Materials Kinetics Fundamentals
Exam Question Bank

The purpose of the Exam Question Bank is to facilitate the easy assembly of exams to test students on important concepts in materials kinetics. The following features are employed to that end.

* The exam questions are preformatted and can be pasted directly in a new document.
* Like the textbook, the problems are broken down into conceptual and calculation sections. Conceptual questions, such as True/False, are better indicators of the understanding of the underlying subject matter, while not getting bogged down into more “plug and chug” type problems.
* There are points assigned to each question. It has been our experience a total of 100 points is typically a manageable exam for a 50-60 minute class period.
* Many of these questions have been used in exams at the Colorado School of Mines over a period of ten years. Having been used previously, the chances of an exam question being far more difficult than intended or having unclear wording is reduced.
* Some of the questions are from the problems from the textbook. They are marked with an asterisk.
* There are far more questions included than will be necessary for a single semester. This allows for variation from year to year. Many of the problems can be thought of more as a template from which changes and completely new exam questions can be developed. The solutions can also be easily edited to accommodate these alterations.

# Chapter 2

## Conceptual Problems

1. (3 ea.) True (T) or False (F).

According to Le Chatelier’s Principle, if a reaction has and ,
the reaction will shift in the forward direction if the temperature is increased.

According to Le Chatelier’s Principle, if a reaction involves a gas
condensing to a solid, the reaction will shift in the forward direction
if the pressure is increased.

For an ideal gas, if the gas pressure is doubled and the temperature (in Kelvin)
is doubled, the gas concentration (moles/volume) will also double.

If and , MUST be negative.

If the reaction quotient, *Q*, is greater than the equilibrium constant, *K*, it is
thermodynamically favorable for the reaction to proceed in the backward direction.

If liquid iron is cooled below its melting point, the thermodynamic driving force
for solidification increases (i.e., for solidification becomes more negative)

1. (3) Based on typical molar weights and densities of solids, the typical concentration of atoms in a solid is around:

a) b) c) d)

1. (3) Based on the ideal gas law, the typical concentration of atoms in a gas at STP is around:

a) b) c) d)

## Calculation Problems

1. \*(15) Metal hydrides are metal alloys that can store significant quantities of hydrogen in their atomic lattice. For this reason, they are considered potentially attractive for the on-board storage of hydrogen for hydrogen fuel cell vehicles. A certain metal hydride alloy can store 2.0 weight% hydrogen and has a density (including the hydrogen) of . Treating hydrogen as an ideal gas, what pressure would be needed to compress gaseous hydrogen to the same equivalent concentration that it attains when absorbed in the metal hydride?

# Chapter 3

## Conceptual Problems

1. (3 ea.) True (T) or False (F).

\*Decreasing a reaction’s activation energy by half will increase
the reaction rate by a factor of 2.

\* is a homogeneous reaction

\* is a first order reaction rate law.

\* For the reaction: , the rate equation must be:

In the derivation of the Langmuir absorption equilibrium, the rate
at which a gas desorbs from a surface depends on the pressure of
that gas above the surface.

In a first order reaction that goes to completion, if the initial concentration
of the reactant is doubled, the initial reaction rate will double.

During CO poisoning of Pt catalysts, increasing the temperature increases
the CO desorption rate and decreases the CO adsorption rate. Thus, if the
temperature is increased, the equilibrium surface coverage of CO on the
Pt catalyst will increase.

For the CO poisoning process described above, if the CO pressure
in the gas phase above the Pt catalyst surface is increased and the
temperature is decreased, the equilibrium surface coverage of CO
on the Pt catalyst will increase.

In a first order radioactive decay process, if the decay rate is doubled,
the half-life will be cut in half (i.e., reduced by a factor of two).

1. \*(15) An exact treatment of equilibrium reaction kinetics for reactions that do not go to completion was discussed in the text. The following two expressions were provided as integrated rate laws for a simple equilibrium first-order reaction between A and B where the forward rate constant is given by and the backward rate constant is given by :

Prove that as , these expressions yield the equilibrium concentrations of species A and B ( and ). Hint: remember that .

