles $\text{Br}_2(\text{g})$ react with n moles $\text{Cl}_2(\text{g})$ to form $2n$ moles $\text{BrCl}(\text{g})$. The Gibbs free energy of this system is:

$$\begin{aligned} G(T, p, n) &= N_{\text{Br}_2} \mu_{\text{Br}_2} + N_{\text{Cl}_2} \mu_{\text{Cl}_2} + N_{\text{BrCl}} \mu_{\text{BrCl}} \\ &= (1-n)[\mu_{\text{Br}_2}^\circ + RT \ln p_{\text{Br}_2}] + (1-n)[\mu_{\text{Cl}_2}^\circ + RT \ln p_{\text{Cl}_2}] + (2n)[\mu_{\text{BrCl}}^\circ + RT \ln p_{\text{BrCl}}] \\ G(T, p, n) &= [\mu_{\text{Br}_2}^\circ + RT \ln p_{\text{Br}_2}] + [\mu_{\text{Cl}_2}^\circ + RT \ln p_{\text{Cl}_2}] \\ &\quad + n[(2\mu_{\text{BrCl}}^\circ - \mu_{\text{Br}_2}^\circ - \mu_{\text{Cl}_2}^\circ) + RT(2 \ln p_{\text{BrCl}} - \ln p_{\text{Br}_2} - \ln p_{\text{Cl}_2})] \end{aligned}$$

The terms in this expression are:

$$\mu_{\text{Br}_2}^\circ + RT \ln p_{\text{Br}_2} = (0) + (8.314)(500) \ln p_{\text{Br}_2} = 4157 \ln p_{\text{Br}_2} \text{ (J/mol)}$$

$$\mu_{\text{Cl}_2}^\circ + RT \ln p_{\text{Cl}_2} = (0) + (8.314)(500) \ln p_{\text{Cl}_2} = 4157 \ln p_{\text{Cl}_2} \text{ (J/mol)}$$

$$2\mu_{\text{BrCl}}^\circ - \mu_{\text{Br}_2}^\circ - \mu_{\text{Cl}_2}^\circ = \Delta G^\circ(500 \text{ K}) = 2(-3694) - (0) - (0) = -7388 \text{ J/mol}$$

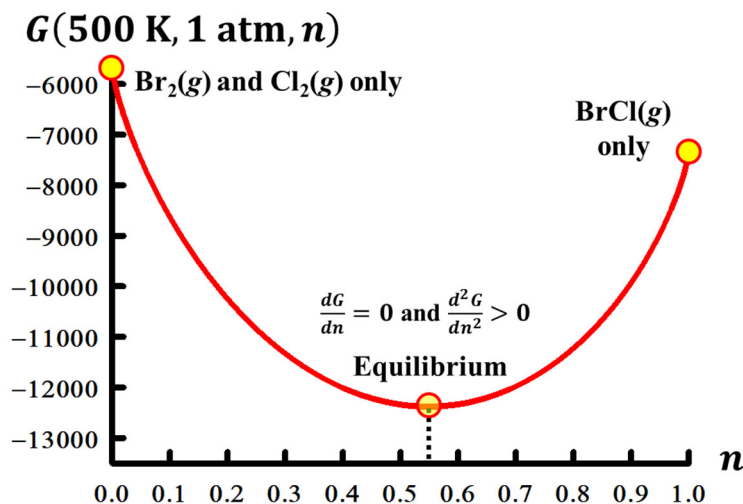
$$RT(2 \ln p_{\text{BrCl}} - \ln p_{\text{Br}_2} - \ln p_{\text{Cl}_2}) = 4157 \ln \frac{p_{\text{BrCl}}^2}{p_{\text{Br}_2} p_{\text{Cl}_2}}$$

$$p_{\text{Br}_2} = x_{\text{Br}_2} p = \frac{1-n}{2} p; \quad p_{\text{Cl}_2} = x_{\text{Cl}_2} p = \frac{1-n}{2} p; \quad p_{\text{BrCl}} = x_{\text{BrCl}} p = \frac{2n}{2} p$$

The plot of $G(500 \text{ K}, 1 \text{ atm}, n)$ vs. n has a minimum value at $n = 0.548$, so that at equilibrium:

$$p_{\text{Br}_2} = 0.226 \text{ atm}; \quad p_{\text{Cl}_2} = 0.226 \text{ atm}; \quad p_{\text{BrCl}} = 0.548 \text{ atm}.$$

This result yields the equilibrium constant $K(500 \text{ K}) = 5.88$ for the chemical equation above.

