

Chemical (Vapor) Transport

Chemical transport is an important technique for growing high quality crystals of many types of solids. The process takes advantage of heterogeneous solid-gas equilibria, which, through appropriate choices of temperature and pressure gradients, can lead to kinetic and thermodynamic control of crystal growth.

READING: H.Schäfer, *Chemical Transport Reactions*, Academic Press, New York, 1964

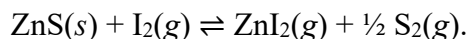
M. Lenz, R. Gruehn, *Chem. Rev.* **1997**, *97*, 2967-2994

R. Gruehn, R. Glaum, *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 692-716

P. Schmidt, M. Binnewies, R. Glaum, M. Schmidt, *Chemical Vapor Transport Reactions-Methods, Materials, Modeling*, IntechOpen, 2012:

<https://www.intechopen.com/chapters/43029>

(47) The essential chemical transport reaction involves moving a nonvolatile species along an activity or temperature gradient at temperatures low compared to those needed to directly volatilize the condensed phase. A good example is the transport of ZnS(*s*) between 900°C and 800°C using iodine as a *transport agent* according to the transport equilibrium:



In a standard experimental set-up, crude ZnS(*s*) and I₂(*s*) are placed into a closed container. The amount of iodine should provide 0.1-1.0 atm I₂(*g*) at ~900°C. The end of the container with the starting reagents is heated to 900° and the other end is heated to 800° C, creating a temperature gradient in the tube. Over time, pure ZnS(*s*) will be transported to the lower temperature region of the tube. To achieve this temperature control, a two-zone furnace is required.

Common transport agents include iodine, hydrogen chloride, and oxygen because these substances can form gas phase molecules with many different elements. The transport agent also provides the primary background gas during transport. For any transport experiment, three important questions arise:

- (1) What is the *rate of transport* of the solid between the two regions?
- (2) What is the *direction of transport*, i.e., will the solid transport from the hot end to the cold end or vice versa?
- (3) What is the *optimum median temperature* for transport? The temperature gradient for the most effective transport will straddle this median value.

(48) Principles: The transport equilibrium is conventionally written as follows:



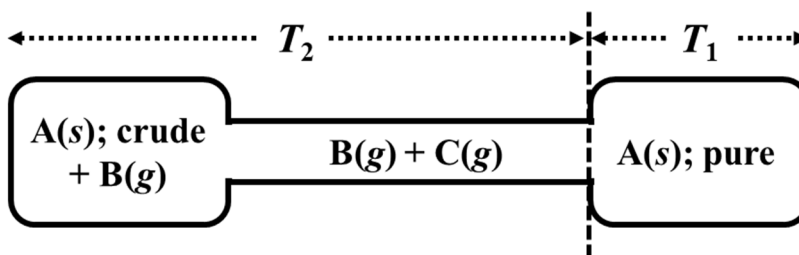
in which the solid to be transported and the transport agent are on the *reactant side* and all other gas-phase species are on the *product side*. In the balanced chemical equation “*k C(g)*” can represent more than one gas-phase species, i.e., “*k*₁ *C(g)* + *k*₂ *D(g)* + ...”. Transport implies gas motion, which can occur by molecular flow, diffusion, or convection, or any combinations of these. Also, the complete transport process can be separated into three stages:

- (1) heterogeneous reaction of the gas **B(g)** on the solid **A(s)**;
- (2) motion of gas molecules, **B(g) + C(g)**, through the chamber; and
- (3) heterogeneous reaction to reform the solid **A(s)**.