## Calculation Problems

1. \*(15) You have synthesized a new radioactive material which you have named OHarium (OHa) in honor of the professor that wrote your favorite undergraduate textbook on materials kinetics…

a) (8) You measure the rate of radioactive emission from one mole of OHa immediately after synthesis to be 6000 disintegrations/sec. Exactly five days later, the rate has decreased to 5800 disintegrations/sec. Based on this information, calculate the first order reaction rate constant () for the nuclear disintegration of OHa.

b) (7) What is the half-life of OHa(in years)?

1. (15) At room temperature () the formation of product from and reactants has . If the initial pressures of , and are , and respectively, calculate the final (equilibrium) pressures of all the species after reaction. (Hint: You should first determine whether this reaction will occur in the forward or reverse directions for the given starting conditions.)
2. (15) Oetzi, the prehistoric man found in a glacier in the Alps in 1991 carrying an almost pure copper axe had radiocarbon dating performed on his remains. If the half-life of is 5730 years:

a) (5) Calculate the reaction rate constant () for this radioactive decay.

b) (10) Calculate the year (AD or BC) that Oetzi died if the concentration in his remains had decreased to 0.5266 of its initial value at the time of sampling in 1991.

1. (35) Plutonium-238, , spontaneously decays by alpha particle, , emission with a half-life of 86 years. The nuclear disintegration reaction is (on a per-atom basis):

where MeV is the energy released in millions of electron-volts. This disintegration rate is sufficiently fast and energetic to produce heat to be used as a power source in spacecraft. There are many spacecraft powered by plutonium heat sources, including the one on the way to Pluto, New Horizons.

a) (5) Calculate the first order reaction rate constant () for the nuclear disintegration of plutonium-238.

b) (5) Calculate the number of disintegrations per second for one mole of plutonium-238 that is **one year old**.

c) (10) Calculate the rate of energy (watts) generated in the plutonium-238 for one mole of the one year old plutonium-238.

d) (5) If the heat source is fueled by PuO2 which has a density of , calculate the molar volume () of PuO2 ().

e) (5) Calculate the power (watts) generated by a 2.0 inch diameter sphere of the one year old PuO2.

f) (5) Calculate what the rate of energy generation (watts) will be when the New Horizons satellite reaches Pluto in 2016 for the initially one-year-old PuO2 in the RTP (radioisotope thermoelectric power) unit sent into space. (Assume the spacecraft was launched in 2007 with a 2.0 inch diameter sphere of PuO2 that was one-year old at the time of the launch).

# Chapter 4

## Conceptual Problems

1. (3 ea.) True (T) or False (F).

If a Pd membrane is doubled in thickness, it will take twice as long for
hydrogen to diffuse through.

For gas-phase diffusion, if the temperature is doubled and the pressure is
doubled, the diffusivity will increase.

If a new pipeline steel alloy reduces the hydrogen diffusivity by a factor of two,
it will now take twice as long for hydrogen to diffuse through the pipe walls.

For solid-state diffusion, if the temperature is exactly doubled
the diffusivity will exactly double.

For gas-phase diffusion, diffusivity decreases with increasing pressure.

Everything else being equal, D2 (a hydrogen gas isotope with molecular mass of
) will diffuse slower than normal hydrogen (molecular mass of ).

1. (10) Chose which of the three schematics best illustrates the situation for the concentration gradient that develops during steady state diffusion across a membrane **when the diffusivity increases with concentration**.



(20) a) (10) Contrast the atomic mechanisms of diffusion in a solid versus a gas. Provide sketches illustrating both diffusion processes.

b) (10) Provide a complete equation describing how diffusivity depends on temperature and pressure in a gas and a complete equation describing how diffusivity depends on temperature in a solid. Define all terms in your equations and indicate typical units for all terms.