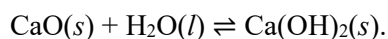


This outcome is equivalent to the statement that the Gibbs free energy difference between the two sides of the chemical equation is 0:

$$\Delta G(T, p) = \Delta G^\circ(T) + RT \ln(K(T)) = 0,$$

and establishes the relationship between the equilibrium constant $K(T)$ and the standard Gibbs free energy difference $\Delta G^\circ(T)$. For homogeneous equilibria, thermodynamic stability generally occurs when all reaction components are present in the mixture.

- (b) *Heterogeneous System:* The chemical species occur in distinct states, such as solid-gas, solid-liquid, or liquid-gas reactions. Consider a mixture of 1.00 mole $\text{CaO}(\text{s})$ and 10.00 moles $\text{H}_2\text{O}(\text{l})$ added to a closed container and allowed to achieve equilibrium at 298 K and 1 atm:



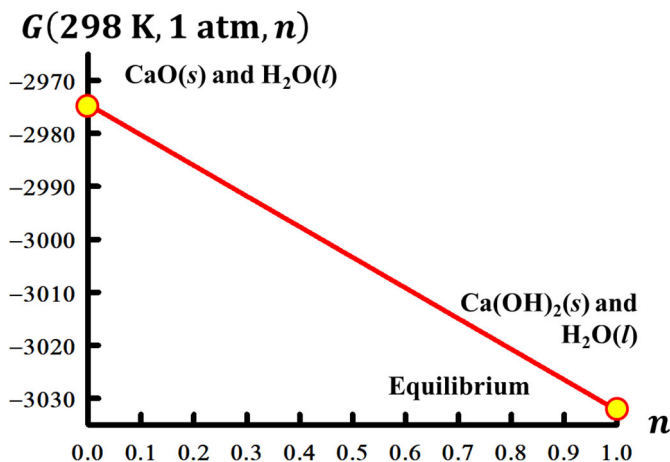
Accordingly, n moles $\text{CaO}(s)$ reacts with n moles $\text{H}_2\text{O}(l)$ to form n moles $\text{Ca}(\text{OH})_2(s)$. Therefore, the initial conditions have $\text{H}_2\text{O}(l)$ in excess. Then, the Gibbs free energy of this system:

$$\begin{aligned} G(T, p, n) &= N_{\text{CaO}}\mu_{\text{CaO}} + N_{\text{H}_2\text{O}}\mu_{\text{H}_2\text{O}} + N_{\text{Ca}(\text{OH})_2}\mu_{\text{Ca}(\text{OH})_2} \\ &= (1-n)[\mu_{\text{CaO}}^\circ + RT \ln a_{\text{CaO}}] + (10-n)[\mu_{\text{H}_2\text{O}}^\circ + RT \ln a_{\text{H}_2\text{O}}] + (n)[\mu_{\text{Ca}(\text{OH})_2}^\circ + RT \ln a_{\text{Ca}(\text{OH})_2}] \\ G(T, p, n) &= [\mu_{\text{CaO}}^\circ + RT \ln a_{\text{CaO}}] + 10[\mu_{\text{H}_2\text{O}}^\circ + RT \ln a_{\text{H}_2\text{O}}] \\ &\quad + n[(\mu_{\text{Ca}(\text{OH})_2}^\circ - \mu_{\text{CaO}}^\circ - \mu_{\text{H}_2\text{O}}^\circ) + RT(\ln a_{\text{Ca}(\text{OH})_2} - \ln a_{\text{CaO}} - \ln a_{\text{H}_2\text{O}})] \end{aligned}$$