In most cases, gas motion is the rate-determining process. The nature of the gas motion depends on the total gas pressure in the reaction chamber, which is considered to be closed. There are three possible conditions:

- Low total pressure (< 0.001 atm): The mean free path of gas molecules exceeds tube dimensions, so gas motion is entirely molecular flow, which is governed by relative molecular speeds. For this condition, the system tends to *equalize total pressure* throughout the tube.
- High total pressure (≥ 0.001 atm): Gas motion is governed by diffusion, which tends to *equalize concentrations*. In this case, there is constant total pressure throughout the system, which means a uniform gas density but a non-uniform molar composition, i.e., a *concentration gradient*. The rate of diffusion decreases as total pressure increases.
- Very high total pressure: Convection, which is the tendency to *equalize temperature* throughout the tube, will dominate because the collision frequency between gas molecules is high.

(49) Kinetics – Transport Rate: How many moles of $A(s)$ can be transported during some time interval t ? To answer this question, the reaction stoichiometry and a combination of diffusion and molecular flow theory are applied.



If $n_A = \#$ moles of $A(s)$ transported, then by the reaction stoichiometry, the $\#$ moles of $B(g)$ and $C(g)$ that migrate through the tube are, respectively, by $n_B = jn_A/i$ and $n_C = kn_A/i$. Therefore, $n_A = (i/j) n_B = (i/k) n_C$.

In the closed tube, we assume a total gas pressure so that gas transport occurs via diffusion. A thorough derivation of the transport rate is presented in the references, but using diffusion models to estimate the rate, the numbers of moles of $B(g)$ and $C(g)$ transported are approximately

$$n_B(\text{moles}) \approx DAt \frac{dc_B}{ds} \quad \text{and} \quad n_C(\text{moles}) \approx DAt \frac{dc_C}{ds}$$

in which $c_B =$ concentration (moles/cm³) of $B(g)$, $c_C =$ concentration (moles/cm³) of $C(g)$, $D =$ diffusion coefficient (in cm²/sec) for $B(g) + C(g)$, $A =$ cross sectional area (cm²) of the diffusion path, $s =$ length (in cm) of the diffusion path, and $t =$ time (sec) of the transport experiment. Since $c_{\text{gas}} = n_{\text{gas}}/V = p_{\text{gas}}/RT$ and, by assuming $dc_{\text{gas}}/ds \sim \Delta c_{\text{gas}}/s$, then these equations become

$$n_B(\text{moles}) \approx \frac{DAT}{sRT} \Delta p_B \quad \text{and} \quad n_C(\text{moles}) \approx \frac{DAT}{sRT} \Delta p_C.$$

To complete semi-quantitative estimates of the transport rate (n_A/t), we must estimate the diffusion coefficient D for the gas mixture and the pressure differences for the gaseous species across the transport tube, Δp_B or Δp_C . The diffusion coefficient is a function of total pressure and

temperature, and from mechanical arguments, $D \propto T^{1.5}/p_{\text{TOT}}$.⁶⁶ Another empirical relationship is $D/D_0 = (p_0/p_{\text{TOT}})(T/T_0)^{1.8}$. For $p_0 = 1$ atm, $T_0 = 273$ K, and $D_0 \approx 0.1$ cm²/sec, then

$$D(\text{cm}^2/\text{sec}) = (4.1 \times 10^{-6}) \left(\frac{T^{1.8}}{p_{\text{TOT}}} \right).$$

The temperature can be selected as the average of the hotter and colder ends $T \sim \frac{1}{2}(T_1 + T_2)$. Lastly, we use this empirical relationship for D , the stoichiometric relationship between n_{A} and n_{B} , and convert time to hours to obtain the transport rate (n_{A}/t) in terms of parameters of the transport agent $\text{B}(\text{g})$ and the reaction chamber:

$$\text{Transport rate} = \frac{n_{\text{A}}}{t} \approx (1.8 \times 10^{-4}) \left[\left(\frac{i}{j} \right) \left(\frac{\Delta p_{\text{B}}}{p_{\text{TOT}}} \right) \right] \left[\frac{T^{0.8} A}{s} \right] \text{ (moles/hr)}$$

In this expression for the transport rate, the first term is a numerical constant to achieve the desired units of moles transported per hour. The second term in brackets identifies *chemical controls* via stoichiometry and thermodynamics of the equilibrium. Lastly, the third term in brackets contains *physical controls* by manipulating tube size and average temperature. According to this expression, faster transport rates arise by maximizing the pressure difference Δp_{B} , minimizing the total pressure for diffusion, maximizing the temperature of the diffusion path, and by maximizing the area while minimizing the tube length. Other references offer slightly different estimates, but the general expressions provide similar outcomes.

