

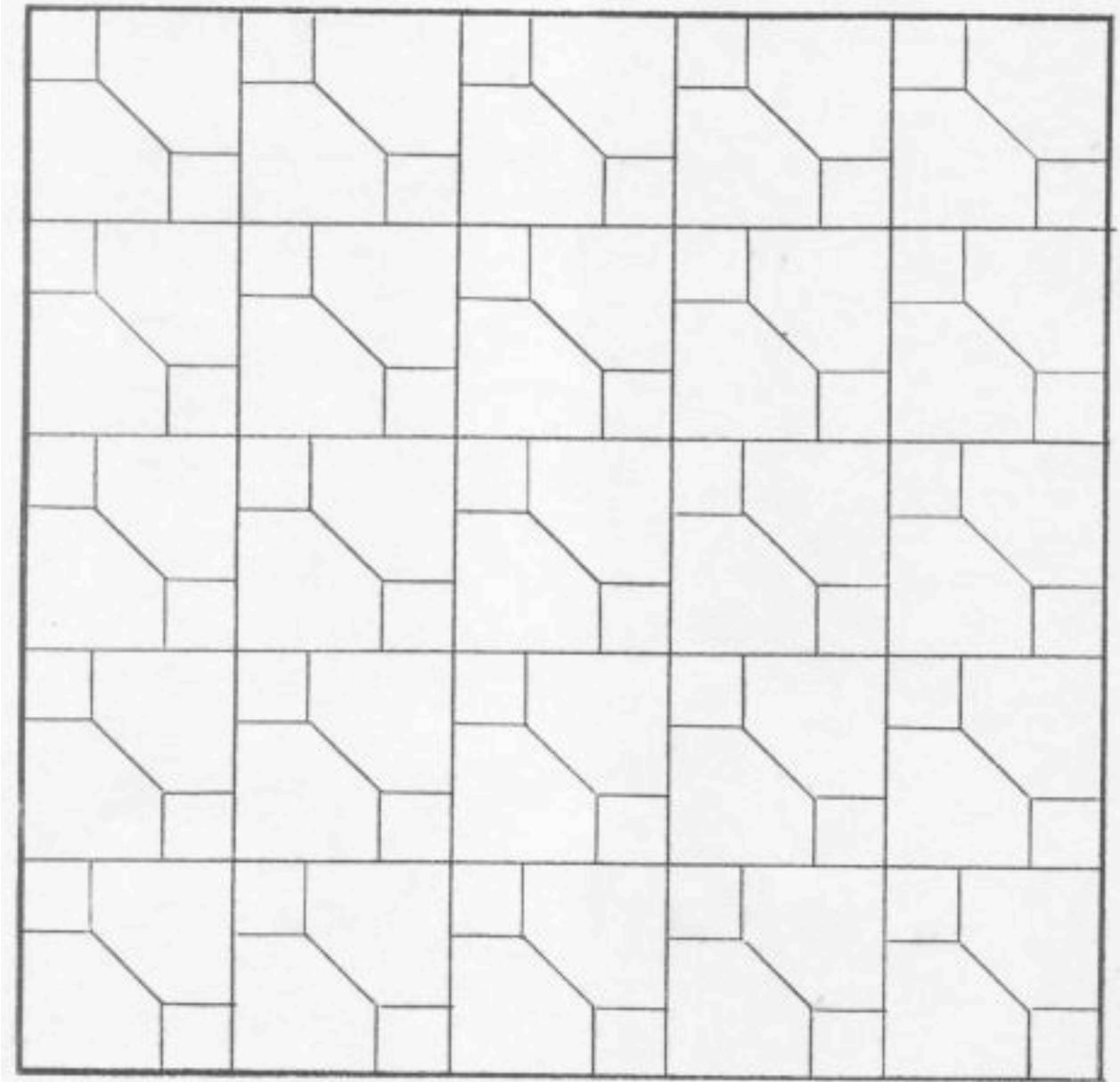
**3.012 PS 4**

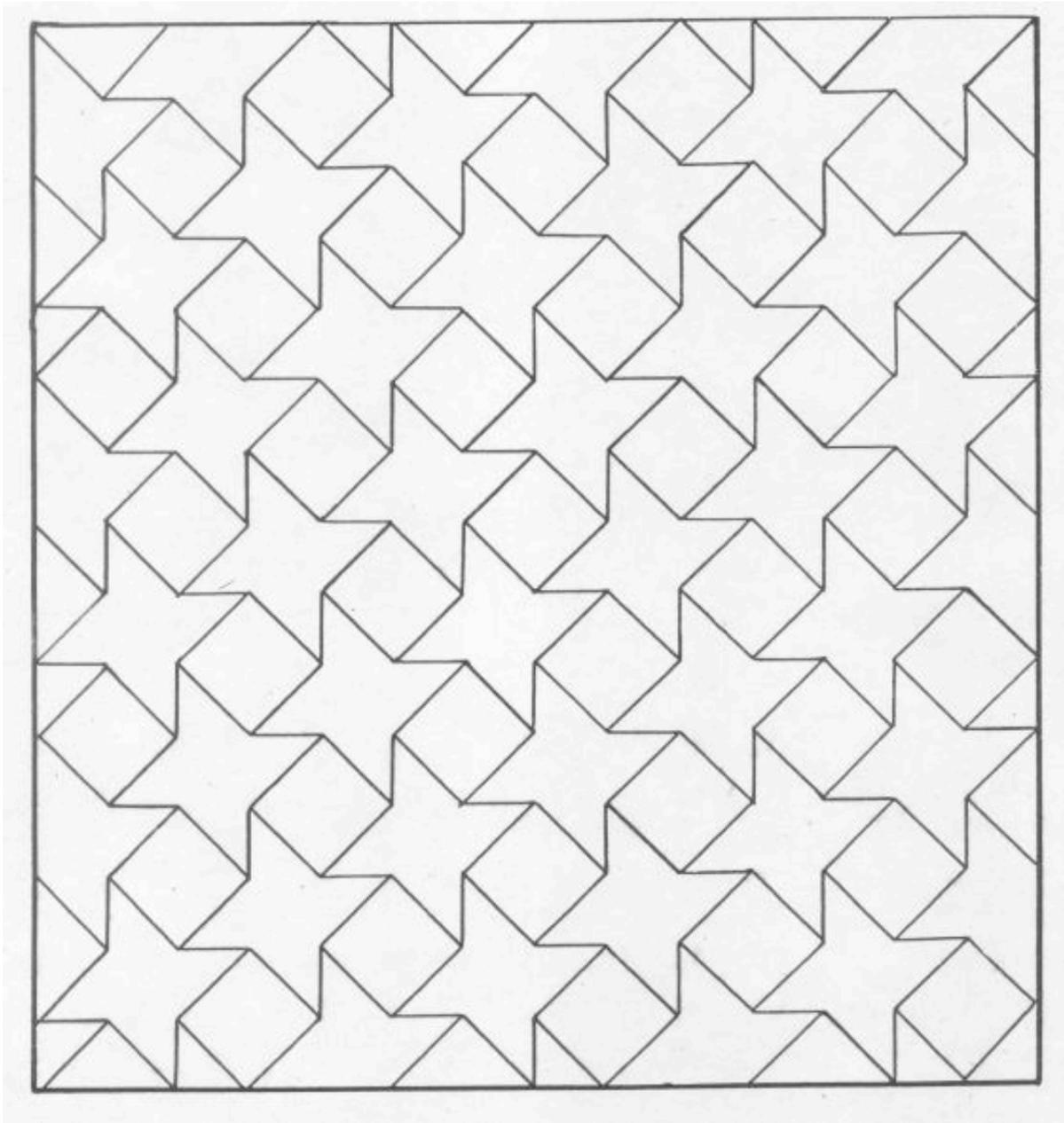
Issued: 10.06.04  
due: 10.13.04 5pm

**3.012**  
**Fall 2004**

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1. A particular cubic crystal has a lattice constant of  $7 \text{ \AA}$ . It is irradiated with X-rays produced by an X-ray tube with a molybdenum target. The strongest intensity produced from such a target (one of the two metals that are most commonly used to produce radiation for diffraction; the other is copper) has a wavelength of  $0.7107 \text{ \AA}$ . Upon irradiating the crystal it is found that the (310) plane produces a diffracted beam at an angle,  $\theta$ , of  $53.384^\circ$ .
  - a. Compute the value of the interplanar spacing,  $d$ , between (310) planes.
  - b. How many wavelengths of path difference are present in the beam scattered from adjacent (310) planes in the stack for the diffraction peak that was observed at  $\theta = 53.384^\circ$  ?
  