1. (10) Provide a sketch of Maxwell’s distribution of gas velocities for three different situations on the same graph: Curve 1 for a gas temperature and molecular mass ; Curve 2 for a gas temperature and molecular mass ; and Curve 3 for gas temperature and molecular mass . Indicate for all three curves. Don’t forget to label your axes!
2. (3) Fick's 2nd law for spherical coordinates and spherical symmetry is given by:
 In this case, the “steady state” is mathematically defined as:
3. \*(25) The following provides the solution for the transient diffusion of a “thin-layer” of material between two semi-infinite bodies:

This thin-film solution yields a Gaussian profile that gradually broadens as a function of time. Derive a mathematical expression quantifying how this Gaussian profile “broadens” as a function of time. Use the peak-width at half-maximum (i.e., the distance between the two points where the concentration is one-half of its peak value at any given time) as the definition of peak breadth.
4. \*(10) Circle the closest (only one) answer for each of the following:

a) The diffusion coefficient of oxygen vacancies in solid ZrO2 at is about:

(1) ; (2) ; (3) ; (4) ; (5)

b) The diffusion coefficient of oxygen vacancies in solid ZrO2 at is about:

(1) ; (2) ; (3) ; (4) ; (5)

c) The diffusion coefficient of Cu atoms in liquid copper at its melting point is about:

(1) ; (2) ; (3) ; (4) ; (5)

d) The diffusion coefficient of water molecules in air at is about:

(1) ; (2) ; (3) ; (4) ; (5)

e) The self diffusion coefficient of water molecules at room temperature is about:

(1) ; (2) ; (3) ; (4) ; (5)

## Calculation Problems

(16) a) (4) Calculate the velocity () of oxygen molecules () at one atmosphere at .

b) (4) Calculate the number of oxygen molecules per cc at and one atmosphere.

c) (4) Calculate the mean free path () of oxygen molecules () at and one atmosphere.

d) (4) Calculate the oxygen diffusion coefficient at and one atmosphere.

1. (15) Scientists are studying the diffusion of toxic chemicals through skin in order to determine its effectiveness as a barrier. In one experiment, 4-cyanophenol (4CP) is permeated through skin specimens as a model toxic chemical. The steady state flux (*J*ss) of 4CP through a thick sample of skin is measured to be when one side of the skin is subjected to a 4CP concentration of and the other side is held at zero concentration (steady state sink conditions).

a) (5) Calculate the diffusivity of 4CP in skin.

b) (5) If the diffusivity of 4CP in pure water is , estimate the “effectiveness” of the skin barrier by calculating the ratio of 4CP diffusivity in water versus skin.

c) (5) Approximately how many times longer would it take for 4CP to transiently diffuse through of skin compared to of water?

1. (35) Most fuels (even biofuels) contain unavoidable sulfur contaminants. These contaminants must often be removed before the fuel can be used. You are tasked to design a new filter system which can remove sulfur contaminants from a gaseous fuel stream. The filter is based on a novel barium-based reactive material that strongly absorbs sulfur. The filter can be modeled as a planar porous membrane of thickness **. As sulfur-contaminated fuel diffuses through the porous membrane, some of the sulfur is absorbed by the barium material. This process can be modeled as a transient reaction-diffusion process, since both diffusion of the sulfur through the membrane and reaction of the sulfur within the membrane occur in parallel. Fick’s second law for this situation therefore includes both diffusion and reaction terms:

where is the sulfur concentration, is the effective diffusivity of sulfur in the porous membrane, and is the reaction rate constant for the absorption of sulfur in the membrane.

a) (4) Assume the porous membrane is initially clean (no sulfur), and at time the “upstream” () face of the membrane is exposed to fuel containing a sulfur concentration of . Provide the boundary condition and the initial condition for this problem.

b) (6) We want to ensure that the membrane is sufficiently thick to prevent “sulfur breakthrough”. Thus, we require a solution for the concentration of sulfur emerging from the downstream face of the filter membrane as a function of time, . This solution is given by:

Based on this *transient* solution, what is the *steady state* solution for the concentration of sulfur emerging from the “downstream face” of this membrane?

c) (15) Sulfur breakthrough occurs when the concentration of sulfur emerging from the downstream face of the membrane exceeds 1% of the upstream concentration. Derive an expression for the minimum membrane thickness required to avoid sulfur breakthrough as a function of the effective diffusivity of sulfur in the porous membrane,, and the reaction rate constant *k*.

d) (5) If , and , what is the minimum filter membrane thickness required to prevent sulfur breakthrough?

e) (5) For an initially clean filter membrane thick, if ,
and , how long can the filter membrane operate before sulfur breakthrough occurs?

