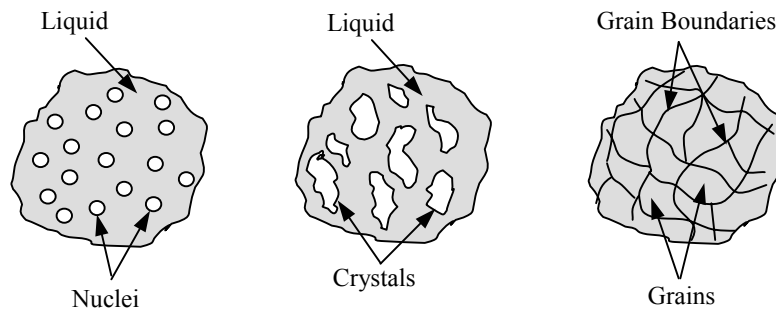


- 4.1 Describe and illustrate the solidification process of a pure metal in terms of the nucleation and growth of crystals.

In general, the solidification of a pure metal involves: the formation of stable nuclei in the liquid melt; the growth of these nuclei into stable nuclei in the liquid melt; and the formation of a solidified structure containing grains formed from the crystals. These three stages are illustrated below.

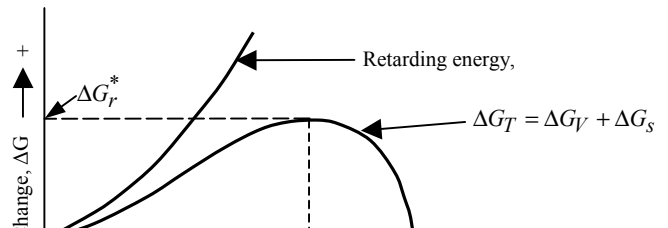


- 4.2 Define the homogeneous nucleation process for the solidification of a pure metal.

In a homogeneous nucleation process, the liquid metal is sufficiently undercooled and thus able to provide the atoms to form nuclei.

- 4.3 In the solidification of a pure metal, what are the two energies involved in the transformation? Write the equation for the total free-energy change involved in the transformation of liquid to produce a strain-free solid nucleus by homogeneous nucleation. Also illustrate graphically the energy changes associated with formation of a nucleus during solidification.

The two energies involved in the solidification of a pure metal are surface free energy and volume free energy. These energies contribute to the total free energy,  $\Delta G_T$ :



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- 4.4 In the solidification of a metal, what is the difference between an embryo and a nucleus? What is the critical radius of a solidifying particle?

An embryo refers to a solidified cluster of atoms which is unstable and can thus redissolve. A nucleus is a comparatively larger stable cluster which can grow into a crystal. The dimension defining the boundary between an embryo and a nucleus is the critical radius.

- 4.5 During solidification, how does the degree of undercooling affect the critical nucleus size? Assume homogeneous nucleation.

In general, the greater the degree of undercooling of a liquid melt, the smaller the critical radius of the nuclei formed.

- 4.6 Distinguish between homogeneous and heterogeneous nucleation for the solidification of a pure metal.

In homogeneous nucleation of a liquid metal, the nuclei are formed from atoms of the metal solidifying. In heterogeneous nucleation, impurity atoms or container surfaces act as nucleating agents.

- 4.7 Calculate the size (radius) of the critically sized nucleus for pure platinum when homogeneous nucleation takes place.  
The critical radius of nucleus is calculated as,

$$r^* = \frac{-2\gamma T_m}{\Delta H_f \Delta T}$$

where  $\gamma = 240 \times 10^{-7} \text{ J/cm}^2$ ,  $\Delta H_f = -2160 \text{ J/cm}^3$ ,  $T_m = 2045 \text{ K}$   
and the undercooling  $\Delta T = 0.2T_m = 0.2(2045 \text{ K}) = 409 \text{ K}$ . Substituting,

$$r^* = \frac{-2(240 \times 10^{-7} \text{ J/cm}^2)(2045 \text{ K})}{(-2160 \text{ J/cm}^3)(409 \text{ K})} = 1.11 \times 10^{-7} \text{ cm}$$

- 4.8 Calculate the number of atoms in a critically sized nucleus for the homogeneous nucleation of pure platinum.

The number of atoms in a critically sized nucleus is found as,

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$$\text{Vol. of critical-sized nucleus} = \frac{4}{3}\pi r^*{}^3 = \frac{4}{3}\pi(1.11 \times 10^{-7} \text{ cm})^3 = 5.73 \times 10^{-21} \text{ cm}^3$$

$$\text{Vol. of unit cell of Pt} = a^3 = (0.32939 \times 10^{-9} \text{ m})^3 = 3.574 \times 10^{-29} \text{ m}^3 = 3.574 \times 10^{-23} \text{ cm}^3$$

$$\text{Vol. per atom} = \frac{3.574 \times 10^{-23} \text{ cm}^3}{4 \text{ atoms/FCC unit cell}} = 8.935 \times 10^{-24} \text{ cm}^3/\text{atom}$$

Substituting,

$$\frac{\text{Volume of nucleus}}{\text{Volume per atom}} = \frac{5.73 \times 10^{-21} \text{ cm}^3}{8.935 \times 10^{-24} \text{ cm}^3/\text{atom}} = \mathbf{641 \text{ atoms}}$$

- 4.9 Calculate the size (radius) of the critical nucleus for pure iron when nucleation takes place homogeneously.

For iron,  $\gamma = 204 \times 10^{-7} \text{ J/cm}^2$ ,  $\Delta H_f = -2098 \text{ J/cm}^3$ ,  $T_m = 1808 \text{ K}$

The amount of undercooling is then  $\Delta T = 0.2T_m = 0.2(1808 \text{ K}) = 361.6 \text{ K}$  and the critical radius becomes,

$$r^* = \frac{-2\gamma T_m}{\Delta H_f \Delta T} = \frac{-2(204 \times 10^{-7} \text{ J/cm}^2)(1808 \text{ K})}{(-2098 \text{ J/cm}^3)(361.6 \text{ K})} = \mathbf{9.72 \times 10^{-8} \text{ cm}}$$

- 4.10 Calculate the number of atoms in a critically sized nucleus for the homogeneous nucleation of pure iron.