2. Two patterns are attached. Both have translational periodicity as well as additional symmetry.
  - a. Sketch in each pattern a set of lattice points that correspond to the translations that map each pattern into congruence with itself. (Use bold, plump points, if you please, so that the grader can readily distinguish the points that you have drawn in.)
  - b. Draw on each pattern the conventional unit cell (that is, one using the shortest pair of translations that describe a cell with the shape that conforms to the symmetry that is present)
  - c. Draw in, using standard symbols (bold lines for mirrors, dashed lines for glides, and small rectangular polyhedra for rotation axes), the location of all symmetry elements that you are able to find within your cell.
  - d. Using the descriptions of the seventeen plane groups taken from the "International Tables for X-Ray Crystallography" (Included in the notes from Lecture #9) identify the plane group that corresponds to each of your patterns and the symbol used to represent it. (And, while you're at it, confirm that you have been successful in finding all the symmetry elements that are present.)





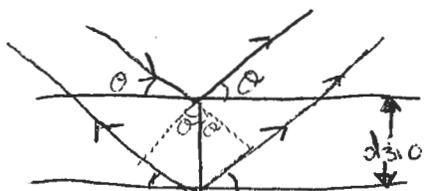
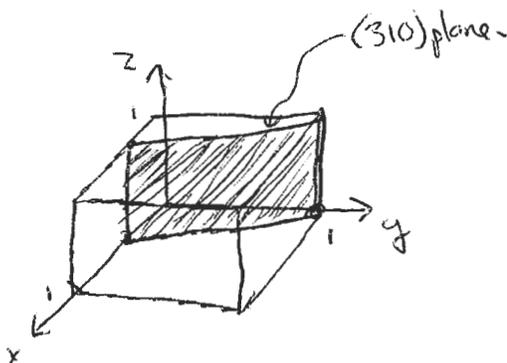
# Solutions to PSET #4 Structure

1)  $a = 7 \text{ \AA}$

$\lambda = 0.7107 \text{ \AA}$

$\theta = 53.384^\circ$

(310) plane corresponds to



$$a) d_{(310)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{7}{\sqrt{3^2 + 1^2}} = \frac{7}{\sqrt{10}} \approx 2.21 \text{ \AA}$$

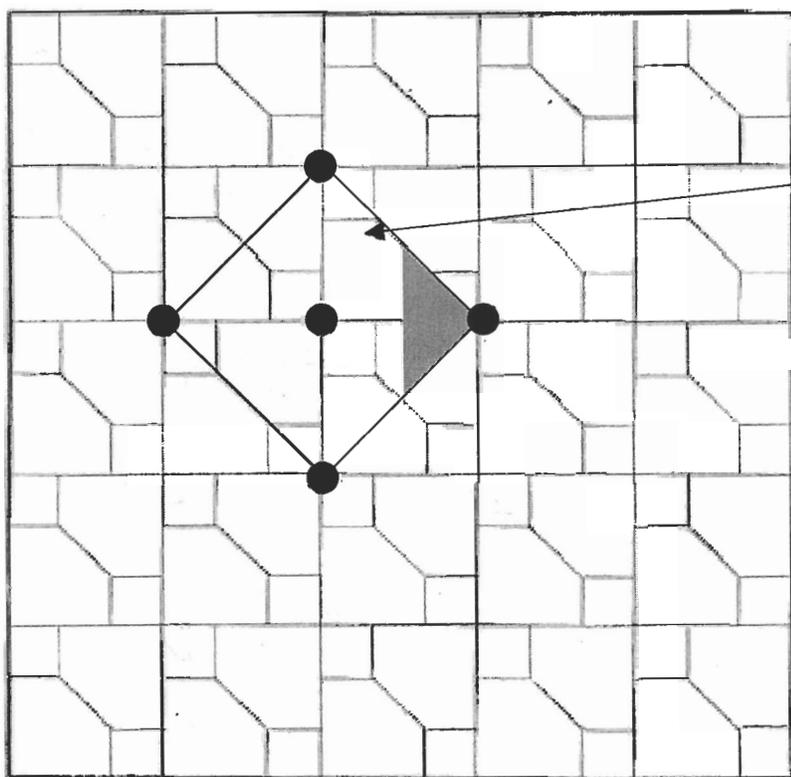
b)  $n\lambda = 2d\sin\theta$

$$n_{\max} = \frac{2d\sin\theta}{\lambda_{\max}} = \frac{2(2.21 \text{ \AA} \times \sin(53.384^\circ))}{0.7107 \text{ \AA}} = 4.999$$