(50) Thermodynamics – Transport Direction: The direction of chemical transport, i.e., whether crystal growth proceeds from high-to-low temperature or low-to-high temperature, is influenced by the enthalpy difference of the balanced chemical equation for the transport equilibrium. If the chemical equation of the equilibrium is endothermic, then K_p increases as T increases and growth of pure $\text{A}(\text{s})$ is favored at lower temperatures. Therefore, transport occurs from high-to-low (hot-to-cold) temperatures for endothermic equilibria. On the other hand, and by a similar argument, an exothermic chemical equation favors formation of $\text{A}(\text{s})$ at higher temperature, so transport of an *exothermic* reaction occurs from low-to-high (cold-to-hot) temperatures.

(51) Thermodynamics – Optimum Temperatures: Another important aspect of transport is the optimum median temperature, which is also based on thermodynamic characteristics of the transport equilibrium. To examine the influence of ΔH° and ΔS° on transport, a simple equilibrium example is examined: $\text{A}(\text{s}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g})$. Experimental parameters include setting the total pressure at 1 atm and the two temperature regimes at 800°C (1073 K) and 1000°C (1273 K). Plots of $\Delta p_{\text{B}} = p_{\text{B}}(1273 \text{ K}) - p_{\text{B}}(1073 \text{ K})$ vs. ΔH° for specific values of ΔS° are generated and interpreted (ΔH° and ΔS° are assumed to be temperature-independent). Using three different values of ΔS° lead to the following results:

- $\Delta S^\circ = 0$ J/mol·K: Δp_{B} is sizable when ΔH° is ca. ± 20 kJ/mol. If the equilibrium reaction is exothermic, the pressure differential favors crystal growth in the hot end because $\Delta p_{\text{B}} > 0$; if the equilibrium reaction is endothermic, the pressure differential favors crystal growth in the cool end because $\Delta p_{\text{B}} < 0$.
- $\Delta S^\circ = +50$ J/mol·K: Δp_{B} is sizable *only* when $\Delta H^\circ > 0$, i.e., an endothermic equilibrium reaction. The pressure differential favors crystal growth in the cool end because $\Delta p_{\text{B}} < 0$.

⁶⁶ see P.W. Atkins, *Physical Chemistry*, W.H. Freeman, New York, 1978, pp. 804-809.

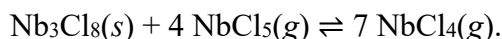
- $\Delta S^\circ = -10 \text{ J/mol}\cdot\text{K}$: $\Delta p_{\mathbf{B}}$ is sizable when $\Delta H^\circ < 0$ and significantly smaller when $\Delta H^\circ > 0$. Therefore, an exothermic equilibrium reaction optimizes transport and provides the greater pressure differential that favors crystal growth in the hot end.

Analysis of all thermodynamic factors leads to a set of rules for effective chemical transport:

- (1) A chemical reaction supports transport only when no solid is present on one side of the chemical equation, such as $i \mathbf{A}(s) + j \mathbf{B}(g) \rightleftharpoons k \mathbf{C}(g)$.
- (2) A chemical reaction with an extreme equilibrium position, i.e., large absolute value of ΔG° , gives no measurable transport. If $\Delta G^\circ \ll 0$, there is a strong driving force to dissolve the solid into the gas phase, but the reverse reaction to reform the solid is prohibited. If $\Delta G^\circ \gg 0$, the solid does not readily dissolve into the gas phase, and transport does not occur.
- (3) An equilibrium reaction with a large absolute value of ΔH° does not promote transport. This rule rationalizes the use of iodine as a popular and convenient transport agent, because M–I bonds are weaker than other metal-anion bonds, so enthalpy values involving making and breaking bonds to iodine will, in general, be small.
- (4) The sign of ΔH° determines the transport direction: exothermic equilibrium reactions transport from low temperature to high temperature; endothermic equilibrium reactions transport from high temperature to low temperature.
- (5) For large values of ΔS° for the equilibrium reaction, transport is only possible if ΔH° and ΔS° have the same sign. If ΔS° is small, then the sign and magnitude of ΔH° control transport.
- (6) Transport is significant when $\ln K_p \sim 0$, or $\Delta G^\circ \sim 0 \text{ J/mol}$. This expression gives the optimum median temperature for transport.

(52) PROBLEM: As an *example* of chemical transport, consider trying to grow crystals of $\text{Nb}_3\text{Cl}_8(s)$ by first reacting $\text{Nb}(s)$ with $\text{NbCl}_5(s)$ to give the correct stoichiometry. Then, place the crude solid “ $\text{Nb}_3\text{Cl}_8(s)$ ” with $\text{NbCl}_5(s)$, which serves as the transport agent (boiling point is 248.2°C) into a closed silica tube (20 cm long, 1 cm diameter). It is known that $\text{NbCl}_4(g)$ is a significant gas-phase component. The amount of $\text{NbCl}_5(s)$ used is designed to give a total pressure of 1 atm in the transport tube.

- (a) What is the transport equilibrium for this system?



- (b) Given the following thermodynamic information for this equilibrium reaction, what is the direction of transport? $\Delta H^\circ = +457.3 \text{ kJ/mol Nb}_3\text{Cl}_8$ and $\Delta S^\circ = +487.9 \text{ J/K}\cdot\text{mol Nb}_3\text{Cl}_8$.

Since the equilibrium reaction is endothermic, transport will occur from the hot zone to the cooler zone, i.e., crystals of $\text{Nb}_3\text{Cl}_8(s)$ grow in the cool end of the transport tube. Therefore, reactants should be placed in the hot end, where crude $\text{Nb}_3\text{Cl}_8(s)$ will form at first.

- (c) What is the optimum median temperature for transport?

Using the thermodynamic data for the equilibrium reaction, $\Delta G^\circ \sim 0$ at $937 \text{ K} = 664^\circ\text{C}$.

- (d) Estimate the transport rate, in moles $\text{Nb}_3\text{Cl}_8(s)$ per hour, if the pressure difference for $\text{NbCl}_5(g)$ across the transport tube is 0.25 atm.

To estimate the transport rate, use the equation derived above:

$$\frac{n_{\text{Nb}_3\text{Cl}_8}}{t} \approx (1.8 \times 10^{-4}) \left[\left(\frac{1}{4} \right) \left(\frac{0.25 \text{ atm}}{1 \text{ atm}} \right) \right] \left[\frac{(937 \text{ K})^{0.8} (0.785 \text{ cm}^2)}{20 \text{ cm}} \right] \text{ (moles/hr)}$$

$$\approx 1.05 \times 10^{-4} \frac{\text{mole}}{\text{hr}} = 0.059 \text{ g/hr}$$

(53) To examine this problem in more detail, use the transport equilibrium to provide expressions for the total pressure and partial pressures of the gases in the reaction tube:

$$K_p(T) = \frac{(p_{\text{NbCl}_4})^7}{(p_{\text{NbCl}_5})^4}; \quad p_{\text{NbCl}_4} = \sqrt[7]{(p_{\text{NbCl}_5})^4 K_p(T)} = p_{\text{TOT}} - p_{\text{NbCl}_5}.$$