The relevant volumes, based on the solution of Problem 4.9, are:

$$\text{Vol. of critical-sized nucleus} = \frac{4}{3}\pi r^*{}^3 = \frac{4}{3}\pi(9.72 \times 10^{-8} \text{ cm})^3 = 3.85 \times 10^{-21} \text{ cm}^3$$

$$\text{Vol. of unit cell of Pt} = a^3 = (0.28664 \times 10^{-9} \text{ m})^3 = 2.355 \times 10^{-29} \text{ m}^3 = 2.355 \times 10^{-23} \text{ cm}^3$$

$$\text{Vol. per atom} = \frac{2.355 \times 10^{-23} \text{ cm}^3}{2 \text{ atoms/BCC unit cell}} = 1.178 \times 10^{-23} \text{ cm}^3/\text{atom}$$

Thus, the number of atoms in a critically sized nucleus is:

$$\text{Volume of nucleus} \quad 3.85 \times 10^{-21} \text{ cm}^3$$

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cooling occurs during solidification. Elongated columnar grains are formed in the metal ingot interior, in the direction of thermal gradients, due to slow cooling of the metal in the mold interior.

- 4.12 Distinguish between equiaxed and columnar grains in a solidified metal structure.

Equiaxed grain dimensions are approximately equal in all directions whereas columnar grains are elongated in a particular direction.

- 4.13 How can the grain size of a cast ingot be refined? How is grain refining accomplished industrially for aluminum alloy ingots?

The grain size of a cast ingot can be refined by: solidifying the metal at a rapid rate; and adding grain refining agents (heterogeneous nucleating agents). Grain refining of aluminum ingots is accomplished through chill casting and by adding grain refining agents such as titanium and/or boron.

- 4.14 What special techniques must used to produce single crystals?

Single crystals can be produced by introducing a single crystal as a seed crystal. The seed continuously rotates as it is slowly lowered and then withdrawn from the melt.

- 4.15 How are large silicon single crystals for the semiconductor industry produced?

Large single crystals of silicon are produced using a pure silicon seed crystal with a pure silicon melt (Czochralski process).

- 4.16 What is a metal alloy? What is a solid solution?

A metal alloy is a mixture of two or more metals or of a metal (metals) and a non-metal (nonmetals). A solid solution is a type of alloy which is solid and consists of two or more elements atomically dispersed in a single phase structure.

- 4.17 Distinguish between a substitutional solid solution and an interstitial solid solution.

A substitutional solid solution is one in which the solute atoms of the elements replace those of the solvent atoms in the crystal lattice. An interstitial solid solution is one in which the solute atoms of the elements are positioned in the interstitial spaces between the solvent atoms of the crystal lattice.

The logo for Cartagena99 features the text 'Cartagena99' in a stylized, blue, serif font. The '99' is significantly larger and more prominent than the 'Cartagena' part. The text is set against a light blue background with a subtle gradient and a soft shadow effect.

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2. identical valence of the elements;
3. similar electronegativities;
4. common crystal structure of the elements.

4.19 Using the data in the following table, predict the relative degree of solid solubility of the following elements in aluminum:

- (a) copper                      (c) magnesium              (e) silicon  
 (b) manganese              (d) zinc

Use the scale very high, 70–100%; high, 30–70%; moderate, 10–30%; low, 1–10%; and very low, < 1%.

Element	Atom Radius (nm)	Crystal Structure	Electro-negativity	Valence
Aluminum	0.143	FCC	1.5	+3
Copper	0.128	FCC	1.8	+2
Manganese	0.112	Cubic	1.6	+2, +3, +6, +7
Magnesium	0.160	HCP	1.3	+2
Zinc	0.133	HCP	1.7	+2
Silicon	0.117	Diamond Cubic	1.8	+4

- (a) **low**      (b) **very low**      (c) **moderate**      (d) **high**      (e) **low**

4.20 Using the data in the following table, predict the relative degree of atomic solid solubility of the following elements in iron:

- (a) nickel                      (c) molybdenum              (e) manganese  
 (b) chromium              (d) titanium

Use the scale very high, 70–100%; high, 30–70%; moderate, 10–30%; low, 1–10%; and very low, < 1%.

Element	Atom Radius (nm)	Crystal Structure	Electro-negativity	Valence
Iron	0.124	BCC	1.7	+2, +3
Nickel	0.125	FCC	1.8	+2

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- 4.21 Calculate the radius of the largest interstitial void in the BCC  $\alpha$  iron lattice. The atomic radius of the iron atom in this lattice is 0.124 nm, and the largest interstitial voids occur at the  $(\frac{1}{4}, \frac{1}{2}, 0)$ ;  $(\frac{1}{2}, \frac{3}{4}, 0)$ ;  $(\frac{3}{4}, \frac{1}{2}, 0)$ ;  $(\frac{1}{2}, \frac{1}{4}, 0)$ , etc., type positions.

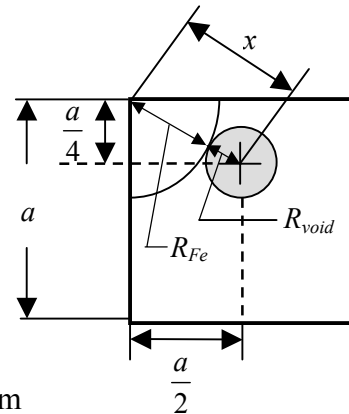
For BCC crystal structure,

$$a = \frac{4R}{\sqrt{3}} = \frac{4(0.124 \text{ nm})}{\sqrt{3}} = 0.286 \text{ nm}$$

Letting  $x = \text{Fe atom radius} + \text{Interstitial void radius}$ ,

$$x^2 = \frac{1}{16}a^2 + \frac{1}{4}a^2 = \frac{5}{16}a^2$$

$$x = \sqrt{\frac{5}{16}}a = 0.559a = (0.559)(0.286 \text{ nm}) = 0.160 \text{ nm}$$



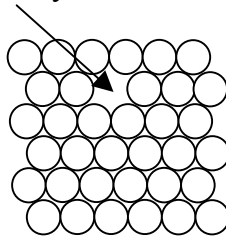
The interstitial void radius is thus,

$$R_{\text{void}} = x - R_{\text{Fe}} = 0.160 \text{ nm} - 0.124 \text{ nm} = \mathbf{0.036 \text{ nm}}$$

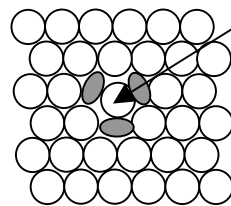
- 4.22 Describe and illustrate the following types of point imperfections that can be present in metal lattices: (a) vacancy, (b) divacancy, and (c) interstitialcy.