In these expressions, a_X is the activity of species X . For this chemical system, all species are pure compounds. As a result:

$$\begin{aligned} a_{\text{CaO}} &= 1; & a_{\text{H}_2\text{O}} &= 1; & a_{\text{Ca}(\text{OH})_2} &= 1 \\ G(T, p, n) &= (1-n)\mu_{\text{CaO}}^\circ + (10-n)\mu_{\text{H}_2\text{O}}^\circ + (n)\mu_{\text{Ca}(\text{OH})_2}^\circ \\ G(T, p, n) &= \mu_{\text{CaO}}^\circ + 10\mu_{\text{H}_2\text{O}}^\circ + n(\mu_{\text{Ca}(\text{OH})_2}^\circ - \mu_{\text{CaO}}^\circ - \mu_{\text{H}_2\text{O}}^\circ) \\ G(T, p, n) &= (-603.5) + 10(-237.1) + n(-898.4 - (-603.5) - (-237.1)) = -2974.5 - 57.8 n \end{aligned}$$

The plot of $G(298 \text{ K}, 1 \text{ atm}, n)$ vs. n has a minimum value at $n = 1$, so that at equilibrium there are 9 moles $\text{H}_2\text{O}(l)$ and 1 mole $\text{Ca}(\text{OH})_2(s)$. That is, the lowest Gibbs free energy occurs when all of the starting compound $\text{CaO}(s)$ is consumed.



There is no equilibrium constant for this chemical equation because all species are pure condensed compounds. For such condensed phase reactions:

$$\Delta G(T, p) = \Delta G^\circ(T) + \int_1^p \Delta V dp.$$

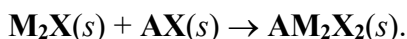
$\Delta G^\circ(T)$ is determined for 1 atm pressure; it is very unusual that $\Delta G^\circ(T) = 0$. For heterogeneous, condensed-phase equilibria, thermodynamic stability corresponds to one side of the chemical equation.

A useful strategy to assess thermodynamic equilibrium for a chemical reaction is to apply different synthetic procedures or starting points and see whether the outcomes are identical for the same external conditions. The different protocols may include modifying heating and cooling profiles or using various starting reagents, but the processes must end at the same temperature and involve the same quantities of the different elements.

(2) Diffusion: Obtaining a *homogeneous (single-phase)* solid-state product requires mass transfer and atomic diffusion within and between solid particles of the reaction mixture. Diffusion is a mechanism of matter transfer through a substance in response to a concentration gradient. Diffusion rates in solids are intrinsically smaller than those in gases and liquids because bulk solids have higher atomic or molecular packing densities and stronger interatomic or intermolecular

forces in all directions. Nonetheless, atoms are constantly vibrating about their equilibrium positions. Therefore, diffusion rates in solids increase with increasing temperature as vibrational amplitudes increase and allow more opportunities for atomic motion.

The traditional reaction between solid-state reactants creates reaction interfaces across which atoms diffuse. To obtain a homogeneous product, i.e., one with no concentration or density gradients, diffusion must also take place within the solid product. Consider the solid-state reaction



The product must form where particles of M_2X and AX meet. To grow AM_2X_2 while consuming the reactants, the atoms must move within phases and between phase boundaries. Factors affecting these diffusion rates include:

- Contact areas between grains of distinct phases: larger contact areas along phase boundaries generally provide larger rates.
- Path lengths atoms or ions travel within a phase before achieving equilibrium: smaller diffusion lengths give larger rates.
- Pore volumes through which atoms or ions move: smaller volumes lower the time for effective mass transfer.
- Temperature: higher temperatures increase diffusion rates.

Therefore, to achieve effective diffusion rates during solid-state reactions, the traditional strategy involves heating compressed powders, a process called *reactive sintering*.

