MS 301300 Problem Set 1

1. An experiment similar to Smith's (sec. 1) is performed on a hollow iron tube with a 1.11-cm outer diameter, a 0.86-cm inner diameter, and a length of 10 cm. In 3.6×10^5 s 3.6 g of carbon passes through the tube. The variation of carbon with radius in the tube is given below. Plot C versus *r*, and from this calculate and plot the diffusion coefficient over the range of carbon contents.

r (cm)	Wt.% Carbon	*r* (cm)	Wt.% Carbon
0.553	0.28	0.491	1.09
0.540	0.46	0.479	1.20
0.527	0.65	0.466	1.32
0.516	0.82	0.449	1.42

2. It is desired to store hydrogen at 673K. A steel tank is available, and you are asked to calculate the steady-state rate of pressure drop for a cubical tank of one liter capacity with a wall thickness of 1 mm when the internal pressure is 9 atm absolute. The tank is to operate in a vacuum. Assume that $D=10^{-4}$ cm^2/sec, independent of the state of stress, that the hydrogen in the steel is in equilibrium with the atmosphere at both the high- and low-pressure sides, that the solubility is proportional to $p^{1/2}$,and that at p = 1 atm the solubility is 3 ppm (by weight). State clearly any additional assumptions made in your analysis.

Data: Density of steel: 7.87 g/cm^3

1 ppm by weight of steel = $7.87/10^6 = 7.87 \times 10^{-6}$ g/cm^3

R=8.314 J/mol.K

1 Pa$\cong 10^{-5}$ atm.

3. A thin shell of pure iron with a thickness of 0.2 cm is carburized at 1000°C in an atmosphere of CO and CO_2 that gives equilibrium carbon concentrations of 0.1 g/cm^3 on one side, and 0.01 g/cm^3 on the other side.

(a) If the diffusivity of carbon (D_C) increases from 2×10^{-7} cm^2/sec at 0.01 g/cm^3 carbon to 6×10^{-7} cm^2/sec at 0.1 g/cm^3 carbon (assuming $D_C = a + b[C]$), what will be the ratio of the concentration gradients at the surfaces under steady state?

(b) Plot the carbon concentration profile in the pure iron under the conditions of (a)?

(c) Calculate the flux of carbon under the conditions of (a)?

(d) Describe one method to double the flux of carbon under the conditions of (c).

4. Movement of gases through solids is described by two different ways including diffusivity (D) and permeability (P*). In other words, the Fick's first law can be rewritten as $J_m = -P^* \dfrac{\partial P}{\partial X}$ where P is the pressure. A sheet of polystyrene (PS) 0.1 cm thick is exposed to moist air on one side and dry air on the other. The pressure of water vapor on the moist side is 0.02 atm. The temperature is 25℃.

(a) What is the rate of permeation of water vapor through the polystyrene sheet in cubic centimeter per centimeter squared per second at steady state?

(b) The polystyrene sheet is coated on one side with a 0.01cm thick layer of polyvinyl chloride (PVC). What is the vapor pressure at the interface between PS and PVC at steady state? Note that no interfacial kinetic resistance exists between PS and PVC.

(c) What is the rate of permeation through the two-layer sheet in cubic centimeters per centimeter squared per second at steady state?

DATA:

Polystyrene (PS) $P^*=1.06\times10^{-5}$ $cm^3/cm\cdot s\cdot atm$,

Polyvinyl chloride (PVC) $P^*=0.27\times10^{-5}$ $cm^3/cm\cdot s\cdot atm$.

5. Often electronic packages are hermetically sealed with polymers, but after being put in service corrosion is sometimes observed. This happens because H_2O molecules can diffuse through polymers. Assume that the equilibrium between water vapor and water dissolved (or absorbed) by the polymer is simply represented by the reaction:

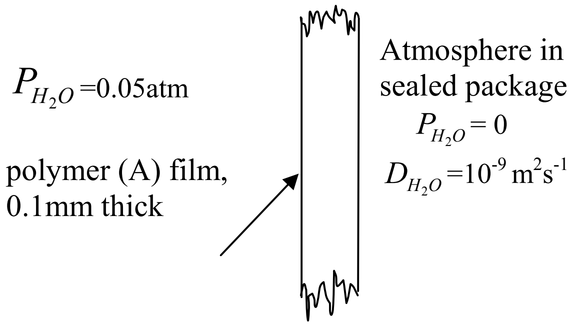
$$H_2O\ (g) = H_2O\ (dissolved)$$

with the equilibrium constant

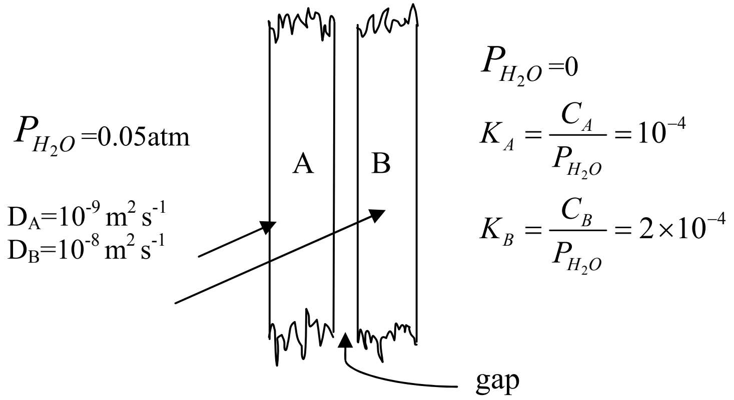
$$K = \frac{C}{P_{H_2O}} = 10^{-4}$$

where C is the concentration of H_2O in the polymer (moles cm^{-3}) and P_{H_2O} is the pressure of H_2O (g) in atm.

a) Assume equilibrium at the surfaces and calculate the flux of H_2O through the polymer (in moles $cm^{-2}s^{-1}$); assume steady state.



b) Now two films, polymer A and B, are used. Each is 0.1 mm thick.



Assume steady state and equilibrium at all interfaces. What is the pressure of H_2O (g) in the gap?

MS 301300 Problem Set 2

1. **A steel bar, 25 cm long and 1 cm in diameter, contains carbon in the amount of 0.15** wt%. A thin layer of carbon, 10^{-4} moles/cm^2, is deposited upon one end of the bar which is then annealed at a temperature of 1200k.
   (a) How long will it take for the composition of the bar to reach 0.25 wt% carbon at a depth of 150 μm from the carbon coated end at the first time?
   (b) Derive an expression for the velocity of the concentration front, $\rho=0.25$ wt% carbon. Comment on the direction of motion of this front at short and long times.
   (c) Hong long will it take for the composition of the bar to drop back down to 0.25 wt% carbon at a depth of 150 μm from the carbon coated end?
   (d) Plot the position of the concentration front, $\rho=0.25$ wt% carbon, as a function of time for times up to 100 h.
   Data: Diffusivity of carbon $D_c=2\text{x}10^{-7}$ cm^{2}sec^{-1}

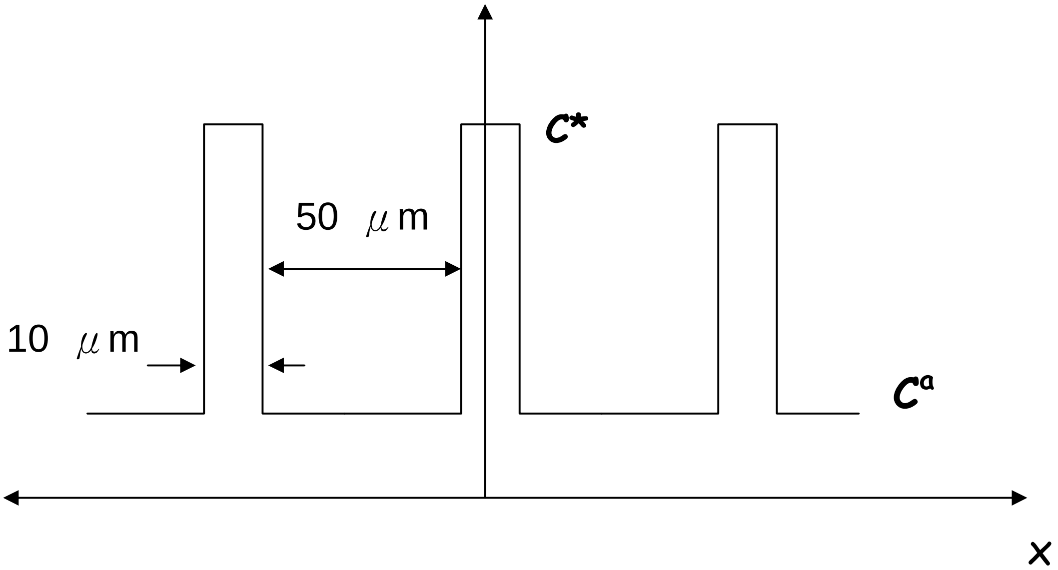
2. **The rule for judging whether a specimen can be modeled as infinite is $x>4.6(Dt)^{1/2}$**, defined in the context of a Leak Test. With reference to the error function solution to the problem of diffusion out of a slab, express this rule in terms of tolerance ($x^2>Dt$, $x^2>4Dt$ and $x^2>16Dt$).

3. **A piece of *p*-type silicon bar with a length of 1 cm contains boron at a uniform** concentration of 10^{16} atoms/cm^3. It is to be used to generate a ***p-n*** junction by diffusing phosphorus at 900^{o}C. Two methods are used. The first method is to deposit a film of phosphorus with a thickness of 10^{-6} cm and a surface concentration of 10^{20} atoms/cm^2 on the surface at low temperature, and the second method is to hold the concentration of phosphorus at the surface at a level of 10^{20} atoms/cm^3 by a flowing gas mixture. The diffusion coefficient of phosphorus in silicon at 900^{o}C is 10^{-12} cm^2/sec.
   (a) If the diffusion is carried out for 3600 sec at 900^{o}C, at what depth will a ***p-n*** junction be formed by the methods (1) and (2), respectively?
   (b) What is the total amount of phosphorus diffusing into silicon at 900^{o}C for 3600 sec in part (a) for the methods (1) and (2), respectively?

4. **Oxygen distribution in the melt-grown silicon crystal is spaced 50 μm apart (see** figure below). Since the oxygen-rich layers cause undesirable local variation in electrical properties, the crystal has to be annealed at 1400K to homogenize the oxygen distribution.
   (a) Write an expression for C(x,t) that is valid at all times.
   (b) Determine the time required to reduce the maximum concentration fluctuation in the oxygen-rich layers to 20% of the initial value, C^*-C^a. Estimate the error in your calculation.
   (c) Estimate the time required to reduce the fluctuation in the oxygen profile to within 1% of average.

Data:
Initial maximum oxygen concentration, $C^*=10^{24}$ atoms/cm^3

Initial minimum oxygen concentration, $C^a=10^{22}$ atoms/cm^3
Diffusion coefficient of oxygen in silicon at 1400K, $D=10^{-10}$ cm^2/sec.