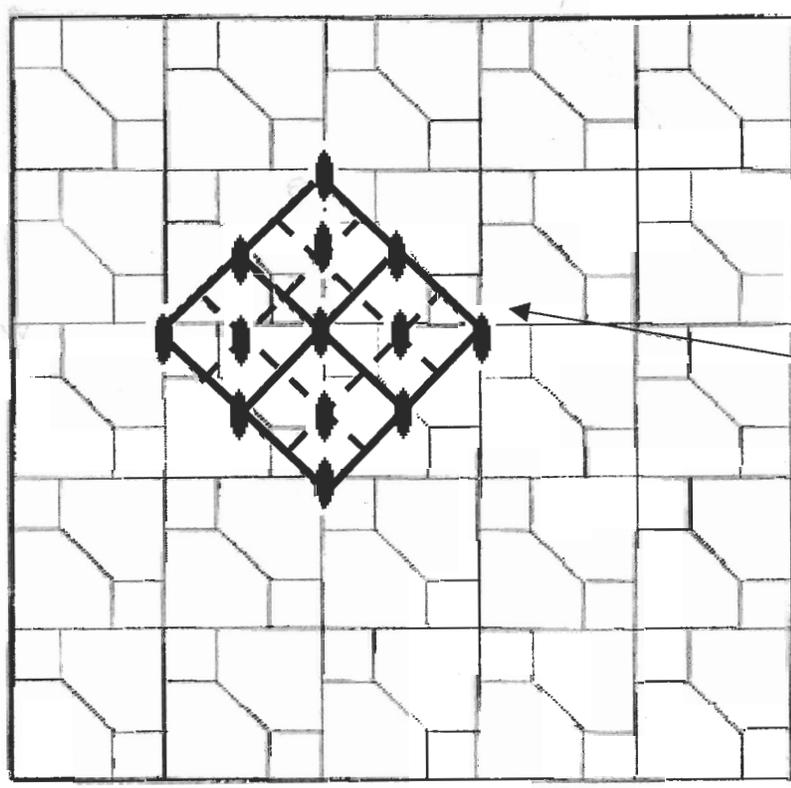
$n_{\max} = 5$

Problem 42

Plane Group:  $c2mm$



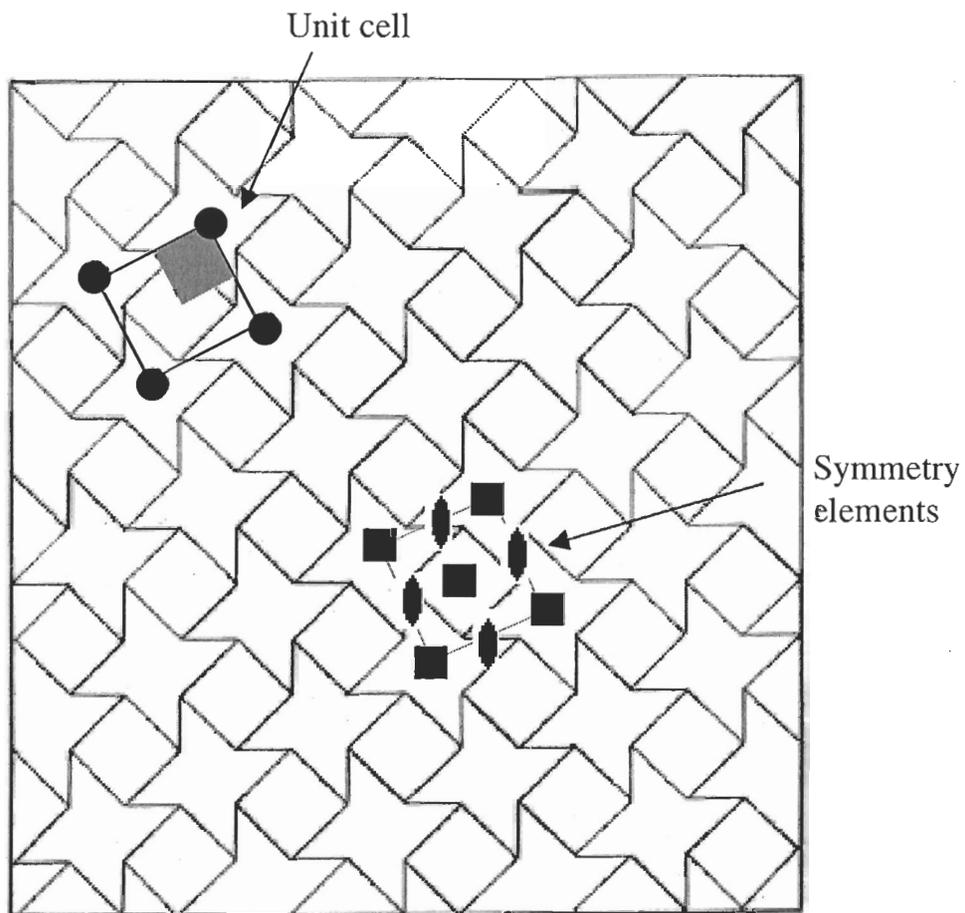
Unit cell  
(Centered - extra  
lattice point at  
center of cell)