- A vacancy, a point defect, is an atomic site which is missing an atom.
- A divacancy is a defect in a crystal lattice where two atoms are missing from adjoining atomic sites.
- An interstitialcy is a point defect where an atom occupies an interstitial site between surrounding atoms in normal sites.

Vacancy



Interstitialcy



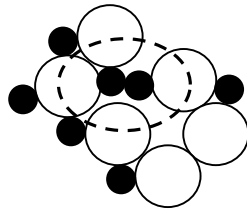
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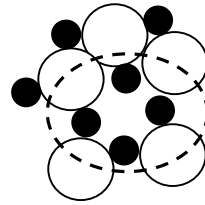
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b) A Schottky imperfection is a cation-anion divacancy which sometimes occurs in ionic crystals.



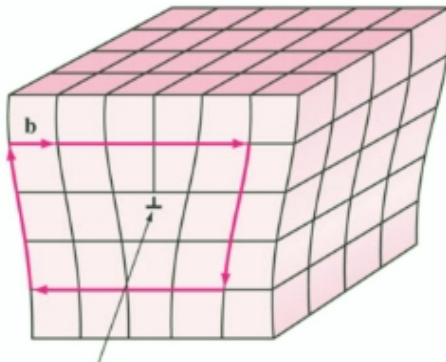
Frenkel Imperfection



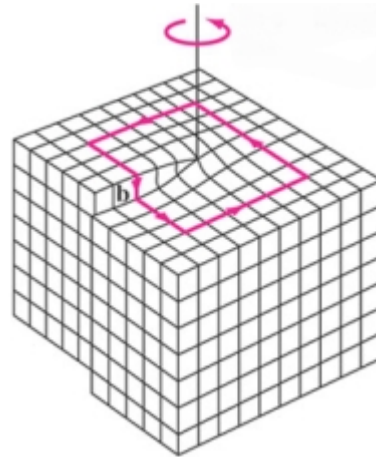
Schottky Imperfection

4.24 Describe and illustrate the edge- and screw-type dislocations. What type of strain fields surround both types of dislocations?

An edge dislocation is a line imperfection caused by an extra half plane of atoms between two normal planes of atoms. Whereas a screw dislocation is a line imperfection created by applying upward and downward shear stress to regions of a perfect crystal separated by a common plane.



Dislocation Line



Screw Dislocation

The strain fields associated with the edge and screw dislocations are shown below:

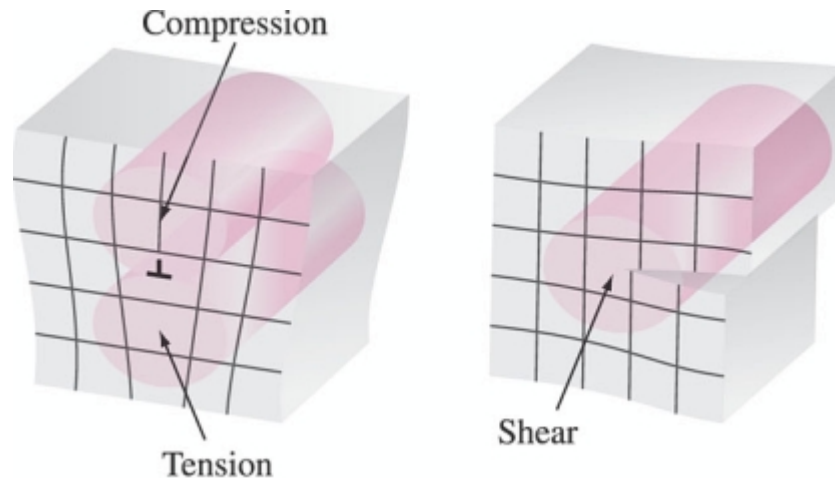
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- 4.25 Describe the structure of a grain boundary. Why are grain boundaries favorable sites for the nucleation and growth of precipitates?

Grain boundaries are surface imperfections that separate grains of different orientations. The grain boundary, a narrow region between two grains, is approximately two to five atomic diameters in width and contains mismatched atoms from adjacent grains. Grain boundaries are favorable sites for the nucleation and growth of precipitates because the irregular atom arrangement at grain boundaries provides lower atomic packing and high energy. Atoms are thus able to diffuse more rapidly to form precipitates.

- 4.26 Why are grain boundaries easily observed in the optical microscope?

Grain boundaries can be easily observed under an optical microscope because they etch more rapidly than grains. Chemical etching thus produces tiny grooves along grain boundaries which appear as dark lines under an optical microscope because they reflect light less intensely.

- 4.27 How is the grain size of polycrystalline materials measured by the ASTM method?

In the ASTM method of measuring grain size of polycrystalline materials, the grain size number,  $n$ , is defined by the equation  $N = 2^{n-1}$ , where  $N$  is the number of grains per square inch, measured on a polished and etched surface at a magnification of 100x.

- 4.28 If there are 600 grains per square inch on a photomicrograph of a metal at 100x, what is its ASTM grain-size number?

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- 4.29 If there are 400 grains per square inch on a photomicrograph of a ceramic material at 200x, what is its ASTM grain-size number?

$$N = 1600 = 2^{n-1}$$

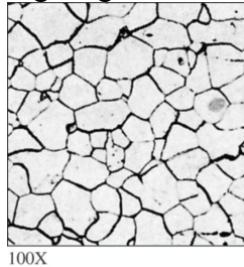
$$\ln 1600 = (n-1)(\ln 2)$$

$$7.378 = (n-1)(0.693)$$

$$n = 10.64 + 1 = \mathbf{11.64}$$

- 4.30 Determine, by counting, the ASTM grain-size number of the low-carbon sheet steel shown in Fig. P4.30. This micrograph is at 100x.