1. (20) In an experiment to determine the diffusion coefficient of sodium interstitials in silica at , is known to be and the error in temperature measurement is . Estimate the error limits on the diffusion coefficient based on these error limits for and temperature.
2. (28) Diffusion coefficients are often measured in materials using a radio isotope “tagging” method. For example, hydrogen gas splits into atomic hydrogen after adsorption onto a palladium (Pd) membrane and then diffuses via solid-state diffusion through the membrane. The atomic hydrogen diffusion can be measured by exposing one side of a Pd membrane to deuterium gas and measuring how long it takes for the deuterium to begin showing up on the other side of the membrane. (Deuterium is a “heavy” isotope of hydrogen gas, and hence can be easily identified based on its mass.)

Figure 1

Consider a Pd membrane of thickness as shown in Figure 1, which is initially devoid of any deuterium (D). At time , one side of the membrane is exposed to a D2 concentration, , while the D2 concentration on the other side of the membrane is effectively maintained (by pumping) at zero for all time.

a) (6) Several different processes can be rate limiting when discussing the transport of gas through a solid membrane. Provide at least three kinetic processes (steps) which might be rate limiting in this system.

b) (6) Assuming that solid-state diffusion of D through the membrane is rate determining, draw a diagram (similar to Figure 1) illustrating the D concentration profile across the membrane at five times:
.

c) (6) Assuming that solid-state D diffusion is rate-determining, provide the two boundary conditions and one initial condition for this transient diffusion problem.

d) (5) By employing your boundary conditions and initial conditions to evaluate this transient diffusion problem (and lots of math), you arrive at the following equation which describes the amount of time it takes before an appreciable amount of deuterium begins to appear at the downstream face of the membrane. This time is referred to as the “lag-time”, :

For a thick Pd membrane at , you measure to be 60 min. Based on this result, what is *D* (cm2/s) for deuterium in Pd at this temperature?

e) (5) You increase the temperature to and decreases to 20 min. Based on this result and the result from part d above, estimate the activation energy (kJ/mol) for deuterium diffusion in Pd.

1. (15) In an experiment to determine the diffusion coefficient of oxygen in nitrogen at and one atmosphere pressure, the error in temperature measurement is , and the error in the pressure measurement is . Estimate the error limits on the diffusion coefficient based on these error limits for temperature and pressure.
2. \*(35) Steel often contains trace amounts of H2, which can lead to embrittlement. To avoid embrittlement, steel is often degassed prior to use in order to **remove** these trace H2 impurities. Degassing steel involves placing the steel in a vacuum, where the H2 concentration in the vacuum can be considered to be zero at all times. Degassing proceeds by three steps: 1) Solid-state diffusion of H2 from the steel bulk to the steel surface. 2) De-sorption of H2 from the surface of the steel. 3) Gas-phase diffusion of the H2 away from the steel surface.

Figure 2

a) (5) Based on what you know about the typical rates of the three steps involved in the steel degasification process, which of these three steps is likely to be the rate determining step and why?

b) (5) Consider a steel plate which initially contains a uniform H2 concentration () of , as shown in Figure 2. Assuming that de-sorption of H2 from the surface of the steel is the rate determining step in steel degasification, draw a diagram (similar to Figure 2) illustrating the H2 concentration profile across the steel plate at five times:
*.*

c) (5) Assuming that solid-state diffusion of H2 from the bulk to the surface of the steel is the rate determining step in steel degasification, draw a diagram (similar to Figure 2) illustrating the H2 concentration profile across the steel plate at five times: .

d) (4) Assuming that solid state H2 diffusion is the rate determining step, is this a finite, semi-infinite, or infinite boundary-value diffusion problem?

e) (6) Assuming that solid-state H2 diffusion is the rate-determining step, provide the two boundary conditions and one initial condition for this transient diffusion problem. Note that corresponds to the center of the steel plate. Assume the steel plate is thick.