5. **A thin shell of pure iron with a thickness of 0.2 cm is carburized at 1000°C** in an atmosphere of CO and CO_2 that gives equilibrium carbon concentration of 0.1 g/cm^3 on one side. The other side of the sample is purged with flowing He. The carburization process is found to be controlled by the diffusion of carbon.

(a) Estimate the time required to reach steady state across the pure iron if the diffusivity of carbon (D_C) is $2\text{x}10^{-7}$ cm^2/sec.

(b) Calculate the **flux** and **concentration** of carbon at t=(i) $4\text{x}10^3$ sec and (ii) ∞ on the surface exposed to carburizing atmosphere and in the middle of iron (i.e., x=0.1 cm). $D_C=2\text{x}10^{-7}$ cm^2/sec.

(c) Plot (i) the carbon concentration profile (C vs. x) and (ii) carbon flux profile (J vs. x) at $t=4\text{x}10^3$ sec and ∞, and (iii) carbon concentration at x=0.1 cm as a function of time (C vs. t indicating the location of t=(i) $4\text{x}10^3$ sec and (ii) ∞).

(d) Calculate the flux of carbon if the diffusivity of carbon (D_C) decreases linearly from $2\text{x}10^{-7}$ cm^2/sec at 0.1 g/cm^3 carbon to $6\text{x}10^{-7}$cm^2/sec at 0.01 g/cm^3 carbon under steady state.

(e) Plot (i) the carbon concentration profile (C vs. x), (ii) carbon flux profile (J vs. x) and (iii) carbon concentration at x=0.1 cm as a function of time (C vs. t) in the pure iron under conditions of (d).

6. **A sample with a three-layer structure of A/B/A metals, where the thickness of** A layer is $1\text{x}10^{-4}$ cm, and B layer is $2\text{x}10^{-4}$ cm. The sample is then covered with a thick alumina layer to prevent evaporation of metals during annealing at 1150K, at which the diffusivity of B in A is 10^{-12} cm^2 s^{-1}.The diffusion of A into B is assumed to be minimal.

(a) Write the differential equation along with the applicable initial and boundary conditions that are valid at all times.

(b) Plot the initial and final (t=∞) concentration profile of B.

(c) Write an expression for C(x,t) of B valid at all times (Two approaches including solutions of error function and Fourier series).

(d) Describe the conditions under which approximate solution will be valid by superposing two error-function solutions.

MS 301300 Problem Set 3

1. **A $4x10^{-7}$ cm film of gold is vapor deposited onto a 0.2 cm thick silver substrate.** The gold film is then coated with a $9.9x10^{-6}$ cm thick silver. This three-layer sample is annealed at 1111 K, at which gold and silver are completely miscible, and the diffusivity of Au in Ag is 10^{-14} cm^2 s^{-1}.
   (a) Describe the conditions under which approximate solutions to the diffusion couple can be obtained from error functions to the Fick's second law. Pointing out the shortcomings of the solution (if any).
   (b) By considering the zero-flux plane at the free surface of the $9.9x10^{-6}$ cm silver coating, develop from the thin-film solution an approximation to the composition profile of gold valid at intermediate times, i.e., long enough that the silver coating can not be considered infinite but short enough that the silver substrate can be considered infinite.
   (c) Estimate the maximum concentration of gold (in terms of initial concentration of Au) at the free surface of the silver coating during the course of a long diffusion anneal.

2. **A piece of *pure* silicon wafer with a thickness of 10 μm is to be doped with** aluminum at 1473K. Two methods are used. The first method is to deposit a film of aluminum with a thickness of 10^{-6} cm and a surface concentration of 10^{18} atoms/cm^2 on the surface at low temperature. The second method is to hold the concentration of aluminum at the surface at a level of 10^{18} atoms/cm^3 by a flowing gas mixture where a chemical reaction of $AlCl_{3(g)}+3/2H_{2(g)} = Al_{(g)}+3HCl_{(g)}$ takes place. Note that only one side of pure silicon is exposed to the flowing gas. The diffusivity of aluminum in silicon at 1473K is $1.05x10^{-11}cm^2$/sec.
   (a) After 30 min, at what depth below the surface of the silicon will the concentration of aluminum be 10^{16} atoms/cm^3 doped by the methods (1) and (2)?
   (b) Calculate the amount of aluminum (in atoms/cm^2) that diffuses into the silicon after 30 min of treatment at 1473K by the method (2)?
   (c) What is the concentration of aluminum on the side of silicon that is not exposed to the flowing gas after 1000 min treatment at 1473K by the method (2)?

3. **An iron plate with a dimension of 4m×1m×1cm has an initial nitrogen content of** 100 ppm. The plate is laid flat on the floor of a furnace heated at 1000 K. The nitrogen concentration in the atmosphere of the furnace is fixed at 5 ppm. The diffusivity of atomic nitrogen in iron is constant at a value of $4\times10^{-7}cm^2s^{-1}$.
   a. Write the differential equation along with the applicable initial and boundary conditions for the denitriding of such a plate. Assume that the reaction to form molecular nitrogen is fast, i.e., not rate-controlling step. Neglect nitrogen losses from the bottom and edges of the plate.
   b. Write an expression for $\rho(x,t)$ valid at all times.

c. Calculate the time required for the average nitrogen concentration in the plate to drop to 50% of the initial value.
d. How does your answer to part (c) change if the diffusivity of nitrogen increases with nitrogen concentration,? Longer or shorter time required? Justify you answer.
e. Calculate the surface flux of nitrogen at t = 0 if the rate-controlling kinetics is diffusive and non-diffusive (e.g., adsorption). Assume, as before, that the kinetics of formation of molecular nitrogen is fast. State your assumptions.

Data: The relationship between atomic nitrogen dissolved in iron and molecular nitrogen gas in the furnace atmosphere is given by the reaction

$$\frac{1}{2}N_2(gas) = N(in\ iron)$$

At 1000K, the equilibrium constant for this reaction is K=50 ppm atm$^{-1/2}$.

4. To dope silicon (Si) with boron (B), Si wafer with a thickness of 0.01 cm is annealed in a furnace with an atmosphere of boron vapor at a pressure of 100 dyne/cm^2 and a temperature of 800 K. Under these conditions the solubility of boron in solid silicon is 5 atomic percent which is equivalent to a surface concentration of 3.5x10^{14} molecule/cm^2, or a volume concentration of 2.5x10^{21} molecule/cm^3.

(a) Calculate the flux of boron at the silicon surface at (i) t=0, (ii) t=1 sec, (iii) t=10^6 sec. In each case justify your choice of rate expression.

(b) How long will it take to reach an average boron concentration of 99% of the equilibrium value?

Datum: Atomic weight: boron: 1.83x10^{-23} g/molecule; silicon: 4.67x10^{-23} g/molecule. Density: boron: 2.5 and silicon:2.3 g/cm^3. Diffusivity of boron in silicon at 800 K over the concentration range of interest, D_B= 10^{-10} cm^{2}sec^{-1}. Sticking coefficient (α) of boron vapor onto the silicon at 800K is 0.5. R= 8.314 J K^{-1} mol^{-1}; k=1.38x10^{-16} erg molecule^{-1}K^{-1}.

5. A steel sheet (0.2 cm thick) with an initial concentration of silicon of 1 wt% is to be exposed on both sides to an atmosphere of $SiCl_4$ which dissociates to Si (g) and Cl_2(g). The Si(g) dissolves in the steel up to 3 wt% at equilibrium, which is established quickly on the surface of steel. Note that the diffusivity of silicon in steel is constant at a value of 8.2x10^{-9} cm^2/s at 1255K.

(a) Indicate what partial differential equation, and boundary and initial conditions would apply in order to calculate the diffusion of silicon into the sheet,
(b) Write an expression for concentration of silicon in steel (C(x,t)) valid at all times,
(c) Calculate the time to achieve an average concentration of 2 wt% Si at 1255K.

MS 301300 Problem Set 4

1. **A thin sheet of pure iron at 740^{o}C is subjected to different gaseous atmospheres on** both of its surfaces such that the composition of one face is always controlled by a thermal decomposition of carbon mono-oxide and the other is a vacuum. The thermal decomposition of carbon mono-oxide takes place quickly as $CO=CO_2+C$ where the equilibrium constant is $4x10^8$ and the concentration of carbon is controlled to be a fixed concentration of 4 at% at the temperature of interest.

   (a) Plot the composition profile in the sample indicating clearly composition profiles and respective distances at time=zero, "short", and "long", and steady state, assuming the whole process controlled by the diffusion of carbon in iron. Pay strict attention to limiting values and their slopes. At 740^{o}C, the diffusivity of carbon in iron is given as $D=10^{-6}$ $cm^2 \cdot s^{-1}$ in ferrite (α) and 10^{-8} $cm^2 \cdot s^{-1}$ in austenite (γ), and independent of carbon concentration.

   (b) Plot the composition profile in part (a) at steady state if the diffusivity of carbon is assumed to increase with carbon concentration.

   (c) Calculate the flux of carbon at the interface between phases in iron (in part (a)) at steady state

   (d) Calculate the advance rate of interface between phases in iron (in part (a)) at steady state.

Note that the thickness of pure iron is 1 mm and density changes during experiment may be neglected.

2. **A composite foil made of metal A bonded to metal B, each 0.1 cm thick, is** subjected to 1.0 atm of pure hydrogen on metal A's face; the other side, metal B's face, is subjected to a perfect vacuum. At the temperature of interest and 1 atm of hydrogen, the solubility of hydrogen in metal A is $1.18x10^{-2}$ g/cm^3 of A and in B it is $1.18x10^{-1}$ g/cm^3 of B. It is also known that the diffusivity of hydrogen is $1x10^{-5}$ cm^2/sec in metal A and $1x10^{-10}$ cm^2/sec in metal B. Moreover, no significant relation between diffusivity of hydrogen and its concentration in both metals is found. The dissolution of H_2 in metals follows $1/2H_2= [H]_{\text{dissolved in metal,}}$ that the equilibrium condition is reached quickly and the solubility of hydrogen obeys the Sievert's law of $C_H=K \cdot P_{H2}^{1/2}$ (K is a constant). No kinetic resistance at the interface of A/B and boundary layers at the surfaces of A and B are assumed.

   (a) Draw the chemical activity profile of hydrogen across the composite foil at steady state. Note that the chemical activity of hydrogen (a_H) is equal to the square root of its partial pressure, i.e., $a_H = P_{H2}^{1/2}$. Pay strict attention to limiting values and their slopes.

   (b) Draw the concentration profile of hydrogen across the composite foil at steady state. Pay strict attention to limiting values and their slopes.

   (c) Calculate the total weight loss of hydrogen through **metal A** within 10^7 sec under steady state. Note that the surface area of metals is fixed at 10 cm^2.

3. **A piece of *p*-type silicon bar with a length of 1 cm contains boron at a uniform** concentration of 10^{16} atoms/cm^3. It is to be used to generate a ***p-n*** junction by

diffusing phosphorus at 900°C. One of methods is to deposit a film of phosphorus with a thickness of 10^{-6} cm and a surface concentration of 10^{20} atoms/cm^2 on the surface at low temperature. The diffusion coefficient of phosphorus in silicon at 900°C is 10^{-12} cm^2/sec. Please solve this question by the method of Laplace Transform given in the Handout.