Estimating 40 grains/in<sup>2</sup> from the micrograph,



$$N = 40 = 2^{n-1}$$

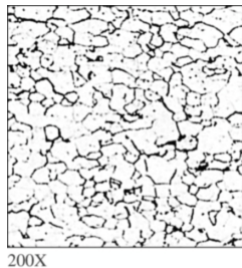
$$\ln 40 = (n-1)(\ln 2)$$

$$3.689 = (n-1)(0.693)$$

$$n = 5.3 + 1 = \mathbf{6.3}$$

- 4.31 Determine the ASTM grain-size number of the type 430 stainless steel micrograph shown in Fig. P4.31. This micrograph is at 200x.

Estimating 100 grains/in<sup>2</sup> from the micrograph,



$$\text{No. of grains at } 100\times = \frac{200^2}{100^2} (100)$$

$$= 400 \text{ grains/in}^2$$

$$N = 400 = 2^{n-1}$$

$$\ln 400 = (n-1)(\ln 2)$$

$$5.99 = (n-1)(0.693)$$

$$n = 8.64 + 1 = \mathbf{9.64}$$

- 4.32 What is a thermally activated process? What is the activation energy for such a process?

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$$n_v = N C e^{-E_v/kT}$$

- where  $n_v$  = number of vacancies per cubic meter of metal  
 $N$  = total number of atom sites per cubic meter of metal  
 $E_v$  = activation energy to form a vacancy (eV)  
 $T$  = absolute temperature (K)  
 $k$  = Boltzmann's constant =  $8.62 \times 10^{-6}$  eV/K  
 $C$  = constant

- 4.34 (a) Calculate the equilibrium concentration of vacancies per cubic meter in pure copper at 850°C. Assume that the energy of formation of a vacancy in pure copper is 1.00 eV.  
 (b) What is the vacancy fraction at 800°C?

- a) In general, the equilibrium number of vacancies is  $n_v = N C e^{-E_v/kT}$ . For copper,

$$N = \frac{N_o \rho_{Cu}}{\text{at. mass Cu}} = \frac{(6.02 \times 10^{23} \text{ atoms/at. mass})(8.96 \times 10^6 \text{ g/m}^3)}{(63.54 \text{ g/at. mass})} = 8.49 \times 10^{28} \text{ atoms/m}^3$$

Substituting and assuming  $E_v = 1.00$  eV at 1123 K,

$$n_v = (8.49 \times 10^{28} \text{ atoms/m}^3) \left\{ \exp \left[ -\frac{1.00 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(1123 \text{ K})} \right] \right\}$$

$$= 2.77 \times 10^{24} \text{ vacancies/m}^3$$

- b) The vacancy fraction at 1073 K is,

$$\frac{n_v}{N} = \exp \left[ \frac{-1.00 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(1073 \text{ K})} \right] = e^{-10.81} = 2.02 \times 10^{-5} \text{ vacancies/atom}$$

- 4.35 (a) Calculate the equilibrium concentration of vacancies per cubic meter in pure silver at 750°C. Assume that the energy of formation of a vacancy in pure silver is 1.10 eV. (b) What is the vacancy fraction at 700°C?

- a) The equilibrium number of vacancies is calculated as  $n_v = N C e^{-E_v/kT}$ . Thus for silver.



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$$n_v = (5.86 \times 10^{28} \text{ atoms/m}^3) \left\{ \exp \left[ -\frac{1.10 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(1023 \text{ K})} \right] \right\}$$

$$= 2.24 \times 10^{23} \text{ vacancies/m}^3$$

b) The vacancy fraction at 973 K is,

$$\frac{n_v}{N} = \exp \left[ \frac{-1.10 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(973 \text{ K})} \right] = e^{-13.12} = 2.01 \times 10^{-6} \text{ vacancies/atom}$$

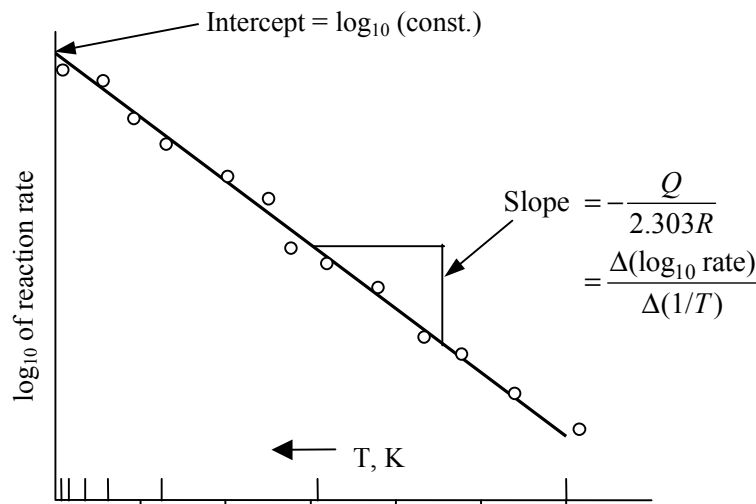
4.36 Write the Arrhenius rate equation in the (a) exponential and (b) common logarithmic forms.

a) Rate of reaction =  $Ce^{-Q/RT}$

b)  $\log_{10} \text{ rate} = \log_{10} \text{ constant} - \frac{Q}{2.303RT}$

4.37 Draw a typical Arrhenius plot of  $\log_{10}$  of the reaction rate versus reciprocal absolute temperature, and indicate the slope of the plot.

A typical Arrhenius plot of the logarithmic reaction rate is shown below for the SI absolute Kelvin temperature scale. The relationship between the  $\log_{10}$  of the reaction rate and the inverse absolute temperature is linear with a slope of  $-Q/(2.303R)$ .



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During substitutional diffusion of atoms in a solid alloy crystal lattice, solute atoms move into positions of solvent atoms in the matrix through a vacancy mechanism. In interstitial diffusion, small solute atoms move between the interstices of the solvent lattice.

- 4.39 Write the equation for Fick's first law of diffusion, and define each of the terms in SI units.