Diffusion is described by Fick's laws, which relate diffusion rates to concentration gradients via temperature-dependent diffusion coefficients $D(T)$, units of cm^2/sec . Examples of these coefficients for various solids are listed in the last column of the following table⁴:

Diffusing Species	Host Species	D_0 (cm^2/sec)	Q (kJ/mol)	T (K)	$D(T)$ (cm^2/sec)
Fe	α -Fe (BCC)	2.8	251	1100	3.4×10^{-12}
Fe	γ -Fe (FCC)	0.49	284	1500	6.3×10^{-11}
Cu	Cu (FCC)	1.64	218	1100	7.3×10^{-11}
Zn	Cu (FCC)	0.24	189	1100	2.5×10^{-10}
Al	Al (FCC)	2.25	144	700	4.0×10^{-11}
Cu	Al (FCC)	0.65	136	700	4.6×10^{-11}
Ge	Ge (Diamond)	13.6	298	1100	9.6×10^{-14}
Ge	Cu (FCC)	0.40	187	1100	5.3×10^{-10}
Ge	Al (FCC)	0.48	121	700	4.5×10^{-10}
C	α -Fe (BCC)	0.098	94.6	1100	3.2×10^{-6}
C	γ -Fe (FCC)	0.23	148	1500	1.6×10^{-6}
N	α -Fe (BCC)	0.010	81.1	1100	1.4×10^{-6}
N	γ -Fe (FCC)	0.91	169	1500	1.2×10^{-6}

The values of diffusion coefficients depend on the nature of the diffusing atoms as well as the host matrix, and suggest two primary diffusion mechanisms in solids:

- *Vacancy* or *Substitutional Diffusion*: Movement of an atom from one atomic site to a neighboring vacant atomic site. For some temperature T , the equilibrium concentration of

⁴ Information obtained from W.F. Gale, T.C. Totemeier, *Smithells Metals Reference Book*, 8th Ed., Elsevier, Amsterdam, 2004. D values are calculated using an Arrhenius equation (see following text).

vacancies C_{vac} follows a Boltzmann distribution, $C_{\text{vac}} = e^{-E_V/kT}$, in which E_V is the energy required to create a vacancy ($E_V > 0$). This mechanism applies to substitutional solid solutions and includes “self-diffusion” of atoms of the host solid (solvent).

- *Interstitial Diffusion*: Movement of an atom from one interstitial site to another within the host solid. Since interstitial sites are occupied by atoms or ions smaller than the atoms forming the host packing, this mechanism generally has larger diffusion rates than the vacancy diffusion mechanism.

Both diffusion mechanisms involve an activation energy Q , so that the temperature-dependent diffusion coefficients follow an Arrhenius equation:

$$D(T) = D_0 e^{-Q/RT}.$$

The prefactors D_0 and activation energies are included in the table above. According to this information, relative diffusion rates depend on the types of crystal structure and bonding characteristics of the host solid, the nature of the diffusing species, and temperature. Diffusion is

faster for...

- Open crystal structures
- Lower density solids
- Lower melting point solids
- Smaller atoms and cations
- van der Waals solids

slower for...

- Close packed crystal structures
- Higher density solids
- Higher melting point solids
- Larger atoms and anions
- Covalently-bonded solids

In general, actual diffusion processes are fastest at surfaces and interfaces. Also, there may be significant changes to molar volumes or grain boundary surface areas during a reaction, changes which affect nucleation and growth of the product.

(3) Nucleation: The formation of a solid during a chemical or physical process typically begins with *nucleation* of a small particle from its environment that can continue to grow into a crystal.⁵ This process often occurs at nucleation sites on surfaces in contact with the environment, called *heterogeneous nucleation*. On the other hand, *homogeneous nucleation* proceeds when a solid particle forms because of thermal fluctuations within the environment itself. As a result, homogeneous nucleation occurs randomly but also spontaneously.