f) (5) By employing your boundary conditions and initial conditions to evaluate this transient diffusion problem, you arrive at the following solution for the time-dependent concentration of H2 at the center of the steel plate :

where is the thickness of the steel plate and is the initial () concentration of H2 in the steel plate. H2 embrittlement is avoided if the H2 concentration in the steel is reduced below . If the diffusivity of H2 in steel under degassing conditions is , how long must the steel be degassed to ensure the H2 concentration at the center of the plate falls below ? Assume the steel plate is thick.

g) (5) How long must a thick steel plate be degassed to avoid H2 embrittlement?

(20) a) (8) The migration barrier () for the diffusion of carbon in BCC iron is . Calculate the diffusion coefficient for carbon in iron at given that the diffusion coefficient for carbon in iron at is .

b) (8) Calculate the diffusion coefficient for carbon in FCC iron at 500 °C given
 and .

c) (4) Compare the diffusivity of carbon in FCC iron vs. BCC iron at . Why do you think the values are different?

1. (20) Nitridation of a thick steel plate can be modeled using transient one-dimensional infinite diffusion. The “diffusion depth”, which describes the characteristic depth to which nitrogen diffuses into the steel plate as a function of time can be approximated with the following equation:

where is the characteristic diffusion depth, is the diffusivity of nitrogen in steel, and is the time.

a) (5) If it takes an amount of time for nitrogen to diffuse into a steel plate a characteristic distance at a temperature , derive an expression for the amount of time, , that would be required for nitrogen to diffuse *four* times as far into the steel plate, assuming the same temperature was used in both cases (so that does not change).

b) (15) If it takes an amount of time for nitrogen to diffuse into a steel plate a characteristic distance at a temperature , derive an expression for the temperature, , that would be required to enable nitrogen to diffuse *four* times as far into the steel plate *in the same amount of time* (i.e. in this case, but ). Assume that diffusion obeys a simple Arrhenius relationship with an activation energy for diffusion of  **Hint: your answer for *T*2 should be in terms of , *R*, and *T*1.**

1. (35) A p-n junction is formed in a boron-doped silicon wafer by diffusing arsenic from the surface. The junction is formed at the depth where the arsenic concentration equals the boron concentration. The silicon wafer has a uniform boron concentration of . Initially, the concentration of arsenic in the wafer is zero. During the diffusion process, the concentration of arsenic at the silicon surface is held at . The diffusion coefficient for arsenic at the process temperature is .

**INSTRUCTOR’S NOTE: It is recommended to provide an error function table to the students in order to work this problem.**

a) (5) Provide a sketch for this transient diffusion problem, clearly illustrating your expectation for the evolution of the arsenic concentration profile as a function of time and the location of the p-n junction as a function of time.

b) (3) Assuming the silicon wafer can be treated as a semi-infinite medium, what is the general solution for the time-dependent arsenic concentration profile, ?

c) (4) Provide the boundary condition and the initial condition for this problem.

d) (6) Use your boundary and initial conditions to determine the constants *A*, and *B* in your general solution for .

e) (10) If the diffusion is carried out for one hour, at what depth will the p-n junction be formed?

f) (4) What total diffusion time is required to place the p-n junction depth below the silicon surface?

g) (3) Provide a rough graph showing how the p-n junction depth increases as a function of diffusion time.

1. (10) For interstitial sodium ion diffusion in pure SiO2 (silica) glass, the following important diffusion parameters are given: and .

a) (6) Calculate the diffusion coefficient (cm2/s) of sodium ion impurities in silica at .

b) (4) Make a sketch of free energy versus distance for an interstitial sodium ion atom making a jump from one interstitial site in silica glass to another interstitial site.

# Chapter 5

## Conceptual Problems

1. (3 ea.) True (T) or False (F).

To improve film conformity during CVD, it is best to operate at high
temperatures where gas phase diffusion is rate limiting.