Fick's first law of diffusion is given by:

$$J = -D \frac{dC}{dx} \quad \text{or in SI unit form, } \left\{ \frac{\text{atoms}}{\text{m}^2 \cdot \text{s}} \right\} = \left\{ \left( \frac{\text{m}^2}{\text{s}} \right) \left( \frac{\text{atoms}}{\text{m}^3} \times \frac{1}{\text{m}} \right) \right\}$$

where  $J$  = flux or net flow of atoms;

$D$  = proportionality constant called the *diffusivity* (atomic conductivity) or *diffusion coefficient*;

$\frac{dC}{dx}$  = concentration gradient.

- 4.40 What factors affect the diffusion rate in solid metal crystals?

The diffusion rate in solid metal crystals is affected by five factors:

1. Type of diffusion mechanism;
2. Temperature of diffusion;
3. Concentration of the diffusion species (concentration gradient);
4. Type of crystal structure;
5. Type of crystal imperfections present.

- 4.41 Write the equation for Fick's second law of diffusion in solids and define each of the terms.

Fick's second law of diffusion in solids, written for the  $x$ -direction, is:

$$\frac{dC_x}{dt} = \frac{d}{dx} \left( D \frac{dC_x}{dx} \right)$$

where  $\frac{dC_x}{dt}$  = rate of change of the concentration of the diffusing species in the  $x$ -direction;

$\frac{dC_x}{dx}$  = concentration gradient of the diffusing species in the  $x$ -direction;

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Fick's second law of diffusion, for the diffusion of a gas into the surface of a solid metal crystal lattice is:

$$\frac{C_s - C_x}{C_s - C_o} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

where  $C_s$  = surface concentration of element in gas diffusing into the surface;

$C_o$  = initial uniform concentration of element in solid;

$C_x$  = concentration of element at distance  $x$  from surface at time  $t$ ;

$x$  = distance from surface;

$D$  = diffusivity of diffusing solute element;

$t$  = time.

- 4.43 Describe the gas-carburizing process for steel parts. Why is the carburization of steel parts carried out?

In the gas carburizing process for steel parts, the parts are placed in a furnace in contact with a gas rich in CO at about 927°C. The carbon from the gas diffuses into the surface of the steel part and increases the carbon content of the outer surface region of the part. The higher carbon concentration at the surface makes the steel harder in this region. A steel part can thus be produced with a hard outer layer and a tough low carbon steel inner core. This duplex structure is important, for example, for many types of gears.

- 4.44 Consider the gas carburizing of a gear of 1018 steel (0.18 wt %) at 927°C (1700°F). Calculate the time necessary to increase the carbon content to 0.35 wt % at 0.40 mm below the surface of the gear. Assume the carbon content at the surface to be 1.15 wt % and that the nominal carbon content of the steel gear before carburizing is 0.18 wt %.  $D$  (C in  $\lambda$  iron) at 927°C =  $1.28 \times 10^{-11}$  m<sup>2</sup>/s.

The time required for this diffusion process is calculated using Fick's second law,

$$\frac{C_s - C_x}{C_s - C_o} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

where:  $C_s = 1.15\%$   $C_o = 0.18\%$   $C_x = 0.35\%$

$x = 0.40$  mm =  $4 \times 10^{-4}$  m  $D_{927^\circ\text{C}} = 1.28 \times 10^{-11}$  m<sup>2</sup>/s



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Interpolating from Table 4.5,

erf z	z
0.8209	0.95
0.8247	x
0.8427	1.0

$$\frac{0.8247 - 0.8209}{0.8427 - 0.8209} = \frac{x - 0.95}{1.0 - 0.95} \quad x = 0.959$$

Thus,

$$z = \frac{55.90}{\sqrt{t}} = 0.959$$

$$t = 3397.7 \text{ s} = \mathbf{56.6 \text{ min.}}$$

- 4.45 The surface of a steel gear made of 1022 steel (0.22 wt % C) is to be gas-carburized at 927°C (1700°F). Calculate the time necessary to increase the carbon content to 0.30 wt % at 0.030 in. below the surface of the gear. Assume the carbon content of the surface to be 1.20 wt %.  $D$  (C in  $\lambda$  iron) at 927°C =  $1.28 \times 10^{-11} \text{ m}^2/\text{s}$ .

Given:  $C_s = 1.20\%$   $C_o = 0.22\%$   $C_x = 0.30\%$

$$x = 0.03 \text{ in.} \left( \frac{0.3048 \text{ m/ft}}{12 \text{ in.}} \right) = 7.62 \times 10^{-4} \text{ m} \quad D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.20 - 0.30}{1.20 - 0.22} = \text{erf} \left[ \frac{7.62 \times 10^{-4} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})t}} \right]$$

$$0.9184 = \text{erf} \left[ \frac{106.49}{\sqrt{t}} \right] = \text{erf } z$$

Interpolating from Table 4.5,

erf z	z
0.9103	1.2
0.9184	x
0.9340	1.3

$$\frac{0.9184 - 0.9103}{0.9340 - 0.9103} = \frac{x - 1.2}{1.3 - 1.2} \quad x = 1.234$$

Thus,

$$t = \left[ \frac{106.49}{z} \right]^2 = \left[ \frac{106.49}{1.234} \right]^2 = 7,446.6 \text{ s} = \mathbf{124 \text{ min.}}$$

- 4.46 A gear made of 1020 steel (0.20 wt % C) is to be gas-carburized at 927°C (1700°F). Calculate the carbon content at 0.90 mm below the surface of the gear after a 4.0-hour carburizing time. Assume the carbon content at the surface of the gear is 1.00 wt %.

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$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.00 - C_x}{1.00 - 0.20} = \operatorname{erf} \left[ \frac{9.0 \times 10^{-4} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})(14,400 \text{ s})}} \right]$$

$$1.25(1 - C_x) = \operatorname{erf}(1.0482)$$

Interpolating from Table 4.5,

erf z	z
0.8427	1.00
x	1.0482
0.8802	1.10

$$\frac{1.0482 - 1.00}{1.10 - 1.00} = \frac{x - 0.8427}{0.8802 - 0.8427} \quad x = 0.8608$$

Thus,  $0.8608 = \operatorname{erf}(1.0482)$

Substituting,

$$1.25(1 - C_x) = 0.8608 \quad C_x = \mathbf{0.311 \text{ wt \%}}$$

- 4.47 A gear made of 1020 steel (0.20 wt % C) is to be gas-carburized at 927°C (1700°F). Calculate the carbon content at 0.04 in. below the surface of the gear after a 7.0-hour carburizing time. Assume the carbon content at the surface of the gear is 1.15 wt %.  $D$  (C in  $\lambda$  iron) at 927°C =  $1.28 \times 10^{-11} \text{ m}^2/\text{s}$ .