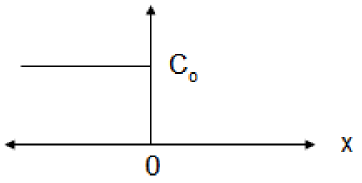
(a) If the diffusion is carried out for 3600 sec at 900°C, at what depth will a ***p-n*** junction be formed by this method?

(b) What is the total amount of phosphorus diffusing into silicon at 900°C for 3600 sec in part (a)?

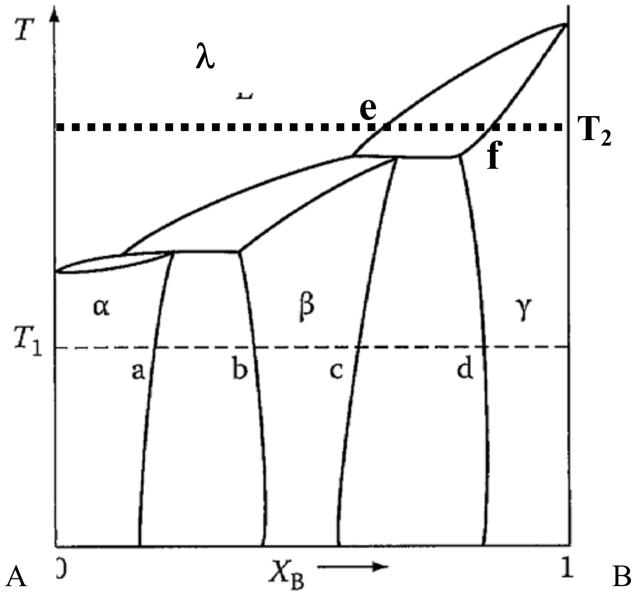
4. **For one-dimension concentration-driven diffusion experiment, the concentration** profile at time t=0 is a step function shown below. The specimen is annealed at a constant temperature, and the annealing time (t) is short (i.e., the sample can be assumed infinite).

   (a) How will the concentration profile C(x,t) change across the sample after time t, assuming a constant diffusivity? Solve the problem by the method of **Laplace Transform.** Note: $L^{-1}(\frac{e^{-\sqrt{p/D}x}}{p}) = erfc(\frac{x}{2\sqrt{Dt}})$

   (b) For a system in which diffusivity increases rapidly with concentration, sketch the concentration profile after time t, and compare it with a constant diffusivity. Note that the original and Matano interfaces should be indicated clearly.



5. **Draw (a) concentration and (b) chemical activity profiles for each diffusion** couple which has been annealed at each indicated temperature for a finite time, and (c) for the temperature T_2, write down the set of equations which would need to be solve to find the interface (S) velocity (V=dS/dt). Note that the rate-limiting step has been identified to be diffusion, and no interfacial resistance is found.



Note: Concentrations at a ,b, c, d, e and f are C_a, C_b, C_c, C_d, C_e and C_f, respectively.

(6) An 1mm sheet of steel with a carbon concentration of 0.76wt% at 800°C is annealed in a tube furnace with flowing He. Only one surface is exposed and the rest are deposited with alumina. No density change is assumed during annealing.

(a) Plot the **i) composition and ii) chemical activity** profiles in the sample at different times from 0 to ∞ (7 distinct stages), assuming the whole process controlled by the diffusion of carbon in the steel. Pay strict attention to limiting values and their slopes. At 800°C, the diffusivity of carbon in iron is given as $D=10^{-6}$ $cm^2 \cdot s^{-1}$ in ferrite (α) and 10^{-8} $cm^2 \cdot s^{-1}$ in austenite (γ), and independent of carbon concentration.

(b) Write down the set of equations which would need to be solved to find the interface (S) velocity (V=dS/dt) at "short" time.

(7) A 0.2 at% carbon alloy steel with a two-phase mixture of α-Fe and γ-Fe is carburized at 800°C in an atmosphere of CO and CO_2, which quickly reaches equilibrium with a surface concentration of 3.0 at% carbon. Under these conditions some γ-Fe forms on the surface after 3×10^7 sec treatment. At 800°C, the diffusivity of carbon in α-Fe and γ-Fe is 10^{-6} cm^2/sec and 10^{-8} cm^2/sec, respectively. The thickness of steel is 1 cm, and the change in density during the experiments may be neglected. The density of alloy steel is 7.9 g/cm^3.

(a) Calculate the thickness of γ-Fe formed on the surface,
(b) Calculate the flux of carbon (in at%) across the phase boundary,
(c) Plot the concentration of carbon as a function of distance. Pay strict attention to limiting values and their slopes.

Data: $0.56(C_s-C_I^*)/(C_I^*-C_o)=\beta\exp(\beta^2)\mathrm{erf}(\beta)$, which has a value of 0.21 for $\beta \approx 0.41$. The C_s is the concentration at the surface, C_I^* is the concentration at the phase boundary, and C_o is the initial concentration. β is related to the thickness (S) of a new phase formed and diffusivity of diffusing species in the new phase (D) as $\beta=S/(2(Dt)^{1/2})$

(8) A thin shell of 3.2 at% carbon alloy steel is decarburized at 800°C in an atmosphere of CO and CO_2, which quickly reaches equilibrium with a surface concentration of 0.01 at% carbon. After $2\text{x}10^4$ sec treatment α-Fe forms on one surface only. At 800°C, the diffusivity of carbon in α-Fe and γ-Fe is $2\text{x}10^{-6}$ cm^2/sec and $3\text{x}10^{-8}$ cm^2/sec, respectively. The thickness of steel is 1 cm, and the change in density during the experiments may be neglected.

(b) Calculate the thickness of α-Fe formed on the surface,
(b) Calculate the net flux of carbon (in at%) across the phase boundary,
(c) Plot the **concentration** and **chemical activity** of carbon ($a_C^\alpha = 1.1X_C^\alpha$) as a function of distance. Pay strict attention to limiting values and their slopes.

Data: $C_{II}^* - C_I^* = \frac{C_s - C_{II}^*}{f(\beta)} - \frac{C_I^* - C_0}{f(\sigma)}$ where the C_s is the concentration at the surface, C_I^* and C_{II}^* are the concentrations at the phase boundary, and C_o is the initial concentration. β is related to the thickness (S) of a new phase formed and diffusivity of diffusing species in the new phase (D) as $\beta=S/(2(Dt)^{1/2})$. The values of f(β) and f($\sigma=\beta\Phi^{1/2}$), where $\Phi=D_{II}/D_I$, are given in the following table:.

β	0.1	0.125	0.15	0.2
f(β)	0.02	0.031	0.046	0.082
σ	0.81	1.02	1.22	1.62
f(σ)	0.7	0.818	0.826	0.85

MS 301300 Problem Set 5

1. A composite foil made of metal A bonded to metal B, each 0.1 cm thick, is subjected to 10^6 dyne/cm^2 (1 atm) of flowing hydrogen on metal A's surface; the other side, metal B's surface, is subjected to a perfect vacuum at 673 K. The dissolution of H_2 in metals follows $1/2H_2= [H]_{\text{dissolved in metal,}}$ that the equilibrium condition is reached quickly and the solubility of hydrogen obeys the Sievert's law of $C_H=K\cdot P_{H2}^{1/2}$ (K is a constant). At 1 atm of hydrogen, the solubility of hydrogen in metal A is $2.19\text{x}10^{-3}$ g/cm^3 and in metal B is $1.18\text{x}10^{-1}$ g/cm^3. It is also known that the diffusivity of hydrogen is $4.9\text{x}10^{-6}$ cm^2/sec in metal A and $6.4\text{x}10^{-5}$ cm^2/sec in metal B. Moreover, no significant relation between diffusivity of hydrogen and its concentration in both metals is found. No kinetic resistance at the interface of A/B and boundary layers at the surfaces of A and B are assumed **at most of experimental conditions**. Justify your assumptions quantitatively. (45%)

(a) Calculate the hydrogen flux at the metal A surface at t=0 and t=1 sec, assuming that the sticking coefficient of hydrogen (α) is (i) $\alpha=1$ and (ii) $\alpha=10^{-10}$.

(b) Estimate the time required to reach steady state across the composite when (i) $\alpha=1$ and (ii) $\alpha=10^{-10}$.

(c) Make a plot for the chemical activity profile of hydrogen across the composite at 10^3, 10^6 and 10^9 sec heat treatment when (i) $\alpha=1$ and (ii) $\alpha=10^{-10}$. Note that the activity of hydrogen (a_H) is equal to the square root of its partial pressure, i.e., $a_H=P_{H2}^{1/2}$ where P_{H2} is in atm . Pay strict attention to limiting values and their slopes.

(d) Make a plot for the concentration profile of hydrogen across the composite at 10^3, 10^6, and 10^9 sec heat treatment when (i) $\alpha=1$ and (ii) $\alpha=10^{-10}$. Pay strict attention to limiting values and their slopes.

(e) Calculate the total weight loss and gain of hydrogen from metal A and B surfaces between 10^6 and 10^9 sec heat treatment when (i) $\alpha=1$ and (ii) $\alpha=10^{-10}$. The surface area of metals for hydrogen transfer is 200 cm^2.

Data: $K_B=1.38\text{x}10^{-16}$ erg/(molecule K); molecular weight of hydrogen =2 g/mole ($3.3\text{x}10^{-24}$ g/molecule), density of hydrogen=$8.92\text{x}10^{-5}$ g/cm^3; atomic weight of metal A=59 g/mole ($9.8\text{x}10^{-23}$ g/molecule), density of metal A=8.8 g/cm^3 ($8.9\text{x}10^{22}$ molecule/cm^3); atomic weight of metal B=106 g/mole ($1.8\text{x}10^{-22}$ g/molecule), density of metal B=11.8 g/cm^3 ($6.6\text{x}10^{22}$ molecule/cm^3).

2. A thin layer of a new element Pn, which has distinct properties of interest, is grown on its own wafer at elevated temperature. A flowing gas with a concentration of Pn of $3\text{x}10^{16}$ atoms/cm^3 is injected into the reactor continuously. The mass transfer coefficient of Pn(g) in the gas film (K_g) is $K_g=D_g/\delta$ where D_g is the diffusivity of Pn(g) and the thickness of stagnant layer (δ) adjacent to Pn wafer. The δ remains relatively unchanged to be 0.0001 cm at the experimental conditions investigated, and $D_g=2\text{x}10^{-5}\exp(-9000/T)$ cm^2/sec. The flux at the surface of Pn wafer (J_s) is $J_s=K_sC_s$ where K_s is the surface reaction rate constant and C_s is the surface concentration of Pn, and $K_s=1\text{x}10^{-5}\exp(-1000/T)$. Please justify your answers quantitatively if any assumption is made. (35%)

(a) What is the relative importance of various kinetic steps in the deposition of Pn layer (or the rate-controlling kinetic step) if the temperature increases from 600, 800, 1000, 1200 to 1400K? Please justify it quantitatively.