In the passive oxidation of silicon, oxygen diffusion controls the oxidation
rate because oxygen atoms diffuse more slowly through
SiO2 than silicon atoms diffuse through SiO2

In the passive oxidation of silicon, when starting with a bare silicon surface,
the oxidation rate is initially linear , before switching to parabolic
 at longer times.

If a passive oxidation process obeys the following rate law: ,
where A and B are constants, *t* is the time, and *x* is the oxide thickness, then
the “switchover” time between linear and parabolic oxidation is given by
 and the “switchover” thickness is given by

1. (10) Explain with *both* diagrams and equations, how a halogen light bulb works in comparison to a traditional incandescent light bulb.
2. (10) Using the principles of materials kinetics, explain how strong temperature gradients in the snowpack of the Colorado Rocky Mountains leads to coarsening and corrosion of the snowpack near the ground and a densification of the snowpack near the surface. Be as detailed as possible in your answer using equations and diagrams as appropriate.

## Calculation Problems

1. (14) The Parabolic Oxidation Law for the passive oxidation of Silicon is:

a) (4) Why are there two terms in the above equation?

b) (6) On a single plot of time versus oxide thickness, draw the overall growth and the two contributing factors that lend to its shape. Label each of the three lines.

c) (4) Identify critical values on the plot and explain why they are significant.

1. \*(26) Titanium undergoes active gas corrosion in HCl according to the reaction

The rate of etching of Ti surface is found to be . Given the following,

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a) (10) Calculate the rate constant for the reaction.

b) (8) Calculate the activation energy *G*act for the reaction.

c) (4) What is the time required to remove of Ti?

d) (4) What is the corrosion rate after a time hours.

1. (25) During the calcination of limestone, calcium carbonate (CaCo3) is decomposed into lime (CaO) and carbon dioxide:

a) (6) For this solid-gas decomposition process, either the reaction at the surface or the gas-phase diffusion of CO2 away from the surface could be rate limiting. Provide sketches illustrating how the CO2 pressure would vary between the surface of the CaCO3 and the bulk atmosphere of the furnace for each of these two cases.

b) (4) At 1000 K, assume that the rate of calcination is controlled by the rate of diffusion of CO2 from the surface of the solid to the surrounding atmosphere. Assuming that the calcining furnace operates at a total pressure of 1.0 atm and that the only CO2 present in the furnace is due to the calcium carbonate decomposition, calculate the equilibrium CO2 pressure at the surface of the limestone at 1000 K.

c) (10) Assume that the rate of calcination is controlled by the rate of diffusion of CO2. Assume that the CO2 leaving the surface diffuses through a stagnant gas diffusion layer of air 1mm thick ( = 1.0 mm) and that the CO2 pressure in the bulk of the calcining furnace is effectively zero. Calculate the rate of decomposition of limestone (J) in units of moles/cm2s at 1000 K given that m2/s at 1000 K.

d) (5) At lower temperatures (below 900 K), the calcination rate is controlled by the rate of the surface reaction. Provide a sketch of the overall calcination rate vs. (1/*T*) illustrating this transition from diffusion control to reaction control. Your sketch should clearly indicate the temperature dependencies of both the surface reaction and diffusion processes as well as the overall calcination rate.

1. \*(15) A vacuum reactor is used to synthesize WO3 nanoparticles for use in an electrochromic window device. To create the WO3 nanoparticles, a tungsten (W) metal filament 1 mm in diameter and 10 cm long is heated to 2200 °C in a vacuum with a trace pressure of oxygen gas. W evaporates from the filament as W metal, and then rapidly oxidized in the reactor atmosphere to produce WO3 nanoparticles. Assuming all of the W evaporating from the surface of the filament is rapidly and completely oxidized to WO3, determine the maximum rate of production of WO3 from this reactor (grams/sec). The equilibrium vapor pressure of W at 2200 °C is approximately . The evaporation flux (J’s) from a material with an equilibrium vapor pressure at a temperature is given by the following expression:

where  (the sticking coefficient) is assumed to be 1 and *M* is the molecular weight of the evaporating material (, ).

# Chapter 6

## Conceptual Problems

1. (3 ea.) True (T) or False (F).