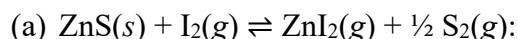
It is challenging to achieve analytical solutions for p_{NbCl_5} and p_{NbCl_4} as a function of temperature, but we can use a graphical approach, and an estimate that the main gaseous component will be $\text{NbCl}_5(\text{g})$, because it is used as a reactant as well as the transport agent. The approach is to target a total pressure close to 1 atm, and to select various $p(\text{NbCl}_5)$ values close to, but smaller than 1 atm. Then, use the equilibrium constants to evaluate $p(\text{NbCl}_4)$ and choose the result that give p_{TOT} closest to 1 atm. So, we obtain the following data table:

T (K)	K_p	p_{NbCl_5} (atm)	p_{NbCl_4} (atm)	p_{TOT} (atm)
600	4.73×10^{-15}	0.995	0.009	1.004
650	5.46×10^{-12}	0.975	0.024	0.999
700	2.30×10^{-9}	0.945	0.056	1.001
750	4.33×10^{-7}	0.885	0.115	1.000
800	4.24×10^{-5}	0.795	0.208	1.003
850	2.42×10^{-3}	0.665	0.335	1.000
900	8.80×10^{-2}	0.520	0.486	1.006
950	2.19	0.368	0.631	0.999
1000	3.97×10^1	0.245	0.757	1.002

As calculated above, the optimum median temperature for transport is ~ 950 K. However, $\text{Nb}_3\text{Cl}_8(\text{s})$ decomposes into $\text{Nb}(\text{s})$ and $\text{NbCl}_5(\text{g})$ when temperatures exceed 875 K. Therefore, transport conditions must be set up below 870 K. A graph of the partial pressure of each gas vs. temperature, shows that to avoid decomposition of $\text{Nb}_3\text{Cl}_8(\text{s})$, we can choose a temperature gradient 750-850 K, which creates $\Delta p_{\text{GAS}} \sim 0.25$ atm. Using this temperature gradient, in a tube that is 20 cm long, 1 cm diameter, the estimated transport rate ($T = 850$ K; $\Delta p(\text{NbCl}_5) = 0.25$ atm) is 9.28×10^{-5} mole/hr = 0.052 g Nb_3Cl_8 /hr.

The Nb-Cl phase diagram has several phases and an important competing phase is “ Nb_3Cl_7 ” = $\text{Nb}_6\text{Cl}_{14}$, which can grow in Nb tubes in the presence of $\text{NbCl}_5(\text{g})$ at high temperatures. Thus, in actual experiments, it may be necessary to carry out the transport of $\text{Nb}_3\text{Cl}_8(\text{s})$ below 700 K.

(54) *Reactions*: Some examples of transport reactions include (NOTE: anything that can be transported, can be synthesized under transport conditions):



- 2 mg I_2/cm^3 in a temperature gradient between 800°C and 1000°C gives nearly complete conversion.

- The straightforward reaction $\text{Zn}(l) + \text{S}(g) \rightarrow \text{ZnS}(s)$ at 800°C , which occurs above the melting point of Zn, gives low conversion due to a protective sulfide skin that grows on the liquid metal and prevents further reaction.

(b) $\text{Ni}(s) + 4 \text{CO}(g) \rightleftharpoons \text{Ni}(\text{CO})_4(g)$:

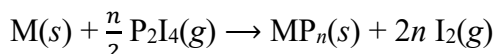
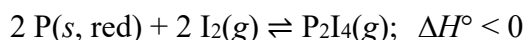
- $\Delta H^\circ = -300 \text{ kJ/mol}$ and $\Delta S^\circ < 0$, so transport occurs from low-to-high temperature.
- This reaction is typically run from 80° to 200°C .
- $\text{CO}(g)$ forms carbonyl complexes with many noble metals, so this is an effective method to purify noble metals,

(c) $\text{W}(s) + 3 \text{Cl}_2(g) \rightleftharpoons \text{WCl}_6(g)$:

- W filaments in an atmosphere with a small partial pressure of $\text{WCl}_6(g)$ can sustain themselves by transport.
- $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$, so W in the cold (thicker) parts of the filament transport to the hot (thinner) parts of the filament.