(b) What is the growth rate of Pn layer at 600, 800, 1000, 1200 and 1400K?

(c) What is the concentration profile of Pn at 600, 800, 1000, 1200 and 1400K?

(d) What temperatures should be recommended to grow Pn layer from processing viewpoint? Justify it quantitatively.

Data: the Pn has a density of $5\text{x}10^{22}$ atoms/cm^3

3. **A wafer of pure silicon is doped with boron generated through the decomposition** of boron trichloride according to BCl_3 (gas)=B (in silicon) + 3/2 Cl_2(gas). The gas mixture has an effective boron concentration (ρ^{eq}) of $2\text{x}10^{16}$ atoms/cm^3, which is invariant with time. The rate of mass transfer across the gas boundary layer can be expressed as $J = K(\rho^s - \rho^{eq})$ where K is the effective mass transfer coefficient and ρ^s is the concentration of boron in silicon at the wafer surface. Assume that only one surface is exposed to the gas stream and neglects edge effects.

(a) Calculate the boron flux at the wafer surface at $t \approx 0$

(b) Estimate the time to achieve an average concentration of 10^{16} atoms/cm^3 across a wafer of thickness of 0.05 cm

(c) Suppose now that instead of a wafer, a thin film of pure silicon, 0.5 μm thick deposited onto a sapphire substrate is borided under the same conditions described above. Estimate the time to achieve an average concentration of 10^{16} atoms/cm^3.

Data:

diffusion coefficient of boron in Si: $D = 10^{-14}$ cm^2/s
effective mass transfer coefficient: K = 0.1 cm/s
density: boron: 2.5 and silicon: 2.3 gm/cm^3
atomic mass: boron = 10.81 and silicon = 28.09 gm/mol

4. **Silica (SiO_2) is formed on the surface of a pure silicon wafer in an atmosphere of** pure oxygen with a pressure of 10 atm at 1200K. Since it is dry oxidation at a high oxygen pressure, no stagnant layer existing between gas and solid can be assumed. Moreover, no interfacial resistance exists at the interfaces of $O_2/SiO_2/Si$. The thickness of the oxide X (in μm) as a function of time t (in sec) is given by the following equation: $X^2 + AX = Bt$, assuming that the initial oxide thickness is zero.

(a) What is the rate-controlling step at the oxide thickness of 0.001 and 1.0 μm? At what <u>time</u> and <u>thickness</u> of oxide layer the rate-controlling step changes? Please justify it.

(b) What is the oxidation rate for the oxide thickness of 0.001 and 1.0 μm if the oxygen pressure in the reaction chamber is reduced from 10 atm to 5 atm?

(c) What are the reaction rate constants (K_R) of $Si+O_2 \rightarrow SiO_2$ and the diffusivity of oxygen in silica at the oxide thickness of 0.001 and 1.0 μm if the oxygen pressure in the reaction chamber is 10 atm?

(d) Sketch the concentration profile of oxygen for the oxide thickness of 0.001, and 1.0 μm. Pay strict attention to limiting values and their slopes.

DATA: A=0.2 μm and B=0.02 μm^2/sec at 1200K. At 1200K, the pressure of oxygen in equilibrium with Si and SiO_2 is approximately 10^{-22} atm. Molecular weight of oxygen is

32 g/mol, and the density of SiO_2 is 2.2 g/cm^3. R=0.082 atm·liter/mol·K

5. When Iron (Fe) is induction melted at 1873K under vacuum, the manganese (Mn) content of the liquid decreases with time. This transfer of Mn from liquid to vapor occurs in two steps including (i) mass transfer from the bulk liquid to the free surface, and (ii) vaporization from the melt surface into the vacuum. Assuming that due to induction stirring the melt composition is uniform everywhere except across the surface liquid boundary layer, and that mass transfer coefficient of Mn in liquid Fe (K_{Mn}) (step (i)) is determined by $K_{Mn}= (D_{Mn}/\theta)^{0.5}$ where $D_{Mn}=10^{-6}$ cm^2/sec and θ, the lifetime of Mn, is 1 sec. Moreover, the mass transfer coefficient of vaporization (step (ii)) is 10^{-1} cm/sec at 1873K.

(a) What is the relative importance of the various kinetic steps in the loss of Mn from Fe? Please justify it quantitatively.

(b) Sketch the concentration profile of Mn as a function of time. Pay strict attention to limiting values and their slopes. Justify your assumptions.

(c) How long does it take for the average concentration of Mn in Fe to become one half? Note that the ratio of surface area/volume of the melt is 0.1.

6. When Iron (Fe) is induction melted under vacuum, the manganese (Mn) content of the liquid decreases with time. This transfer of Mn from liquid to vapor occurs in two steps, (i) mass transfer from the bulk liquid to the free surface, and (ii) vaporization from the melt surface into the vacuum. An Fe-Mn alloy with a concentration of Mn of 4 at% is induction melted and stirred under vacuum at time, t, in a crucible of volume of 10 cm^3 and surface area of 1 cm^2. Assuming that (i) due to induction stirring the melt composition is uniform everywhere except across the surface liquid boundary layer, and that (ii) mass transfer coefficient of Mn in liquid Fe (K_{Mn}) is determined by $K_{Mn}=2(D_{Mn}/\pi\theta)^{0.5}$ where θ is the lifetime of Mn. In the case of induction stirring, θ is in the order of 1 sec or less.

(a) What is the relative importance of the various kinetic steps in the loss of Mn from Fe if the lifetime (θ) decreases from 1 sec, 0.1 sec, 0.01 sec to 0.00001 sec? Please justify it quantitatively.

(b) Sketch the concentration profile of Mn as a function of time when the lifetime (θ) varies from 1sec, 0.1 sec, 0.01 sec to 0.00001 sec. Pay strict attention to limiting values and their slopes. Justify your assumptions.

(c) How long does it take for the average concentration of Mn in Fe to drop to 2 at% at 1600°C, assuming the lifetime (θ) = 0.00001 sec?

Datum: At T=1873K, $D_{Mn}=9\times10^{-5}$ cm^2·s^{-1}, $\alpha=1$, $\gamma_{Mn}=1.0$, $P_{Mn}=4.665\times10^4$ dyne·cm^{-2}, and density of Fe=8.35×10^{22} molecule/cm^3. Molecular weight of Mn= 9.15×10^{-23} g/molecule, and gas constant (k_B)=1.38×10^{-16} erg/(molecule·K).

7. When Iron (Fe) is induction melted at 1873K under vacuum, the manganese (Mn) content of the liquid decreases with time. This transfer of Mn from liquid to vapor occurs in two steps including (i) mass transfer from the bulk liquid to the free surface, and (ii) vaporization from the melt surface into the vacuum. Assuming that due to induction stirring the melt composition is uniform everywhere except across the surface liquid boundary layer, and that mass transfer coefficient of Mn in liquid Fe (K_{Mn}) (step (i)) is determined by $K_{Mn}= (D_{Mn}/\theta)^{0.5}$ where $D_{Mn}=10^{-6}$ cm^2/sec and θ, the lifetime of Mn, is 10^{-4} sec. Moreover, the mass transfer coefficient of vaporization (step (ii)) is 10^{-3} cm/sec at 1873K.

(a) What is the relative importance of the various kinetic steps in the loss of Mn from Fe? Please justify it quantitatively.

(b) Plot the concentration profile of Mn as a function of time. Pay strict attention to limiting values and their slopes. Justify your assumptions.

(c) How long does it take for the average concentration of Mn in Fe to become one half? Note that the ratio of surface area/volume of the melt is 0.1.

8. **Quantum dots are very fine particles of materials such as high purity silicon.** We are interested in keeping the "dots" clean. The "dots" in question is a sphere with a diameter of 10^{-4} cm. Its residence time in a vacuum apparatus is 37 sec. The pressure in the apparatus is 10^{-5} dynes/cm^2, and the temperature is 300K. Assume that all the gas molecules in the apparatus are oxygen, and all the molecules that strike the surface of the "dots" stick to it. Estimate how many molecules of oxygen gas are adsorbed on the surface of one of the "dots" based upon the conditions described above. Datum: molecular weight of oxygen: $5.33\text{x}10^{-23}$ g/molecule, $k_B=1.38\text{x}10^{-16}$ erg/molecule K.

9. **A wafer of pure silicon is doped with boron generated through the decomposition** of boron trichloride according to BCl_3 (gas)=B (in silicon) + 3/2 Cl_2 (gas).The gas mixture has an effective boron concentration (ρ^{eq}) of $2\text{x}10^{16}$ atoms/cm^3, which is invariant with time. The rate of mass transfer across the gas boundary layer can be expressed as $J = K(\rho^{eq} - \rho^s)$ where K is the effective mass transfer coefficient and ρ^s is the concentration of boron in silicon at the wafer surface. Note that only one surface is exposed to the gas stream and the rest covered with alumina.
   (a) After 10^6sec, at what depth below the surface will the concentration of boron be 10^{16} atoms/cm^3 across a wafer with a thickness of 10^{-2} cm.
   (b) Calculate the amount of boron (in atom/cm^2) that diffuses into the Si under condition of (a).
   (c) What is the concentration of boron on the side of silicon that is not exposed after 10^8 sec annealing for a wafer with a thickness of 10^{-2} cm.
   (d) Estimate the time to achieve an average concentration of 10^{16} atoms/cm^3 across a wafer with a thickness of 10^{-2}, and 10^{-6} cm.
   (e) Plot the concentration profile of boron across a wafer with a thickness of 10^{-2}, and 10^{-6} cm under the conditions of (d). Pay strict attention to limiting values and their slopes.

   Data:
   diffusion coefficient of boron in Si: $D = 10^{-12}$ cm^2/s
   effective mass transfer coefficient: $K = 10^{-8}$ cm/s
   density: boron: 2.5 and silicon: 2.3 gm/cm^3
   atomic mass: boron = 10.81 and silicon = 28.09 gm/mol

10. **A thin-film Qx can be produced by physical vapor deposition** (PVD) on a sapphire substrate. At 873K, the substrate is exposed to a beam of Qx for 1000 sec to

produce a deposit with a thickness of 3x10^{-6} m. This is inconsistent with product literature of the PVD equipment, which should be able to deposit a thicker film, i.e., 6x10^{-6} m, under the same conditions. Experimental results confirm that the above difference in thickness is caused by the **sublimation loss** of Qx during deposition. Please estimate the partial pressure of Qx (P_{Qx}^{o}) at 873K.

Data: Properties of Qx: density: 4x10^{3} kg/m^{3}; molecular weight: 0.1 kg/mol. R=8.314 J/mole K. 1 Pa (=N/m^{2}) =9.86x10^{-6} atm.

11. A pure silicon wafer is being oxidized in an atmosphere of pure oxygen with a pressure of 10 atm at 1200K. Since it is dry oxidation at a high oxygen pressure, no stagnant layer existing between gas and solid can be assumed. Moreover, no interfacial resistance exists at the interfaces of $O_2/SiO_2/Si$. The thickness of the oxide X (in μm) as a function of time t (in sec) is given by the following equation:
$X^2 + AX = Bt$, where A=0.4 μm and B=0.04 μm^2/sec at 1200K. Please justify your answers quantitatively if any assumption is made.