Heterogeneous nucleation decreases the critical nuclei size () required for
nucleation compared to homogeneous nucleation.

The greater the undercooling, the faster the overall rate of transformation
during a solid-state phase transformation.

For a solid-state transformation process, as the undercooling increases,
the critical radius for nucleation () also increases.

The energy of a surface is lower than the energy of a bulk material because
there are fewer neighboring atoms on a surface.

If the critical activation barrier for nucleation () is cut in half,
the nucleation rate will double.

For a liquid cooled *below* its solidification temperature, for
solidification is positive.

To minimize heterogeneous nucleation on a surface, the contact angle between
the nuclei and the surface should be as low as possible.

Spinodal decomposition reactions do not require diffusion. They are
“displacive” reactions that involve the collective cooperative movement
of many atoms simultaneously in a shearing action.

1. (8) Provide a sketch of system free energy (*G*) versus nucleus size (*r*) during a solid-state phase transformation. Include four curves on your sketch:

i) a curve indicating how the interfacial energy of the system varies with nucleus size,

ii) a curve indicating how the volumetric energy of the system varies with nucleus size,

iii) a curve indicating how the net total free energy of the system varies with nucleus size, and

iv) a curve indicating how the total net free energy of the system varies with nucleus size for the case of heterogeneous nucleation where . Indicate *r*\* and *G*\* on your sketch for both the homogeneous and heterogeneous nucleation cases.

 (12) a) (6) Provide a sketch of rate versus temperature (*T*) describing how both the nucleation rate and the growth rate vary as a function of temperature for a solidification process (for a pure single-phase material). Your sketch should have two curves on it: the overall nucleation rate as a function of temperature, and the overall growth-rate as a function of temperature. Indicate TM and three additional temperatures (*T*1, *T*2, and *T*3 smaller than *T*M) on your sketch as well.

b) (6) Provide three sketches (one each for temperatures *T*1, *T*2, and *T*3 indicated on your sketch above) showing how the solidified microstructure changes with solidification temperature.

 (14) a) (5) Explain the difference between stable growth and dendritic growth. Be sure to use diagrams in your explanation.

b) (5) Use a plot of temperature versus rate to identify the region where dendrite formation is favored and the region where it is suppressed. Explain the reasoning behind this. Be sure to label *T*interface and *T*perturbation in each of the regions and explain why one is always below the other.

c) (4) List the conditions that encourage dendrite growth and explain why they do so?

1. \*(8) You are tasked to design a new mold material for iron casting that ensures the best possible wetting of the mold surface with molten iron. To ensure that iron wetting on the mold surface is energetically favorable, should the surface energy between the mold and the molten iron be much greater, or much smaller than the surface energy between the mold and air? Fully explain your answer, using diagrams/equations as appropriate.

## Calculation Problems

1. \*(35) A small droplet of molten silver is cooled until it solidifies via a homogeneous nucleation and growth process. Calculate the amount of undercooling required to initiate the onset of solidification (i.e., the temperature at which at least one viable homogeneous nuclei forms in the volume of the droplet).

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|  |  |
| Droplet volume  |  |
|  |  |

1. (15) You are provided with the following thermodynamic data for the solidification of gold:

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a) (2) At *T*=*T*m, what is the driving force (*G*) for solidification

b) (8) If liquid gold is cooled 300 °C below its melting temperature, the free energy driving force (*G*) for solidification is determined to be . What are the enthalpy (*H*) and entropy (*S*) of solidification for this reaction?

c) (5) If liquid Au is cooled 300 °C below its melting temperature, what is the free energy driving force per unit volume (*Gv*) for solidification?