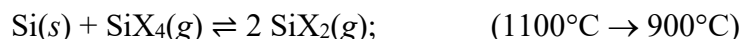
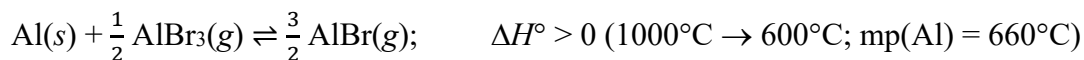
(d) Metal phosphides, $\text{M}(s) + n \text{P}(s, \text{red}) \longrightarrow \text{MP}_n(s)$

- Metal phosphides often form very sluggishly by reaction of the metal with red phosphorus, although they are thermodynamically favorable reactions. These reaction rates can be increased by introducing a small amount of iodine, which reacts with red phosphorus to produce $\text{P}_2\text{I}_4(g)$. This gas then reacts with the metal to give the phosphide and regenerate iodine to continue the transport reaction. The formation of $\text{P}_2\text{I}_4(g)$ is exothermic, so the metal phosphide will grow in the cold end of the tube. The relevant reactions are:



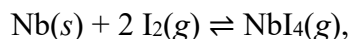
(55) Additional Reactions:

(e) Synproportionation Reactions: These are often endothermic processes with positive ΔS° values, so they are good candidates for transport equilibria. Two examples include:



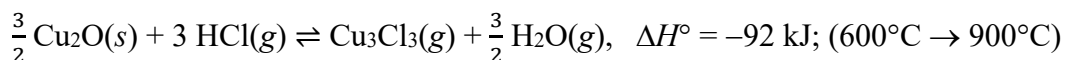
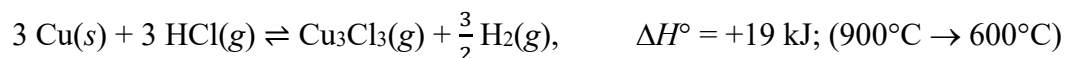
(f) Separation/Purification Reactions: Chemical transport can also be used to separate two different solids $\text{M}(s)$ and $\text{M}'(s)$; the technique is therefore useful for purification. Two important cases include

(1) $\text{M}(s)$ transports whereas $\text{M}'(s)$ does not. An example is a mixture of $\text{Nb}(s)$ and $\text{NbC}(s)$ using iodine as a transport agent. $\text{Nb}(s)$ can be transported using I_2 as follows:



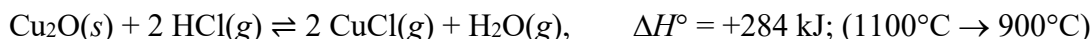
which is an exothermic equilibrium reaction. Therefore, $\text{Nb}(s)$ will transport from the cold end to the hot end of the transport tube. Also, load the $\text{Nb}(s)/\text{NbC}(s)$ mixture with $\text{I}_2(s)$ in the eventual cold end of the tube.

(2) $\text{M}(s)$ transports by an *exothermic* equilibrium and $\text{M}'(s)$ transports by an *endothermic* equilibrium. An example is a mixture of $\text{Cu}(s)$ and $\text{Cu}_2\text{O}(s)$ using $\text{HCl}(g)$ as the transport agent:



Therefore, a Cu(s)/Cu₂O(s) mixture placed in the middle of a reaction vessel in which the temperatures at each end are set to 600°C and 900°C will eventually separate the two solids, with Cu(s) growing in the colder end and Cu₂O(s) growing in the hotter end.

At higher temperatures, Cu₂O(s) transports via CuCl(g):



Therefore, a film of Cu₂O(s) spread out over an entire transport tube whose ends are kept at 600° and 1100°, will transport into the middle.