Given:  $C_s = 1.15\%$   $C_o = 0.20\%$   $C_x = ?$   $t = 7 \text{ h} = 25,200 \text{ s}$

$$x = 0.040 \text{ in.} = 1.02 \times 10^{-3} \text{ m} \quad D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.15 - C_x}{1.15 - 0.20} = \operatorname{erf} \left[ \frac{1.02 \times 10^{-3} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})(25,200 \text{ s})}} \right]$$

$$\frac{1.15 - C_x}{0.95} = \operatorname{erf}(0.89798)$$

Interpolating from Table 4.5,

$$\frac{0.89798 - 0.85}{0.90 - 0.85} = \frac{x - 0.7707}{0.7970 - 0.7707} \quad x = 0.7959$$

erf z	z
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4.48 The surface of a steel gear made of 1018 steel (0.18 wt % C) is to be gas-carburized at 927°C (1700°F). Calculate the time necessary to increase the carbon content to 0.35 wt % at 1.00 mm below the surface. Assume the carbon content of the surface of the gear is 1.20 wt %.  $D$  (C in  $\lambda$  iron) at 927°C =  $1.28 \times 10^{-11}$  m<sup>2</sup>/s.

Given:  $C_s = 1.20\%$   $C_o = 0.18\%$   $C_x = 0.35\%$

$$x = 1.0 \text{ mm} = 1.0 \times 10^{-3} \text{ m} \quad D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.20 - 0.35}{1.20 - 0.18} = \text{erf} \left[ \frac{1.00 \times 10^{-3} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})t}} \right]$$

$$0.8333 = \text{erf} \left[ \frac{139.75}{\sqrt{t}} \right] = \text{erf } z$$

Interpolating from Table 4.5,

$$\frac{0.8333 - 0.8209}{0.8427 - 0.8209} = \frac{x - 0.95}{1.0 - 0.95} \quad x = 0.978$$

erf z	z
0.8209	0.95
0.8333	x
0.8427	1.0

Thus,

$$t = \left[ \frac{139.75}{z} \right]^2 = \left[ \frac{139.75}{0.978} \right]^2$$

$$t = 20,400 \text{ s} = \mathbf{340 \text{ min.} = 5.67 \text{ h}}$$

4.49 A gear made of 1020 steel (0.20 wt % C) is to be gas-carburized at 927°C (1700°F). Calculate the carbon content at 0.95 mm below the surface of the gear after an 8.0-hour carburizing time. Assume the carbon content at the surface of the gear is 1.25 wt %.  $D$  (C in  $\lambda$  iron) at 927°C =  $1.28 \times 10^{-11}$  m<sup>2</sup>/s.

Given:  $C_s = 1.25\%$   $C_o = 0.20\%$   $C_x = ?$   $t = 8 \text{ h} = 28,800 \text{ s}$

$$x = 0.95 \text{ mm} = 9.5 \times 10^{-4} \text{ m} \quad D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.25 - C_x}{1.25 - 0.20} = \text{erf} \left[ \frac{9.50 \times 10^{-4} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})(28,800 \text{ s})}} \right]$$



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Interpolating from Table 4.5,

erf z	z
0.7112	0.75
x	0.7823
0.7421	0.80

$$\frac{0.7823 - 0.75}{0.80 - 0.75} = \frac{x - 0.7112}{0.7421 - 0.7112} \quad x = 0.7312$$

Thus,  $0.7312 = \text{erf}(0.7823)$

Substituting,

$$\frac{1.25 - C_x}{1.05} = 0.7312 \quad C_x = \mathbf{0.48 \text{ wt \%}}$$

- 4.50 A gear made of 1018 steel (0.18 wt % C) is to be gas-carburized at 927°C (1700°F). If the carburizing time is 7.5 h, at what depth in millimeters will the carbon content be 0.40 wt %? Assume the carbon content at the surface of the gear is 1.20 wt %.  $D$  (C in  $\lambda$  iron) at 927°C =  $1.28 \times 10^{-11} \text{ m}^2/\text{s}$ .

Given:  $C_s = 1.20\%$   $C_o = 0.18\%$   $C_x = 0.40\%$

$$t = 7.5 \text{ h} = 27,000 \text{ s} \quad D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.20 - 0.40}{1.20 - 0.18} = \text{erf} \left[ \frac{x}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})(27,000 \text{ s})}} \right]$$

$$0.7843 = \text{erf}(850.52x) = \text{erf } z$$

Interpolating from Table 4.5,

erf z	z
0.7707	0.85
0.7843	$x_1$
0.7970	0.90

$$\frac{0.7843 - 0.7707}{0.7970 - 0.7707} = \frac{x_1 - 0.85}{0.90 - 0.85} \quad x_1 = 0.8759$$

Substituting,

$$z = 0.8759 = 850.52x$$

$$x = 0.00103 \text{ m} = 1.03 \text{ mm}$$

- 4.51 If boron is diffused into a thick slice of silicon with no previous boron in it at a temperature of 1100°C for 5 h, what is the depth below the surface at which the concentration is  $10^{17} \text{ atoms/cm}^3$  if the surface concentration is  $10^{18} \text{ atoms/cm}^3$ ?