1. (25) You are provided with the following thermodynamic data for the solidification of gold:

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a) (2) At *T*=*T*m, what is the driving force () for solidification

b) (2) What is the entropy of solidification for this reaction?

c) (2) If liquid Au is cooled 100 °C below its melting temperature, what is the free energy driving force () for solidification?

d) (3) If liquid Au is cooled 100 °C below its melting temperature, what is the free energy driving force per unit volume () for solidification?

e) (8) Solid Au has the FCC crystal structure. If the average *bulk* gold atom in solid gold has twelve nearest neighbors () and the average *surface* gold atom has eight neighbors, what is the approximate surface energy () for solid gold? (Assume that the average surface density of gold is )

f) (6) Assuming that for gold (note: don’t expect this value to be the same as what you calculated in part e above, since this is for the l/s interface), calculate *r*\*, the critical nuclei size, for the solidification of gold from the liquid 100 °C below its melting temperature.

g) (2) If liquid gold is cooled to 200°C below its melting temperature, will *r*\* *increase* or *decrease* compared to the situation at 100°C below the melting temperature? Explain your answer.

1. (15) The following data is provided for the solidification of water:

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The temperature required for nuclei of solid water (ice) to form homogeneously from undercooled water is .

a) (10) Calculate the critical radius of a solid water (ice) nucleus at this temperature.

b) (5) Why do ponds freeze when the temperature is just a few degrees below the equilibrium freezing point (0 °C)?

1. (15) At 700 K, a solid-solid transformation process has the following nucleation and growth kinetics:
 Nucleation rate Growth rate

a) (6) Using the Johnson-Mehl equation, calculate the time (in hours) for this solid state transformation to reach 50% conversion, assuming that we start from zero % conversion initially (at *t* = 0).

b) (4) At 800 K, and cm/s, while at 600 K, and cm/s. For each of these two temperatures, again calculate the time (in hours) required for this solid state transformation to reach 50% conversion.

c) (5) Based on your answers to parts a. and b. above, provide a graph *quantitatively illustrating* the fraction transformed *F*(*t*) as a function of time for each temperature (600, 700, and 800 K) for this solid state transformation process. Provide all three curves on a single plot.

1. (25) Part of the beryllium-copper (Be-Cu) phase diagram is given in Figure 3. Copper is age-hardened by precipitating the γ phase from the α solid solution. The alloy composition being heat-treated contains 1.0 wt.% Be and the γ phase precipitates by a nucleation and growth process.

a) (2) Estimate the equilibrium temperature for the precipitation of γ particles from the 1 wt.% Be alloy.

b) (5) Sketch a schematic time-temperature-transformation (TTT) curve for the transformation of α to γ. Provide curves for 10% and 90% transformation curves and note the equilibrium temperature for the transformation.

Figure 3

c) (10) For a 1.0 wt.% Be solid solution at 400 °C, the Gibbs Free Energy of transformation for α to γ is . Given that γ has a density of , a molecular weight of approximately , and the surface energy of the α/γ interface is , calculate *r*\* and Δ*G*\* for this transformation.

d) (4) If the temperature is lowered from 400 °C to 300 °C, will *r*\* increase or decrease? Why?

e) (4) If the temperature is lowered from 400 °C to 300 °C, will Δ*G*\* increase or decrease? Why?

# Chapter 7

## Conceptual Problems

1. (3 ea.) True (T) or False (F).

Capillary forces drive the transport of matter from surfaces/interfaces of
high concavity to areas of high convexity.

Coarsening leads to an increase in both the number of particles and the
mean particle size as a function of time.

The *rule of six*, derived for 2D grain growth, holds that grains with more than
six sides tend to grow while grains with fewer than six sides tend to shrink.

Bulk-diffusion controlled sintering is densifying, while vapor-transport
controlled sintering is nondensifying.

According to 2D models, during grain growth, grain size
increases with the cube-root of time.

1. (6) Solid gold, in the bulk form, melts at 1337 K. Would you expect a *very* small particle of gold (with a radius of several nm) to melt at *higher* or *lower* temperatures than bulk gold? Make sure to explain your answer.
2. (20) Calculate the equivalent spherical diameter of:

a) (5) A regular 2D octagonal grain with sides of length *a*.

b) (5) A regular 2D hexagonal grain with sides of length *a*.

c) (5) A regular 2D square grain with sides of length *a*.

d) (5) A regular 2D triangular grain with sides of length *a*.

## Calculation Problems

1. (15) Thermal analysis can be used to approximate particle size. You test a sample of gold nanoparticles and get a melting point of 890 °C. Given the following information, how small are the particles?

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