(a) Initial thickness of SiO_2 on pure silicon?
(b) Flux of oxygen at the oxide thickness of 1.0 μm?
(c) What total oxidation time is required to reach an oxide thickness of 1.0 μm?
(d) Sketch the concentration profile of oxygen for the oxide thickness of 1.0 μm. Pay strict attention to limiting values and their slopes.

Data: Molecular weight of oxygen is 32 g/mole, the density of SiO_2 is 2.2 g/cm^3, and R=0.082 atm·liter/mol·K

MS301300 Problem Set 6

(1) The diffusivity of Bi atoms in Pb at 600 K is $1\text{x}10^{-9}$ cm^2/sec. The lattice constant of the FCC Pb crystal is $4.95\text{x}10^{-8}$ cm. Calculate the total distance traveled by the Bi atoms after 3600 sec and compare it to the expected root-mean-square displacement for the same period. Note that Pb has an FCC structure and the diffusion of Bi atoms in Pb takes place mainly by a substitutional mechanism.

(2) Estimate the γ for an isotope tracer in a pure BCC metal where γ is defined by the equation: $D=\gamma \boldsymbol{a}^2\boldsymbol{\Gamma}$ where $\boldsymbol{a}$ is the lattice constant, and $\boldsymbol{\Gamma}$ is the successful jump frequency. Note that the diffusion of tracer is dominated by vacancy mechanism.

(3) Calculate the γ for a nitrogen tracer in a pure BCC-Fe where γ is defined by the equation: $D=\gamma \boldsymbol{a}^2\omega \mathbf{N_i}$ where $\boldsymbol{a}$ is the lattice constant, $\boldsymbol{\omega}$ is the possible jump frequency and $\mathbf{N_i}$ is the concentration of interstitial tetrahedral site.

(4) The diffusivity of carbon in γ-Fe is D=0.04 exp(-10200 cal/RT) cm^2/sec. If the average vibration frequency of the carbon atom in the lattice is $5\text{x}10^{13}$ sec^{-1}, calculate the entropy of motion, ΔS_m, for carbon diffusion. Note that the lattice constant of γ-Fe is $2.48\text{x}10^{-8}$ cm, γ-Fe has a FCC lattice structure and the carbon atom occupies the interstitial tetrahedral site of γ-Fe. R=1.987 cal/K mol.

(5) The diffusivity of carbon in γ-Fe is D=0.04 exp(-10200 cal/RT) cm^2/sec. If the average vibration frequency of the carbon atom in the lattice is $5\text{x}10^{13}$ sec^{-1}, calculate the entropy of motion, ΔS_m, for carbon diffusion. Note that the lattice constant of γ-Fe is $2.48\text{x}10^{-8}$ cm, γ-Fe has a fcc lattice structure and the carbon atom occupies the interstitial octahedral site of γ-Fe. R: 1.987 cal/mol-K.

(6) The lattice constant, successful jump frequency and vacancy concentration at 1000°C for a pure simple cubic metal are $3\text{x}10^{-8}$ cm, 10^{10} sec^{-1} and $3\text{x}10^{-4}$, respectively. Calculate the diffusivity of vacancy at 1000°C.

(7) Please calculate the correlation factors of (i) vacancy and (ii) interstitial (tetrahedral site) diffusivities for FCC, BCC and SC.

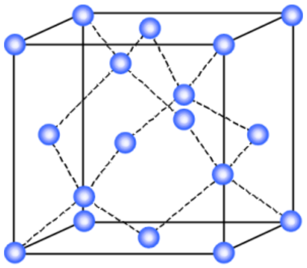
(8) An adsorbed W atom on an atomically smooth surface of W can be observed at low temperatures with a field ion microscope. If the sample is heated, then cooled again and observed, the W atoms have moved a mean-square displacement $\boldsymbol{\Delta x^2}$.

(a) Derive an equation that can be used to calculate the surface diffusion coefficient (2-dimensional diffusion) for the adsorbed W atoms ($\mathbf{D_s}$) in terms of jump distance ($\boldsymbol{\alpha}$) and successful jump frequency ($\boldsymbol{\Gamma}$).

(b) Calculate D_s if the mean-square displacement $\boldsymbol{\Delta x^2}$ is $1\text{x}10^{-7}$ cm^2 after annealing for 100 sec.

(9) (a)Estimate the γ for an isotope tracer in a pure diamond where γ is defined by the equation: $D^*=\gamma \boldsymbol{a}^2\omega \mathbf{N}_v$ where $\boldsymbol{a}$ is the lattice constant, ω is the possible jump frequency and $\mathbf{N}_v$ is the concentration of vacancy. Note that the diffusion of tracer is dominated by vacancy mechanism.

(b) Estimate D* at 2500K if diamond has a lattice constant of $3\text{x}10^{-8}$ cm, average vibration frequency of the carbon atom in the lattice is $5\text{x}10^{13}$ $\text{sec}^{-1}(\nu)$, vacancy formation energy (ΔG_v)=400 kJ/mol, and migration activation energy (ΔG_m)=200 kJ/mol.


Diamond Structure

(10) Please estimate the value of

(a) The self diffusion coefficient of solid Ar (FCC) at its melting point

(b) The activation energy for motion by self diffusion of solid Ar (FCC) at its melting point

(c) ^{39}Ar, which is a radiotracer, is doped into solid Ar. Please estimate its diffusion coefficient at the melting point of solid Ar.

(d) A **fluid** Ar is observed at its critical point (T_C=151K). Please estimate the value of the self diffusion coefficient of Ar, assuming a simple cubic lattice which has a lattice constant of $5\text{x}10^{-8}$ cm.

(e) Ne, which forms a substitutional solid solution with Ar, is present as an impurity at a concentration of 1 ppma (part per million on an atomic basis). Please estimate its diffusion coefficient at the melting point of solid Ar.

Data: Gas constant, R=8.314 J/mol K; Boltzmann constant, $k_B=1.38\text{x}10^{-23}$ J/K; Planck constant, $h=6.6\text{x}10^{-34}$ J s.

Successful jump frequency (Γ) = Debye frequency (ν_D) x successful jump rate. The successful jump rate is approximately 10^{-1} for liquids and 10^{-4} for materials near melting point.

Data of Ar and Ne for question (10)

	Ar	**Ne**
Atomic mass (g/mol)	39.95	20.18
Melting point (K)	83.7	24.5
Boiling point (K)	87.4	27.2
Critical temperature (T_C) (K)	151	44.4
Critical pressure (MPa)	4.86	2.65
Critical volume (cm^3/mol)	75.2	41.2
Atomic radius (Solid) (cm)	$1.74\text{x}10^{-8}$	$1.60\text{x}10^{-8}$
Lattice constant (Solid) (cm)	$4.92\text{x}10^{-8}$	$4.53\text{x}10^{-8}$
Density (Solid) (g/cm^3)	1.66	0.839
Enthalpy of sublimation (ΔH_{sub}) (kJ/mol)	7.65	2.08
Entropy of sublimation (ΔS_{sub}) (J/mol)	8.32	8.12

MS301300 Problem Set 7

1. **Interdiffusion experiments were recently performed on the urbium-suurbium (Ub-Su)** binary alloy system. The diffusion couple, which is annealed at 1000K for 3.6×10^5 sec, is formed by a pair of pure single crystals. Markers placed at the original interface were found to move with the concentration front, $N_{Ub}=0.4$, where N represents molar fraction. The concentration gradient here was measured to be $\partial N_{Ub}/\partial x = -20\ \mathrm{cm}^{-1}$.

(a) Calculate the marker displacement. Be careful the direction of marker moving.

(b) Suppose that the marker displacement of part (a) is zero due to pore formation, and the pore volume is calculated to be $0.196\ \mathrm{cm}^3$ on the Ub-rich side. Calculate the cross-sectional area of the Ub-rich side.

Data: The Ub-Su system is sub-regular with the concentration dependence of the activity coefficient given as

$$\ln(\gamma_{Ub}) = -0.75(1-N_{Ub})^2 + 0.01(1-N_{Ub})^3$$

$$\partial \ln(\gamma_{Ub}) / \partial \ln(N_{Ub}) = 1.5\, N_{Ub}(1-N_{Ub}) - 0.03\, N_{Ub}(1-N_{Ub})^2$$

The relevant self diffusion coefficients are

$D_{Ub}^{self} = 2.5 \times 10^{-8}\ \mathrm{cm^2/s}$, $D_{Su}^{self} = 2.0 \times 10^{-8}\ \mathrm{cm^2/s}$.

2. **A Kirkendall-type experiment was performed in the A-B alloy system.** Marker placed at the original interface was found to move with the iso-concentration front of $N_A = 0.45$. After a 1.8×10^5 sec anneal the following data were obtained:

Concentration gradient at $N_A = 0.45$, $\partial N_A / \partial x = 3\ \mathrm{cm}^{-1}$

Self diffusion coefficient of tracer A, $D_A^{self\text{-}*} = 2.0 \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$

Self diffusion coefficient of tracer B, $D_B^{self\text{-}*} = 1.5 \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$

(a) Assume that A and B form a solution, which has $\partial(\ln \gamma_A)/\partial(\ln N_A) = N_A N_B$. Note that γ_A is the activity coefficient of A. **State your assumptions.**

  (i) Calculate the marker displacement relative to the end of A-rich.

  (ii) Calculate the Matano interface displacement relative to the end of A-rich.

  (iii) Calculate the Matano interface displacement relative to the marker.

(b) Suppose now that the marker displacement of part (a) was 1.73×10^{-3} cm due to the presence of porosity (or voids)

  (i) Calculate the volume of porosity at $t = 1.8 \times 10^5$ sec if the diffusion area is $5\ \mathrm{cm}^2$.

  (ii) In which part of the specimen do you expect the pores to form?

3. **A Kirkendall-type experiment was performed in the A-B alloy system.** Marker placed at the original interface was found to move toward the A-rich end with the iso-concentration front, $N_A = 0.35$. After a 100-hour anneal the following data were obtained:

Concentration gradient at $N_A = 0.35$, $\partial N_A / \partial x = 2\ \mathrm{cm}^{-1}$

Marker velocity, $V_M = 3.2 \times 10^{-10}$ cm/sec

Interdiffusion coefficient, $\check{D} = 1.1 \times 10^{-10}\ \mathrm{cm^2\ s^{-1}}$

Molar volume, V_{mol}=12 cm^3/mol

(a) Calculate the intrinsic diffusivities of A (D_A^I) and B (D_B^I).

(b) Calculate the vacancy flux (J_V) across the plane of the marker at t=100 hour.

(c) Qualitatively plot concentrations (C_A, C_B and C_V), fluxes (J_A, J_B and J_V) and change of vacancy concentration ($\partial C_V/\partial t$) as a function of distance.

(d) Be sure to indicate clearly in part (c) where the vacancies need to be created and destroyed, and the voids could form to restore equilibrium at t=3.6x10^5.