Let's consider crystallization (precipitation) of a solid from the liquid. For temperatures above the melting point T_m , the liquid is thermodynamically favored and has a lower chemical potential than the solid: $\mu^{(l)}(T) < \mu^{(s)}(T)$. On cooling, the chemical potentials of the liquid and solid become equal at the melting point: $\mu^{(l)}(T_m) = \mu^{(s)}(T_m)$. Therefore, we expect solidification to ensue. In the case of heterogeneous nucleation, the presence of seed crystals or imperfections on the container surface facilitates nucleation of the solid. In the bulk liquid, however, spontaneous crystallization does not usually occur. At temperatures below the melting point, the solid is thermodynamically favored and has a lower chemical potential than the liquid: $\mu^{(l)}(T) > \mu^{(s)}(T)$. The solid nuclei on the seed crystals or imperfections grow, but in the liquid, which becomes supersaturated, thermal fluctuations enhance the formation of nuclei of varying sizes. Although the solid phase has a lower chemical potential than the liquid phase at temperatures below the melting point, a small solid particle in the melt may not be stable compared to the liquid because of the solid-liquid interfacial energy. Therefore, the change in free energy to form a solid particle in a liquid, $\Delta G_{\text{Nuc}}(T)$, has two components:

⁵ H. Meyer, “The Kinetics of Crystal Growth,” *Angew. Chem. Intl. Ed.* **1966**, *5*, 67-77.

ΔG_V = free energy change to form a volume of solid from the liquid. This depends directly on the volume of the particle and is negative below the melting point ($\Delta G_V < 0$).

ΔG_I = free energy change to form the liquid-solid interface. This depends on the surface area of the particle and is positive due to disrupting the bulk to form the surface ($\Delta G_I > 0$).

For a spherical particle⁶ of radius R

$$\Delta G_{\text{Nuc}}(R) = \Delta G_V + \Delta G_I = -V_{\text{Nuc}} \cdot \frac{\Delta\mu}{v^{(s)}} + A_{\text{Nuc}} \cdot \gamma = -\left(\frac{4\pi R^3}{3}\right) \frac{\Delta\mu}{v^{(s)}} + 4\pi R^2 \gamma,$$

in which $v^{(s)}$ = molar volume of the solid, $\Delta\mu = \mu^{(l)} - \mu^{(s)}$ = difference in chemical potentials between the liquid and bulk solid, and γ = surface tension of the solid. This model for *homogeneous nucleation* concludes that there is a *critical size* for which growth will continue after nucleation, and an *activation energy* (energy barrier) for the growth process to ensue.

$$\text{CRITICAL SIZE:} \quad \frac{d\Delta G_{\text{Nuc}}(R)}{dR} = 0 = -4\pi R^2 \frac{\Delta\mu}{v^{(s)}} + 8\pi R \gamma; \quad R_C = \frac{2v^{(s)}\gamma}{\Delta\mu}.$$

$$\text{ACTIVATION ENERGY:} \quad \Delta G_{\text{Nuc}}(R_C) = -\frac{32\pi(v^{(s)})^2 \gamma^3}{3(\Delta\mu)^2} + \frac{16\pi(v^{(s)})^2 \gamma^3}{(\Delta\mu)^2} = \frac{16\pi(v^{(s)})^2 \gamma^3}{3(\Delta\mu)^2} = \frac{1}{3}(4\pi R_C^2) \gamma.$$

Both features are inversely related to $\Delta\mu$ and directly related to γ , an outcome which suggests that the critical radius and activation energy are inversely related to the degree of supercooling ΔT below the melting point of the liquid,⁷ as given by the Gibbs-Thomson equation.

Relation between supercooling ΔT and size of solid nuclei R : When a small solid particle forms in a liquid, there is a pressure difference, called the *Laplace pressure*, between the interior (solid) and exterior (liquid), $\Delta p = p^{(s)} - p^{(l)}$, which can be evaluated by using the Helmholtz free energy at equilibrium and constant T :

$$dF^{(l)} = dF^{(s)}, \text{ where}$$

$$dF^{(l)} = -p^{(l)}dV - S^{(l)}dT = -p^{(l)}dV, \text{ and}$$

$$dF^{(s)} = -p^{(s)}dV - S^{(s)}dT + \gamma dA = -p^{(s)}dV + \gamma dA.$$

Then, for a spherical particle of radius R ,

$$\Delta p = \frac{\gamma dA}{dV} = \frac{\gamma(8\pi R \cdot dR)}{(4\pi R^2 \cdot dR)} = \frac{2\gamma}{R}.$$

In these equations, $(\Delta p)dV$ is the tendency to expand the particle, and γdA is the tendency to shrink the particle. When these terms are equal, then the equilibrium size of the particle is inversely related to the Laplace pressure. Furthermore, $\Delta p \rightarrow 0$ as $R \rightarrow \infty$, which corresponds to the bulk solid.