Additional examples of transportable compounds include:

Oxides	Agent	Chalcogenides	Agent	Others	Agent
SiO ₂	HF	TiS ₂ , NbS ₂ , TaS ₃ , WS ₂ , Cr ₂ S ₃ , FeS ₂ , PtS	S	AlOCl	NbCl ₅
V _n O _{2n-1} ; n = 4-8, ∞	TeCl ₄	Nb ₅ Se ₄	I ₂	CrOCl	Cl ₂
RuO ₂ , IrO ₂	O ₂	LaTe ₂ , La ₂ Te ₃	I ₂	ZrOS, ZrSiS	I ₂
MgTiO ₃ , NiTiO ₃	Cl ₂	Cu ₃ NbS ₄ , Cu ₃ TaS ₄	I ₂		
MgFe ₂ O ₄ , MnFe ₂ O ₄ , CoFe ₂ O ₄ , NiFe ₂ O ₄	HCl	MnIn ₂ S ₄ , CoIn ₂ S ₄ , ZnIn ₂ S ₄ , CdIn ₂ S ₄	I ₂	CuCr ₂ S ₃ Cl	Cl ₂
MnGeO ₃ , MnFeO ₃ , CoGeO ₃	HCl	Cd ₄ SiSe ₆	I ₂	NbS ₂ Cl ₂	NbCl ₄
FeGeO ₃ , MnGeO ₃	NH ₄ Cl	HgCr ₂ Se ₄	AlCl ₃	BiSBr	Br ₂
MgNb ₂ O ₆ , CaNb ₂ O ₆ , CoNb ₂ O ₆ , NiNb ₂ O ₆ , ZnNb ₂ O ₆	Cl ₂ , HCl				
CrTaO ₄	Cl ₂			BP	HCl
MgWO ₄ , ZnWO ₄ , MnWO ₄ , FeWO ₄ , NiWO ₄	Cl ₂			ZnSiP ₂	I ₂

(56) SUMMARY: Effective synthetic protocols involve controlling certain thermodynamic and kinetic factors, and becoming acquainted with various techniques will establish a broad synthetic “toolbox”. Understanding heterogeneous equilibria and learning how to interpret phase diagrams are two important skills for the solid-state chemist. In this unit, we discussed

- Synthetic fundamentals include an understanding of stability, an appreciation of atomic or ionic diffusion in condensed states, and recognition that crystal nucleation and growth is a process representing a conflict between bulk and surface thermodynamic features. To achieve the temperatures that allow reasonable diffusion rates require different types of furnaces and careful choices of containers. Creative synthetic strategies generally seek to control reaction mechanisms and provide effective means to obtain products of high purity and yield. Succumbing only to thermodynamic control significantly limits the breadth of compounds that can be obtained.
- Preparative strategies of solids involve forming crystals for further study. Crystalline solids can be grown using vapor-phase, liquid-phase, solution-phase, or solid-phase approaches. Methods include using gaseous reactants or creating driving forces by evolving gases; applying high pressures via diamond-anvil cells, high-pressure reactive gases, or solvothermal methods; achieving temperatures sufficiently high to melt one of the components or using eutectic mixtures of solvents; among others. In general, the chemist must eliminate or minimize reaction impurities and develop ways to purify or separate desired products from other reaction byproducts.
- Reading and interpreting phase diagrams are important skills. These diagrams rely on the Gibbs phase rule, which relates the number of degrees of freedom to the numbers of phases and distinct components in the system, and map out the overall minima in the molar Gibbs free energies of the various phases that can exist in a system. The Gibbs phase rule is the foundation of understanding heterogeneous equilibria. One-component **A** diagrams are p - T maps; two-component **A-B** diagrams are T - x_B maps at fixed pressure (1 atm). Three-phase equilibria are represented by constant-temperature (horizontal) lines; two-phase equilibria are regions with the two phases related by a tie-line. Phase composition in two-phase regions are determined by the lever rule.
- Chemical vapor transport is an especially effective technique to grow high-quality crystals of various compound types by taking advantage of heterogeneous solid-gas equilibria at different temperatures. Important experimental parameters are the transport rate, direction of transport, and the optimal temperature around which the transport reaction occurs.