(e) Indicate at least one mechanism to create and destroy vacancies in part (d).

(4) Mo wires, which are placed at the interface of Cu/Zn, move with the iso-concentration front of N_{Cu} =0.4. After a 100-hour anneal the following data were obtained: concentration gradient ($\partial N_{Cu=0.4}/\partial X$) on Mo wires= 2.7 cm^{-1}; self diffusion coefficient of tracer Cu, D_{Cu}^{self-*} = 2.0x10^{-8} cm^2 s^{-1}; self diffusion coefficient of tracer Zn, D_{Zn}^{self-*} = 1.5x10^{-8} cm^2 s^{-1}. Assume that Cu and Zn form a solution, which has $ln\, \gamma_{Cu}= -(1-N_{Cu})^2$. Note that γ_{Cu} is the activity coefficient of Cu. State your assumptions.

(i) Calculate the Mo wire displacement relative to the end of Cu side.

(ii) Calculate the Matano interface displacement relative to the Mo wires.

(iii) Suppose now that the Mo wires displacement of part (ii) is zero due to the presence of porosity (or voids), and the volume of porosity at t=100 hr is 1.44x10^{-3} cm^3. Calculate the diffusion area.

(iii) In which part of the specimen do you expect the pores to form?

(5) (a) Describe the definition of self diffusivity (D^S), tracer diffusivity (D^T), intrinsic diffusivity (D^I), and chemical diffusivity (D^C), and experiments that allow each of them to be measured.

(b) Can any of the four diffusivities listed above be negative? Why?

(6) Match column II to column I (multiple choices)

I	II
(A) Ideal solution (1-12 in II)	(1) ΔS_M=0
	(2) ΔS_M^{exe}= $-R(X_A lnX_A+X_B lnX_B)$
	(3) ΔH_M=0
(B) Regular solution (1-12 in II)	(4) $\Delta H_M=\Omega X_A X_B$ and $\Omega \neq 0$
	(5) Ω<0
	(6) Ω>RT/($2X_A X_B$)
(C) Down-hill diffusion (1-12 in II)	(7) Chemical diffusivity ($\tilde{D}$)>0
	(8) Chemical diffusivity($\tilde{D}$)<0
(D) Up-hill diffusion (1-12 in II)	(9) Chemical potential gradient ($\nabla\mu_i$)>0
	(10) Chemical activity gradient (∇a_i)<0

	(11) $\tilde{D} = X_B D_A^* + X_A D_B^*$
	(12) $\tilde{D} = X_B D_A^I + X_A D_B^I$
	(13) Self diffusivity(D^{self})
	(14) Tracer diffusivity(D_i^*)
	(15) Intrinsic diffusivity (D_i^I)
(E) Stationary coordinate (11-20 in II)	(16) $J_i = -D_i^I \nabla C_i$
	(17) $J_i = -\tilde{D} \nabla C_i$
(F) Moving coordinate (11-20 in II)	(18) $J_i = -D_i^I \nabla C_i + V_M C_i$
	(19) $J_i = -\tilde{D}_i \nabla C_i + V_M C_i$
	(20) $V_M = (X_B D_A^I - X_A D_B^I)\frac{\partial X_A}{\partial X}$

* $\Omega = ZN_o \varepsilon = ZN_o[0.5(\varepsilon_{AA} + \varepsilon_{BB}) - \varepsilon_{AB}]$ where Z is the coordination number, No is the total number of atoms, and bonding strength of A-A(ε_{AA}), B-B (ε_{BB}) and A-B(ε_{AB}).
V_M: velocity of marker displacement

(7) The marker is placed at the interface of a diffusion couple of *A/B*. The maker with a concentration of N_A=0.35 and a concentration gradient of 1×10^{2} cm^{-1} moves at a velocity of 3×10^{-9} cm/sec. The chemical diffusivity under these conditions is found to be 1.03×10^{-10} cm^2/sec. Assuming that an ideal solution is formed between A and B.

(a) Determine the values of the intrinsic diffusivity of the components *A* and *B*.
(b) What is the direction of net vacancy flux?
(c) What is the moving direction of lattice flow?
(d) What is the moving direction of marker?
(e) Which side will porosities form?

(8) A diffusion couple was formed in the A-B alloy system at elevated temperatures. Marker placed at the original interface was found to move with the iso-concentration plane of N_A =0.35. The following data were obtained after a 3.6×10^5 sec anneal.

Concentration gradient at N_A = 0.35, $\partial N_A/\partial x$ = 2 cm^{-1}
Intrinsic diffusivity of A (D_A^1) =1.66×10^{-10} cm^2/sec
Intrinsic diffusivity of B (D_B^1) =6×10^{-12}cm^2/sec
Molar volume, V_{mol}=12 cm^3/mol (15%)

(a) Calculate the chemical diffusivity at N_A =0.35.
(b) Calculate the marker displacement relative to the end of A-rich?
(c) Calculate the Matano interface displacement relative to the marker.
(d) Calculate the vacancy flux (J_V) across the marker at t =3.6×10^5 sec.
(e) In which side of the specimen the vacancies need to be created to restore its

thermodynamic equilibrium? Suggest one mechanism at least.

(f) Suppose that the location of marker remains unchanged at the original interface due to pore formation, calculate the pore volume if the cross-sectional area of the specimen is 2 cm^2

MS301300 Problem Set 8

1. **Estimate the maximum supercooling of pure, liquid copper at which nuclei of** solid copper form homogeneously. Note that homogeneous nucleation is observed when the density of nuclei per unit volume (#/cm^3) is measured to be unity.
   DATA: Melting point: 1083°C,
   Surface energy ($\gamma_{S\text{-}L}$) = 200 ergs/cm^2
   Heat of fusion = 3120 cal/mol
   Molar volume for both liquid and solid= 7 cm^3/mol.

2. **The temperature at which nuclei of solid water (ice) form homogeneously from** undercooled water is -40°C.

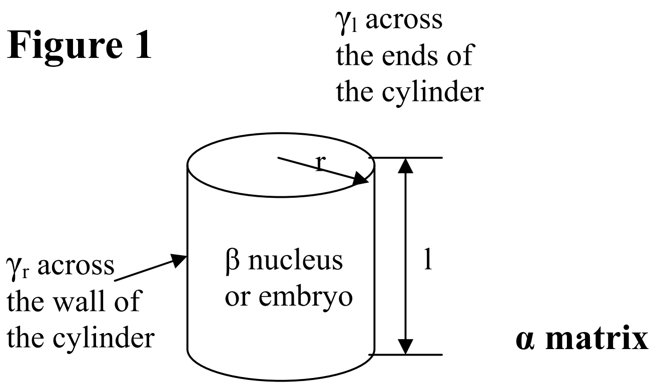
(a) What is the critical radius of the solid water nuclei at this temperature?

(b) Why do ponds freeze when the temperature is just a few degrees below the equilibrium freezing point (0°C)?
   DATA: Surface energy ($\gamma_{S\text{-}L}$) = 25 ergs/cm^2
   Heat of fusion = 335 J/g
   Density of Ice=0.92 g/cm^3

(3) **(a) Pure metal, M, undergoes a transformation from α-solid to β-solid by** nucleation of rod-shapes precipitates which can be modeled as cylinders. In this system embryos and nuclei from only with an aspect ratio (radius/length) with minimizes surface energy. As shown in Figure 1, this last property is anisotropic. Calculate the size of the critical nucleus for an undercooling of 50 K.

Data: Equilibrium transition temperature, T_e=400 K
Enthalpy of transition (α-β), ΔH_{tr}=1.25x10^8 J/m^3
Axial solid-solid surface energy, γ_l=0.2 J/m^2
Radial solid-solid surface energy, γ_r=0.1 J/m^2

Figure 1



(b) **Pure metal, M, undergoes a transformation from α-solid to β-solid by** nucleation of spherical precipitates which changes the strain energy of the system. To a first approximation in this case the strain energy is proportional to the volume of the precipitate. Estimate the nucleation rate, I, for an undercooling of 50 K.

Data: Equilibrium transition temperature, T_e=400 K
Enthalpy of transition (α-β), $\Delta H_{tr}=5x10^9$ J/m^3
Solid-solid surface energy, $\gamma_{\alpha\beta}=0.15$ J/m^2
Solid-solid strain energy, $E_{\alpha\beta}=2.25x10^8$J/m^3

4. The rate of nucleation of solid tin from its liquid has been determined at various temperatures below the melting point by rapidly supercooling a large number (10^{10}) of small tin droplets, separated by an oxide film, and measuring the change in volume of the sample as a function of time. Using "bulk" values of the free energy of transformation, ΔG_v, the investigators were able to show the theory of homogeneous nucleation agreed well with their work and that assumptions of a spherical nucleus and the applicability of the bulk value of the surface energy γ to nucleus formation were correct to within the accuracy of their experiments.

Calculate the values of the following quantities at 113^{o}C:
- (c) The liquid-solid surface energy for tin;
- (d) The critical radius for the nucleation of solid tin;
- (e) The number of tin atoms in a nucleus of critical size.

Data
(1) Accounting for the temperature dependence of ΔG_v,, the slope of ln(I) versus 1/T at 113^{o}C is -23.8x10^3 K for any constant fraction of liquid transformed.
(2) ΔG_v,= -10^8 J/m^3 at 113^{o}C
(3) Radius of tin atom, r =1.5x10^{-10} m

5. For pure, liquid Ni to solidify by homogeneous nucleation.
(i) At its melting point (T_m = 1725 K), what is **(a)** the Gibbs free energy of formation (ΔG_r), **(b)** the number (n_r) of a spherical crystalline cluster of solid (a nucleus of solid) of radius 7x10^{-10} m?
(ii) At T=1715 K ($\Delta T_m=10$ *K*), what is **(a)** the critical nuclei size (r^*), and **(b)** the critical activation energy of nucleation (ΔG^*)? **(c)** Will the nucleation take place?
(iii) To observe homogeneous nucleation, what is the required undercooling (ΔT_m)?
Note that the homogeneous nucleation mechanism is assumed to take place when the concentration of nuclei formed is above one per cubic centimeter ($n_r \geq 1$/cm^3).
Data: For pure Ni:Melting point (T_m) = 1725 K; Surface energy (γ) = 0.25 J/m^2 Molar volume ($\underline{V}$) = 7 cm^3/mol = 7x10^{-6} m^3/mol; Latent heat of fusion (ΔH_m) = 17250 J/mol; Gibbs free energy change per unit volume during solidification (ΔG_v) = $\Delta H_m \Delta T_m/(\underline{V}\, T_m)$; Number of particles with atomic radius in the liquid (n_o)=6x10^{23}/$\underline{V}$ = 8.6x10^{22} cm^{-3}; Number of solid particles with cluster radius (r) in the liquid (n_r) =

$n_o\exp(-\Delta G_r/RT)$ where ΔG_r is the formation energy of cluster with a size of r; $R=1.38\text{x}10^{-23}$ J/atom-K.