The Laplace pressure enters the relationship between chemical potentials between the liquid and the solid particle at some temperature below the melting point $T < T_m$:

$$\mu^{(l)}(T, p^{(l)}) = \mu^{(s)}(T, p^{(s)}), \text{ where}$$

$$\mu^{(l)}(T, p^{(l)}) = \mu^{(l)}(T_m) - \int_{T_m}^T s^{(l)} dT + \int_{p^{(l)}}^{p^{(l)}} v^{(l)} dp = \mu^{(l)}(T_m) - \int_{T_m}^T s^{(l)} dT, \text{ and}$$

$$\mu^{(s)}(T, p^{(s)}) = \mu^{(s)}(T_m) - \int_{T_m}^T s^{(s)} dT + \int_{p^{(s)}}^{p^{(s)}} v^{(s)} dp.$$

Since $\mu^{(l)}(T_m) = \mu^{(s)}(T_m)$, the degree of supercooling $\Delta T = T_m - T$ is

$$\Delta T = T_m - T = \frac{v^{(s)} \Delta p}{\Delta s_{\text{fus}}} = \frac{2\gamma v^{(s)} T_m}{R \Delta h_{\text{fus}}},$$

⁶ Crystalline particles are not strictly spherical. The *Wulff construction*, which differentiates surface tensions of various crystal planes, provides a better evaluation of these energetics. The qualitative conclusions remain as is.

⁷ H. Biloni, W.J. Boettinger, in *Physical Metallurgy*, Eds. R.W. Cahn, P. Haasen, North-Holland, New York, 1991, Vol. 1, Chapter 8.

in which ΔS_{fus} and Δh_{fus} are the entropy and enthalpy of fusion. The following table lists the important parameters for various metals that allow estimation of the critical radius R from homogeneous nucleation:

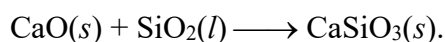
Metal	ΔT_{max} (K)	T_m (K)	Δh_{fus} (kJ/mol)	γ (J/m ²)	$v^{(s)}$ (cm ³ /mol)
Al	175	934	10.71	0.108	9.997
Bi	227	544	11.30	0.088	21.309
Co	330	1767	16.06	0.238	6.652
Cu	236	1357	13.26	0.178	7.114
Fe	420	1811	13.81	0.277	7.092
Ga	174	303	5.59	0.077	11.803
Hg	88	234	2.29	0.031	14.652
Mn	308	1519	12.91	0.216	7.567
Ni	480	1728	17.48	0.300	6.586
Pb	80	600	4.77	0.069	18.268
Pt	332	2045	22.17	0.240	9.091
Sn	191	505	7.03	0.075	16.291
Ti	350	1940	14.15	0.202	10.543

(4) **Furnaces:** There are various ways to provide the high temperatures necessary to carry out solid-state reactions. Examples of furnaces include:

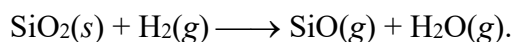
- Tube Furnaces** are electrical heating devices most commonly utilized for solid-state reactions. Their design involves a cylindrical cavity surrounded by a heating coil that is embedded in a thermally insulating material. Temperature is monitored and manipulated by a thermocouple. Resistance of the heating element controls the effective limits for temperature control. Tube furnaces can be oriented horizontally, vertically, or at various angles. They can also be partitioned into separate zones held at different temperatures to promote chemical transport reactions. Tubes containing the reactants include various materials such as Pyrex (strain point $\sim 515^\circ\text{C}$; softening point $\sim 820^\circ\text{C}$), fused silica (strain point $\sim 1120^\circ\text{C}$; softening point $\sim 1600^\circ\text{C}$), alumina (melting point $\sim 2070^\circ\text{C}$), or refractory metals like molybdenum (melting point $\sim 2620^\circ\text{C}$) or tantalum (melting point $\sim 3020^\circ\text{C}$). Metal tubes are typically sealed in a secondary container to prevent oxidation at high temperatures.
- Arc Furnaces** heat metallic substances using an electric arc and can achieve temperatures exceeding 3000°C . Heating occurs when an electric arc is struck between a needle-shaped electrode consisting of thoriated tungsten or graphite and the metal sample, which is placed on a water-cooled copper hearth in an inert gas atmosphere, which is typically argon but may also be helium, although helium suffers from regular shortages and may be prohibitively expensive. The arc arises by providing a sufficiently large electric potential difference between the needle (cathode) and the copper hearth (anode) where the sample rests. When the needle is sufficiently close to the sample, a sustained electrical discharge passes through the ionized gaseous atmosphere and the sample melts. Due to possible density differences among components of the melted sample, the arc melting procedure should be repeated several times after turning over the cooled solid sample to ensure homogeneity throughout the final pellet.
- Induction Furnaces** heat electrically conductive materials by electromagnetic induction, which uses a radio-frequency power supply to send an alternating current through a copper coil (the inductor), inside which the sample is placed. The alternating current generates a magnetic field that causes eddy currents inside the metal sample. Via Joule heating arising from natural electrical resistance of the induced eddy currents in the metal sample, the specimen will be heated internally and rapidly.

(5) Containers: Working at high temperatures means paying careful attention to *containers* for chemical reactions. Certain important criteria for proper selection of a container material include: (i) it should be inert to the reactants; (ii) it should have compatible thermal expansion or compression coefficients with the substances in the container (reactants, products, and solvents = fluxes); and (iii) if gases are involved, it must be constructed to withstand the pressures inside them. Often, reactions are carried out in one container that is itself enclosed in another secondary container to prevent oxidation of the primary one. Common container materials include:

(a) *Fused silica* SiO_2 (often mistakenly called quartz⁸) is a common container substance. Although fused silica melts at $\sim 1715^\circ\text{C}$, its softening point is $\sim 1600^\circ\text{C}$ and its strain point is $\sim 1120^\circ\text{C}$. The strain point realistically sets the upper limit for its use in high-temperature reactions. The more active metals, such as alkali, alkaline earth, and some rare earth elements, can reduce SiO_2 slowly, whereas some metals, especially Zr, Nb, Ta, and Mo, form silicides. Also, basic oxides will react with silica to form silicates, e.g.,

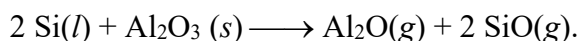
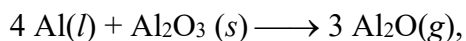


At high temperatures, reduction of water on the silica surface or the presence of adventitious hydrogen in metal reactants, impurities that arise from reduction of metal oxides to obtain “pure” metals, can produce H_2 gas that transports silica and contaminates the eventual product:



When using fused silica for high-temperature solid-state reactions, the tubes or ampoules should be preheated under vacuum and stored in an inert atmosphere to minimize surface water and hydroxide before use.