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$$\frac{C_s - C_x}{C_s - C_o} = \frac{10^{18} - 10^{17}}{10^{18} - 0} = \operatorname{erf} \left[ \frac{x}{2\sqrt{(4.0 \times 10^{-13} \text{ cm}^2/\text{s})(1.80 \times 10^4 \text{ s})}} \right]$$

$$0.90 = \operatorname{erf} \left( \frac{x}{1.697 \times 10^{-4}} \right) = \operatorname{erf} z$$

Interpolating from Table 4.5,

erf z	z
0.8802	1.1
0.9000	x
0.9103	1.2

$$\frac{0.9000 - 0.8802}{0.9103 - 0.8802} = \frac{x_1 - 1.1}{1.2 - 1.1} \quad x_1 = 1.166$$

Substituting,

$$z = 1.166 = \frac{x}{1.697 \times 10^{-4}}$$

$$x = 1.98 \times 10^{-4} \text{ cm}$$

- 4.52 If aluminum is diffused into a thick slice of silicon with no previous aluminum in it at a temperature of 1100°C for 6 h, what is the depth below the surface at which the concentration is  $10^{16}$  atoms/cm<sup>3</sup> if the surface concentration is  $10^{18}$  atoms/cm<sup>3</sup>?

$D = 2 \times 10^{-12} \text{ cm}^2/\text{s}$  for aluminum diffusing in silicon at 1100°C.

Given:  $C_s = 10^{18} \text{ atoms/cm}^3$   $C_x = 10^{16} \text{ atoms/cm}^3$   $C_o = 0.0$

$t = 6.0 \text{ h} = 2.16 \times 10^4 \text{ s}$   $D_{1100^\circ\text{C}} = 2.0 \times 10^{-12} \text{ cm}^2/\text{s}$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{10^{18} - 10^{16}}{10^{18} - 0} = \operatorname{erf} \left[ \frac{x}{2\sqrt{(2.0 \times 10^{-12} \text{ cm}^2/\text{s})(2.16 \times 10^4 \text{ s})}} \right]$$

$$0.99 = \operatorname{erf} \left( \frac{x}{4.157 \times 10^{-4}} \right) = \operatorname{erf} z$$

Interpolating from Table 4.5,

erf z	z
0.9891	1.8
0.9900	x
0.9928	1.9

$$\frac{0.9900 - 0.9891}{0.9928 - 0.9891} = \frac{x_1 - 1.8}{1.9 - 1.8} \quad x_1 = 1.824$$

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4.53 Phosphorus is diffused into a thick slice of silicon with no previous phosphorus in it at a temperature of 1100°C. If the surface concentration of the phosphorus is  $1 \times 10^{18}$  atoms/cm<sup>3</sup> and its concentration at 1 μm is  $1 \times 10^{15}$  atoms/cm<sup>3</sup>, how long must the diffusion time be?  $D = 3.0 \times 10^{-13}$  cm<sup>2</sup>/s for P diffusing in Si at 1100°C.

Given:  $C_s = 10^{18}$  atoms/cm<sup>3</sup>  $C_x = 10^{15}$  atoms/cm<sup>3</sup>  $C_o = 0.0$   
 $x = 1.0 \mu\text{m} = 1.0 \times 10^{-4}$  cm  $D_{1100^\circ\text{C}} = 3.0 \times 10^{-13}$  cm<sup>2</sup>/s

$$\frac{C_s - C_x}{C_s - C_o} = \frac{10^{18} - 10^{15}}{10^{18} - 0} = \text{erf} \left[ \frac{10^{-4} \text{ cm}}{2\sqrt{(3.0 \times 10^{-13} \text{ cm}^2/\text{s})t}} \right]$$

$$0.999 = \text{erf} \left( \frac{91.287}{\sqrt{t}} \right) = \text{erf } z$$

Interpolating from Table 4.5,

$$\frac{0.9990 - 0.9981}{0.9993 - 0.9981} = \frac{x - 2.2}{2.4 - 2.2} \quad x = 2.35$$

erf z	z
0.9981	2.2
0.9990	x
0.9993	2.4

Thus,

$$t = \left[ \frac{91.287}{z} \right]^2 = \left[ \frac{91.287}{2.35} \right]^2$$

$$t = 1508 \text{ s} = \mathbf{25.1 \text{ min.}}$$

4.54 If the diffusivity in Prob. 4.53 had been  $1.5 \times 10^{-13}$  cm<sup>2</sup>/s, at what depth in micrometers would the phosphorus concentration be  $1 \times 10^{15}$  atoms/cm<sup>3</sup>?

Since  $\frac{C_s - C_x}{C_s - C_o} = 0.999$ , erf z is still 2.35. Thus, for the same diffusion period,

$$z = \left[ \frac{x}{2\sqrt{(1.5 \times 10^{-13} \text{ cm}^2/\text{s})(1509 \text{ s})}} \right] = 2.35, \quad x = 7.07 \times 10^{-5} \text{ cm} = \mathbf{0.707 \mu\text{m}}$$

4.55 Arsenic is diffused into a thick slice of silicon with no previous arsenic in it at 1100°C. If

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$$\frac{C_s - C_x}{C_s - C_o} = \frac{5.0 \times 10^{18} - 1.5 \times 10^{16}}{5.0 \times 10^{18} - 0} = \operatorname{erf} \left[ \frac{1.20 \times 10^{-4} \text{ cm}}{2\sqrt{(3.0 \times 10^{-14} \text{ cm}^2/\text{s})t}} \right]$$

$$0.9970 = \operatorname{erf} \left( \frac{346.4}{\sqrt{t}} \right) = \operatorname{erf} z$$

Interpolating from Table 4.5,

$$\frac{0.9970 - 0.9953}{0.9981 - 0.9953} = \frac{x - 2.0}{2.2 - 2.0} \quad x = 2.12 \text{ and,}$$

$$t = \left[ \frac{346.4}{z} \right]^2 = \left[ \frac{346.4}{2.12} \right]^2 = 26,700 \text{ s} = \mathbf{7.42 \text{ h}}$$

- 4.56 Calculate the diffusivity  $D$  in square meters per second for the diffusion of nickel in FCC iron at  $1100^\circ\text{C}$ . Use values of  $D_0 = 7.7 \times 10^{-5} \text{ m}^2/\text{s}$ ;  $Q = 280 \text{ kJ/mol}$ ;  $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ .

The diffusivity of the nickel into FCC iron at  $1373 \text{ K}$  is:

$$\begin{aligned} D &= D_0 e^{-Q/RT} = (7.7 \times 10^{-5} \text{ m}^2/\text{s}) \left\{ \exp \left[ \frac{-280,000 \text{ J/mol}}{[8.314 \text{ J}/(\text{mol} \cdot \text{K})](1373 \text{ K})} \right] \right\} \\ &= (7.7 \times 10^{-5} \text{ m}^2/\text{s})(e^{-24.53}) \\ &= \mathbf{1.71 \times 10^{-15} \text{ m}^2/\text{s}} \end{aligned}$$

- 4.57 Calculate the diffusivity in  $\text{m}^2/\text{s}$  of carbon in HCP titanium at  $700^\circ\text{C}$ . Use  $D_0 = 5.10 \times 10^{-4} \text{ m}^2/\text{s}$ ;  $Q = 182 \text{ kJ/mol}$ ;  $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ .

The diffusivity of carbon into HCP titanium is:

$$\begin{aligned} D &= D_0 e^{-Q/RT} = (5.10 \times 10^{-4} \text{ m}^2/\text{s}) \left\{ \exp \left[ \frac{-182,000 \text{ J/mol}}{[8.314 \text{ J}/(\text{mol} \cdot \text{K})](973 \text{ K})} \right] \right\} \\ &= (5.10 \times 10^{-4} \text{ m}^2/\text{s})(e^{-22.49}) \end{aligned}$$



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$$\begin{aligned}
 D &= D_0 e^{-Q/RT} = (3.40 \times 10^{-4} \text{ m}^2/\text{s}) \left\{ \exp \left[ \frac{-191,000 \text{ J/mol}}{[8.314 \text{ J/(mol} \cdot \text{K)}](623 \text{ K})} \right] \right\} \\
 &= (3.40 \times 10^{-5} \text{ m}^2/\text{s})(e^{-36.88}) \\
 &= \mathbf{3.29 \times 10^{-21} \text{ m}^2/\text{s}}
 \end{aligned}$$

- 4.59 The diffusivity of manganese atoms in the FCC iron lattice is  $1.5 \times 10^{-14} \text{ m}^2/\text{s}$  at  $1300^\circ\text{C}$  and  $1.5 \times 10^{-15} \text{ m}^2/\text{s}$  at  $400^\circ\text{C}$ . Calculate the activation energy in kJ/mol for this case in this temperature range. Data:  $R = 8.314 \text{ J/(mol} \cdot \text{K)}$ .

The activation energy may be calculated using the Arrhenius type equation,

$$\frac{D_{1300^\circ\text{C}}}{D_{400^\circ\text{C}}} = \frac{\exp(-Q/RT_2)}{\exp(-Q/RT_1)} = \exp \left[ \frac{-Q}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

where  $T_1 = 400^\circ\text{C} = 673 \text{ K}$  and  $T_2 = 1300^\circ\text{C} = 1573 \text{ K}$ . Substituting,

$$\begin{aligned}
 \frac{1.5 \times 10^{-14} \text{ m}^2/\text{s}}{1.5 \times 10^{-15} \text{ m}^2/\text{s}} &= \exp \left[ \frac{-Q}{8.314 \text{ J/(mol} \cdot \text{K)}} \left( \frac{1}{1573 \text{ K}} - \frac{1}{673 \text{ K}} \right) \right] \\
 10 &= \exp \left[ (1.0226 \times 10^{-4})Q \right] \\
 \ln(10) &= (1.0226 \times 10^{-4})Q \\
 Q &= 22,518 \text{ J/mol} = \mathbf{22.5 \text{ kJ/mol}}
 \end{aligned}$$

- 4.60 The diffusivity of copper atoms in the aluminum lattice is  $7.5 \times 10^{-13} \text{ m}^2/\text{s}$  at  $600^\circ\text{C}$  and  $2.5 \times 10^{-15} \text{ m}^2/\text{s}$  at  $400^\circ\text{C}$ . Calculate the activation energy for this case in this temperature range. [ $R = 8.314 \text{ J/(mol} \cdot \text{K)}$ .]

The activation energy associated with copper diffusing into aluminum for this temperature range is,

$$\frac{D_{600^\circ\text{C}}}{D_{400^\circ\text{C}}} = \exp \left[ \frac{-Q}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

where  $T_1 = 400^\circ\text{C} = 673 \text{ K}$  and  $T_2 = 600^\circ\text{C} = 873 \text{ K}$ . Substituting,



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$$\frac{7.5 \times 10^{-13} \text{ m}^2/\text{s}}{2.5 \times 10^{-15} \text{ m}^2/\text{s}} = \exp \left[ \frac{-Q}{8.314 \text{ J}/(\text{mol} \cdot \text{K})} \left( \frac{1}{873 \text{ K}} - \frac{1}{673 \text{ K}} \right) \right]$$

$$300 = \exp \left[ (4.094 \times 10^{-5})Q \right]$$

$$\ln(300) = (4.094 \times 10^{-5})Q$$

$$Q = 139,320 \text{ J/mol} = \mathbf{139.3 \text{ kJ/mol}}$$

- 4.61 The diffusivity of iron atoms in the BCC iron lattice is  $4.5 \times 10^{-23} \text{ m}^2/\text{s}$  at  $400^\circ\text{C}$  and  $5.9 \times 10^{-16} \text{ m}^2/\text{s}$  at  $800^\circ\text{C}$ . Calculate the activation energy in kJ/mol for this case in this temperature range. [ $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ .]

The activation energy associated with iron diffusing into BCC iron for this temperature range is,

$$\frac{D_{800^\circ\text{C}}}{D_{400^\circ\text{C}}} = \exp \left[ \frac{-Q}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

where  $T_1 = 400^\circ\text{C} = 673 \text{ K}$  and  $T_2 = 800^\circ\text{C} = 1073 \text{ K}$ . Substituting,

$$\frac{5.9 \times 10^{-16} \text{ m}^2/\text{s}}{4.5 \times 10^{-23} \text{ m}^2/\text{s}} = \exp \left[ \frac{-Q}{8.314 \text{ J}/(\text{mol} \cdot \text{K})} \left( \frac{1}{1073 \text{ K}} - \frac{1}{673 \text{ K}} \right) \right]$$

$$13,111,111.1 = \exp \left[ (6.662 \times 10^{-5})Q \right]$$

$$\ln(13,111,111.1) = (6.662 \times 10^{-5})Q$$

$$Q = 246,007 \text{ J/mol} = \mathbf{246 \text{ kJ/mol}}$$



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