6. One conducted nucleation experiments using mercury, which can be purified by distillation. The results of the experiment are shown schematically in Fig. 1. For large droplets, the undercooling that could be observed was small. Very small droplet could be undercooled to about $0.8T_M$. The transition occurred for a droplet diameter of about 60 μm. This experiment has been repeated hundreds of times by many researchers using a variety of materials. The maximum undercooling is usually about $0.8T_M$ where T_M is the melting point of the material studied. Moreover, it was also found that the observed melting points follow the results shown in Fig. 2, where Au is used as an example. Please explain the results in Figs. 1 and 2 based upon the nucleation theories you have learned.

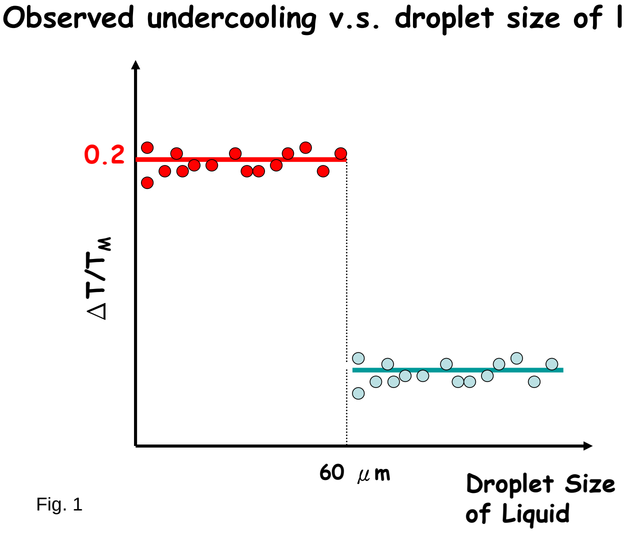

Observed undercooling v.s. droplet size of liquid

Fig. 1

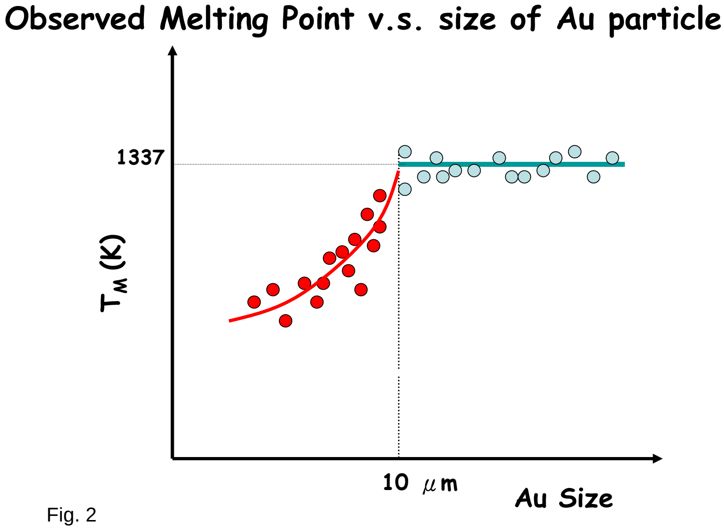

Observed Melting Point v.s. size of Au particle

Fig. 2

MS301300 Problem Set 9

1 To relieve the cold-worked strain generated at room temperature, the pure gold has to be annealed at 717 K. New strain-free gold grains nucleate and grow under the above conditions. The driving force for this transformation, which is known as recrystallization, is the reduction in strain energy left in the sample by cold working. Nucleation mechanism can be either homogeneous or heterogeneous. There are 10^{19} m^{-3} randomly distributed sites that function as heterogeneous nuclei. Normal growth occurs.

(a) Calculate the time to achieve 99% recrystallization. State your assumptions and justify them where the data permit. Note that the critical free energy required (ΔG^*) for homogeneous nucleation is in the range of 60-70 kT for a spherical nuclei, where k_B=1.38x10^{-23} J/K = 8.314 J/mol K. Moreover, the total free energy change (ΔG_{total}) for the transformation should include free energy change ($V\Delta G_V$), surface energy ($A\gamma$) and strain energy ($V\Delta G_e$), where V is the volume and A is the area of new strain-free grains

(b) Sketch the temperature dependence of the growth rate, U, over the temperature range spanning from room temperature to the melting point. Justify with reference to relevant equations.

(c) At 99% recrystallization, what do you estimate the average grain size to be?

Data: Strain energy of cold work, ΔG_e=1.7x10^6 J m^{-3}=17.35 J mol^{-1}

Interfacial energy between transformed and untransformed grains, γ=0.17 J m^{-2}
Melting point of gold, T_m=1336 K
Atomic weight of gold, M=196.97 g mol^{-1}
Density of gold, ρ=19.3 g cm^{-3}
Molar volume of gold, V_M=10.2x10^{-6} m^3 mol^{-1}
Lattice constant of gold, a=4.08x10^{-10} m
Diffusion coefficient of gold across the grain boundary between transformed and untransformed grains, D=10^{-10} m^2s^{-1}.

2. Co melt solidifies by cooling below its melting point. Please answer the following questions:

(a) What is the Gibbs free energy of formation of a spherical crystalline cluster of solid with a radius of 7x10^{-10} m at its melting point? Assuming the nucleation is dominated to be homogeneous.

(b) Repeat the calculation of part (a) except that the nucleation takes place primarily on the surface of CoO particles, which are uniformly dispersed in the melt. Note that the cluster size has an equivalent radius of 7x10^{-10} m and a contact angle to CoO is 90°. The concentration of CoO particles is 8.6x$10^{10}$$cm^{-3}$, and assuming that each CoO particle forms one cluster of solid Co only.

(c) Calculate the concentration of such nucleus (7x10^{-10} m) at its melting point for the parts (a) and (b).

(d) Calculate the critical cluster size for nucleation at the undercooling ($\Delta T=T-T_m$) of 400K for the parts (a) and (b).

(e) Determine the dominant nucleation mechanism at $\Delta T = 400K$ quantitatively.

(f) Calculate the undercooling ($\Delta T = T - T_m$) needed to form detectable number of nuclei, i.e., one cluster/cm^3, for the parts (a) and (b).

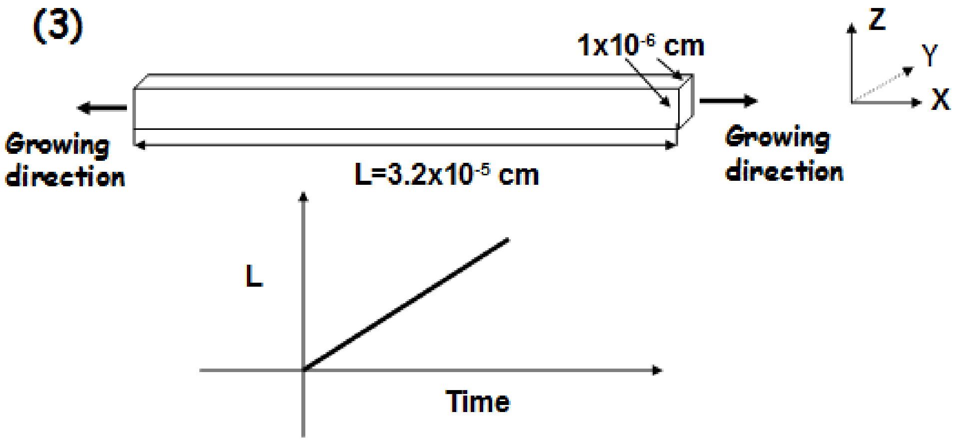
Data: Co: Melting point: 1725K, Latent heat of melting: 17250 J/mol,
Surface energy: 0.25 J/m^2, Molar volume: 7×10^{-6} m^3/mol.
R: 1.38×10^{-23} J/atom-K. N_A: 6×10^{23} molecule/mol.

$$\Delta G^*_{het} = \Delta G^*_{hom}\left(\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right)$$ where θ is the contact angle.

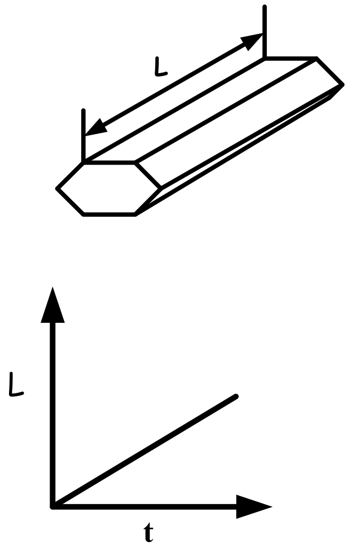
3. **A pure, amorphous metal crystallizes when annealed at 800 K. The** crystallization kinetics can be described by a general equation of $\boldsymbol{x = 1 - \exp(-kt^n)}$ where ***x*** is the degree of transformation. The crystals exhibit a shape of fine filament with a dimension shown below. Experimental results show that spherical nuclei are formed by homogeneous nucleation, and the length of fine filament crystals follows a growth kinetics shown in a figure below.
   - **(a)** Suggest a growth mechanism in the X- and Z-direction of fine filament which is consistent with the experimental results.
   - **(b)** Estimate the growth rate in the X-direction under these conditions. Assuming ***x***=0.99 to represent total transformation and little growth in the Y-and Z-directions.

Data: Enthalpy of transformation $\Delta H = -0.5RT_e$ where R= 8.314 J/mol-K.
Equilibrium transformation temperature, T_e= 950 K
Molar volume of metal, $V_m = 11 \times 10^{-6}$ m^3/mol
Interfacial energy, $\gamma = 0.04$ J/m^2
Pre-exponential factor for nucleation rate, $ND/a^2 = 10^{28}$ $cm^{-3}sec^{-1}$.
k (Boltzmann constant): 1.38×10^{-23} J/atom-K.

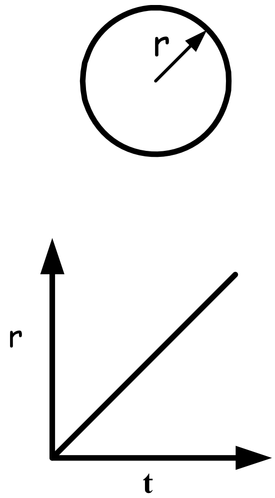
(3)



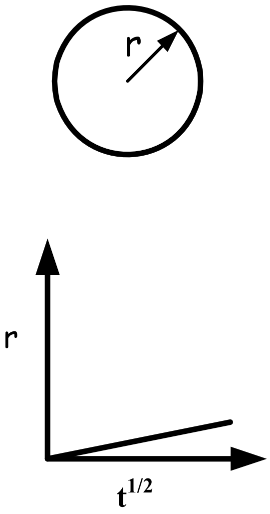
(4) (a) Various solid oxide inclusions nucleate and grow in a steel melt that is being held at constant temperature in a crucible. The growth kinetics and the shape of the inclusion for three different metal oxide species are illustrated in the sketches below. For each example suggest a growth mechanism which would be consistent with the observations. Justify.