(b) *Ceramics* like yttrium-stabilized zirconia ($\text{Y}:\text{ZrO}_2$; melting point 2700°C) or alumina (Al_2O_3 ; melting point $\sim 2070^\circ\text{C}$) allow higher reaction temperatures than fused silica containers. These materials will not further oxidize in air. However, if any reactants are susceptible to oxidation, then these containers will need to be constructed to allow inert gas atmospheres. If aluminum or silicon are reactants, then they can react with alumina under vacuum to form $\text{Al}_2\text{O}(g)$, which is stable above $\sim 1050^\circ$ and can introduce unwanted oxygen into reaction products:



(c) *Elemental metal* containers fall into two different categories:

(i) *Reactive metal* containers, which include Cu, Ni, Co, Ti, Nb, Ta, and Mo, are reactive at high temperatures in air or can act as reducing agents when preparing compounds of these metals in low oxidation states. For example, a Nb container is effective to prepare $\text{Nb}_6\text{I}_{11}(s)$ through the reductive decomposition of NbI_5 . If this kind of metal container does not react with any reactant, then it must be contained in a secondary container that holds an inert atmosphere to prevent oxidation of the metal. In these cases, Nb and Ta are versatile materials due to their ductility, strength, and ease of welding. Ta is especially useful for using active metal reactants because it is permeable to hydrogen and can withstand pressures up to ~ 30 atm. Mo and W are less reactive, but they are also more difficult to seal. Therefore, Mo and W are often used as foils that can be formed to a desired shape, such as a boat or envelope.

⁸ Personal opinion: the German term for fused silica is *quarzglas*, which may be the origin of the misnomer.

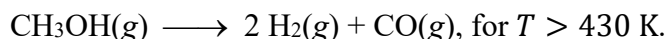
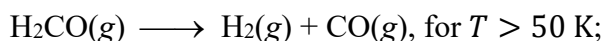
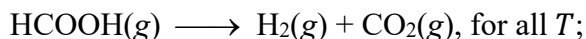
- (ii) *Inert* metal containers, which include Pt and Au, do not react with oxygen. Therefore, they are useful for hydrothermal reactions. Gold is especially effective and easily worked. However, certain caution is warranted because Pt can be transported with reagents such as chlorine, oxygen, and carbon monoxide. Furthermore, if reactants include early metals such as Cs or Zr, then early metal-late metal compounds may form that can disintegrate the metal container, such as CsAu or various Zr-Pt intermetallic compounds.

Sometimes, it is useful to follow a stepwise path from reactants to products due to reactivities with various containers. For example, to prepare certain metal-rich chalcogenides like Nb₂₁S₈, reacting mixtures of Nb and sulfur in silica as far as possible is an effective first step, followed by transferring the reaction mixture with phases known or unknown but controlled composition, to a tungsten cup in an induction furnace. Pre-reacting sulfur with metallic Nb significantly reduces the vapor pressure (activity) of sulfur and prevents it from reacting with the tungsten cup.

(6) Harald Schäfer, the “father” of *chemical vapor transport*, astutely commented on the problems associated with traditional solid-state synthetic strategies.⁹ Some of his conclusions are

- (1) Not knowing a mechanism impedes exploitation and control of the reaction.
- (2) There are no intrinsic purification effects during these reactions. Other incidental processes, such as reactions with the container material, can change the targeted proportions of reactants uncontrollably.
- (3) Correcting errors using physical or mathematical efforts do not replace careful treatment, handling, and preparation of all reactants and containers.
- (4) The principally accessible products are those stable at high temperatures. These products are often the thermodynamically stable solids at the reaction temperature, so products that are either metastable or would be stable at lower temperatures are not formed.

Clearly, the breadth of organic molecules achieved by synthetic organic chemists verifies the significance of these conclusions. As a *gedanken* activity, consider synthesis in the carbon-hydrogen-oxygen system if all reactions are carried out at ~500 K from elemental reactants, graphite C(s) and gaseous H₂(g) and O₂(g), and if all products are governed by thermodynamic control. There are five stable binary compounds, CO(g), CO₂(g), H₂O₂(g), H₂O(g), and CH₄(g), and three stable ternary compounds, HCOOH(g), H₂CO(g), and CH₃OH(g) with favorable Gibbs free energies of formation, i.e., $\Delta G_f^0 < 0$. However, all three ternary compounds are thermodynamically unstable relative to certain binary compounds:



This thermodynamic outcome frequently occurs for solid-state reactions: attempts to prepare ternary, quaternary, or other multi-nary compounds from elements often yield binary compounds.

⁹ H. Schäfer, *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 43-50.