(A)



(B)



(C)

(b) The transformation kinetics in the baking of pizza can be modeled by an Avrami-type equation. At very short times the transformation data indicate that $\frac{dX}{dt} = 4.2\times10^{-3} t^{1.5}\ \text{min}^{-1}$, where X represents the fraction transformed. How long will it take to bake the pizza to 95% of completion?

(c) Suppose the same process in part (b) is used in the baking of cupcakes. Estimate the value of n, the exponent of the time variable in the Avrami equation ($X=1-\exp(-kt^n)$).

Justify. 

(5) The homogeneous nucleation of Cu can be undercooled to a temperature where ΔG_C=30 kT, the exponential term in the nucleation equation.

(a) Estimate the value of the liquid-solid interfacial energy.

(b) Calculate the radius of the critical-sized nucleus of solid copper at 280 K below the melting point.

(c) Estimate the nucleation rate per unit volume of solid copper at 280 K below the melting point.

(6) A concentration of 10^{10} cm^{-3} CuO particles is added into Cu melt, and the nucleation of solid Cu takes place on the surface of CuO particles. Each CuO particle forms one cluster of solid Cu only, and the cluster has a contact angle of 60^o to CuO. Determine the dominant nucleation mechanism of solid copper at 280 K below the melting point.

Data: Melting point =1356K
Entropy of fusion = 10^8 erg/(mol K)
Specific volume = 7 cm^3/mol
Maximum observed undercooling = 280 K
k=1.38x10^{-16} ergs/(mol K)
Diffusivity of liquid Cu (D) ≈10^{-5} cm^2/sec
Jump distance of liquid Cu (a) ≈10^{-8} cm

$\Delta G^*_{het} = \Delta G^*_{\hom}(\frac{2-3\cos\theta+\cos^3\theta}{4})$ where θ is the contact angle.

${}^{V}I \approx \frac{ND}{a^2}\exp(-\frac{\Delta G_c}{kT})$ where N is the number of atoms per unit volume.

MS301300 Problem Set 10

1. **For materials in which the liquid is relatively viscous and the temperature** dependence of the rate of crystal growth, U, from a melt of pure material often has a shape similar to that of GeO_2 in Figure 1 (see next page).
   (a) Explain the shape of the curve in Figure 1.
   (b) For many liquids the viscosity, η, is strongly temperature dependent. On the basis of the additional information in Figure 2, and the Stokes-Einstein equation, state what you believe to be the probable mechanism controlling the rate of growth.

   Figures 3 and 4 show relevant information for the crystallization rate of tri-α-naphthylbenzene (TαNB), a non-polymeric organic which can easily be quenched to form a glass.
   (c) Is the growth mechanism the same for GeO_2 and TαNB? Which simple mechanisms can describe the observed growth rate of each?
   (d) What can you say about the nature of the solid-liquid interface for each material?

   DATA： GeO_2 $T_E = 1115^oC$； $\Delta H_f = 1.3\ RT_E$
   TαNB $T_E = 119^oC$； $\Delta H_f = 10.7\ RT_E$

(2) The system A-B exhibits regular solution behavior in the solid state. Answer parts (a) through (e), each when n, the linear strain per unit composition difference, is equal to (i) 0 and (ii) 0.06.

(a) Calculate the consolute temperature for solid miscibility.
(b) What is the temperature of the spinodal for the solutions of composition $X_A = 0.25$ and $X_A = 0.40$?
(c) What is the critical wavelength at T = 775 K for the two solutions of part (b)?
(d) What is the fastest growing wavelength at T = 775 K anywhere in the A-B system?
(e) What is the maximum value of the amplification factor, $R(\beta)$, at T = 775 K anywhere in the A-B system?

<u>DATA</u>:
regular solution interaction parameter, $\Omega = 15$ KJ mol^{-1}
gradient energy coefficient, $K = 10^{-9}$ J m^{-1}
Young's modulus, $E = 10^{11}$Pa
Poisson's ratio, $\nu = 0.3$
self-diffusion coefficient, $D_A^* = D_B^* = 10^{-3}\exp(-100\ KJ/RT)\ m^2s^{-1}$
atomic masses, $M_A = 195$ g mol^{-1}; $M_B = 197$ g mol^{-1}
densities, $\rho_A = 21.5$ g cm^{-3}; $\rho_B = 19.3$ g cm^{-3}

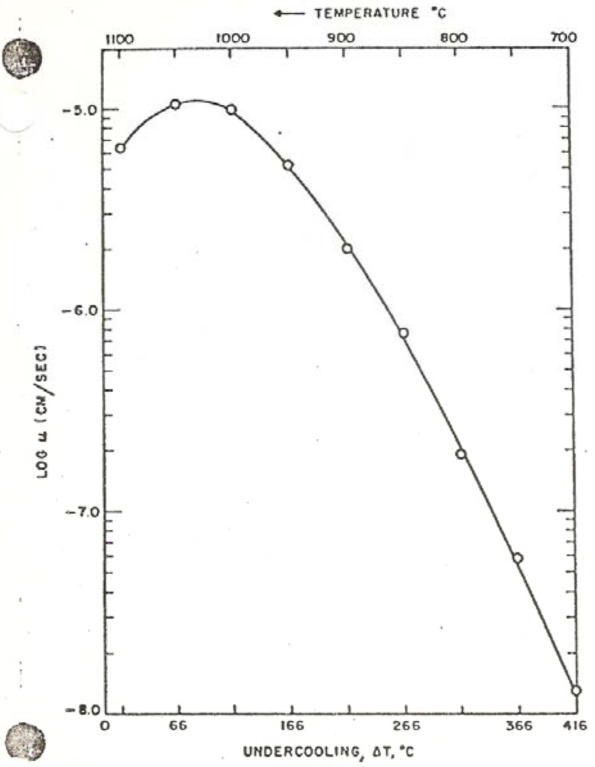


FIGURE 1
Growth rate versus temperature relation
for GeO_2.

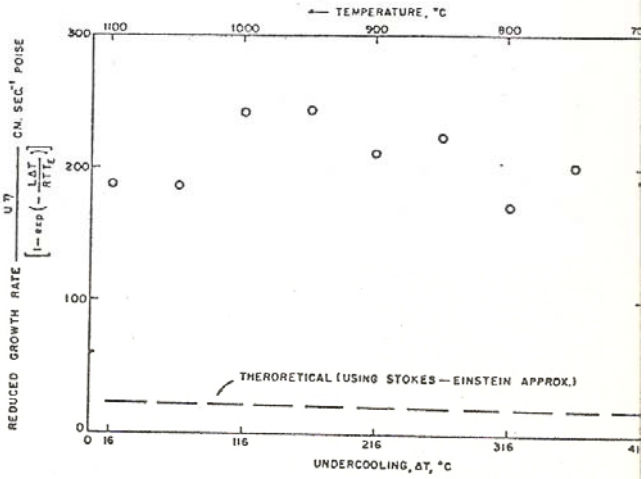


FIGURE 2
Reduced growth rate versus undercooling
relation for GeO_2.

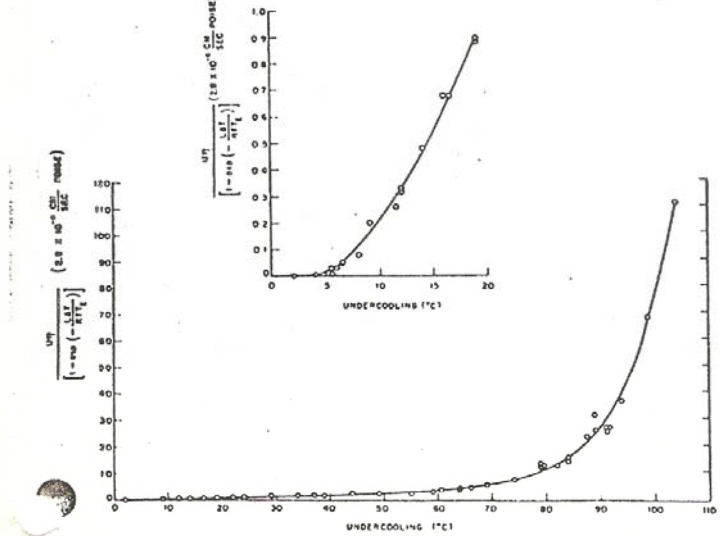


FIGURE 3
Reduced growth rate versus undercooling
relation for tri-α-naphthylbenzene.

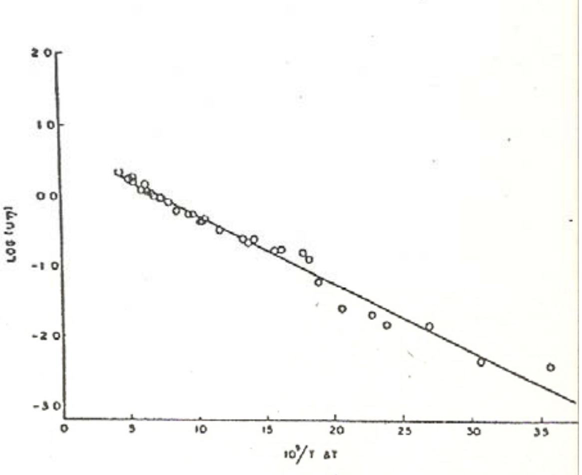


FIGURE 4
Logarithm of (growth rate × viscosity)
versus 1/TΔT for tri-α-naphthylbenzene.

3. It is known that the alloy of Gx-My forms a special microstructure by spinodal decomposition.

(a) The alloy with a characteristic compositional periodicity of 8.0 nm is made by first forming a homogeneous solid solution at an elevated temperature and then cooling to 773K for spinodal decomposition. What must the composition of the alloy be?

(b) For the process described in part (a) estimate a reasonable processing time. Clearly state your criteria and show your calculations.

Data: Gx-My is a regular solution and the free energy of mixing is

$\Delta G = \Omega C(1\text{-}C) + RT\,[C \ln(C) + (1\text{-}C)\ln(1\text{-}C)]$

At 773K in the Gx-My system the miscibility gap extends from 10 mol% to 90 mol% and the spinodal spans the interval 25 mol% to 75 mol%.

The diffusion equation for the spinodal decomposition is

$$\frac{\partial C}{\partial t} = -\frac{M}{Nv}\left(\frac{\Delta G''}{V_m}\frac{\partial^2 C}{\partial x^2} - 2K\frac{\partial^4 C}{\partial x^4}\right)$$

and the amplification factor (R(β) is

$$R(\beta) = -\frac{M}{N_V}\left[\left(\frac{\Delta G''}{V_m}\right)\beta^2 + 2K\beta^4\right]$$

where $M/N_v = 10^{-18}\exp(-Q/RT)\ m^5/J\ s$, $Q = 1.5\times10^5$ J/mol,

M: mobility, and N_V: molar fraction;

regular solution interaction parameter, $\Omega = 1.71\times10^4$ J/mol

molar volume of Gx-My solutions, $V_m=2.1\times10^{-5}\ m^3/mol$

gradient energy coefficient, $K = 3.21\times10^{-11}$ J/m

$\beta=2\pi/\lambda$ where λ is the wavelength of the compositional fluctuation,

R: 8.31 J/mol K.