Symmetry  
elements

Problem 2

Plane Group: p4



3. **Logic of the Second Law.** Following are a collection of statements concerning the second law. Determine if each statement is true or false, and provide a brief (1-2 sentence) explanation.
- When two materials A and B with initial temperatures  $T_A > T_B$  are placed in thermal contact (the two samples are otherwise isolated from their surroundings), the entropy of the 'hot' material decreases, but this does not violate the second law.
  - In a reversible process, the entropy change of a closed system is always zero.
  - The entropy of an isolated system must always increase in a spontaneous process.
  - The Gibbs free energy of a system is minimized at equilibrium under conditions of constant temperature and pressure. Under other conditions, its behavior is unspecified.
- 
- True.** The second law dictates that the entropy of the universe increases in spontaneous processes. For a process involving an isolated system, no heat or work is performed on the surroundings and thus the entropy of the system alone changes. Here we have two sub-systems- material A and material B, and the second law dictates that the sum of the entropy changes in the two blocks,  $\Delta S_A + \Delta S_B > 0$ , but the entropy change in one of the subsystems may be negative, as long as it is balanced by a greater positive change in entropy of the other subsystem.
  - False.** The second law only requires that the entropy change of the universe- system + surroundings- is zero in a reversible process. A closed system can exchange heat with its surroundings, and thus the entropy change of the surroundings may be nonzero in a reversible process on this system.
  - True.** A process operating on an isolated system cannot affect the surroundings, because no heat or work can be transferred through the boundaries of an isolated system. Thus,  $\Delta S_{\text{universe}} = \Delta S_{\text{system}}$  for processes acting on isolated systems, and  $\Delta S_{\text{system}} > 0$  for a spontaneous process in an isolated system.
  - True.** Maximizing the entropy of the universe under conditions of constant pressure and temperature is equivalent to minimizing the free energy of the **system**.

4. **Entropy change of the universe in a heating process**[DJI1]. We heat 1 mole of a material (at an initial temperature  $T_i$ ) by placing it in thermal contact with a large heat reservoir that has a higher temperature  $T_f$  at constant pressure. Assume the heat capacity of this material is a constant approximately independent of temperature, and that the heat reservoir is so large that its temperature is unaffected (remains constant) during moderate heat transfers.

- What is the entropy change in the heat reservoir caused by this process?
- Show that the entropy change of the universe for this process is:

$$\Delta S_{universe} = C_p [x - \ln(1 + x)]$$

...where  $x = -\frac{(T_f - T_i)}{T_f}$ .

- Does this spontaneous heating process obey the second law? Explain why or why not in 1-2 sentences.

a. The second law dictates that temperatures are equal at thermal equilibrium. Here, our system (the one mole of material being heated in contact with the heat reservoir) receives heat from the reservoir until its temperature reaches that of the reservoir,  $T_f$ . The entropy change in the reservoir will be determined from:

$$dS_{reservoir} = \frac{dq_{rev}}{T_f}$$

$$\Delta S_{reservoir} = \frac{q_{reservoir}}{T_f} = \frac{-q_{system}}{T_f}$$

We use the definition of heat capacity to determine what the heat transferred into the system is in this process:

$$C_p = \left( \frac{dq_{rev}}{dT} \right)_p$$

$$q_{system} = \int_{T_i}^{T_f} C_p dT = C_p \int_{T_i}^{T_f} dT = C_p (T_f - T_i)$$

$$\therefore \Delta S_{reservoir} = -\frac{C_p (T_f - T_i)}{T_f} = x C_p$$

b. To calculate the entropy change of the universe, we need to know the entropy change of the system and combine it with the entropy change of the reservoir. We again utilize one of the identities for the heat capacity:

$$C_p = T \left( \frac{\partial S}{\partial T} \right)_p$$

$$\Delta S_{\text{system}} = \int_{T_i}^{T_f} \frac{C_p}{T} dT = C_p \int_{T_i}^{T_f} \frac{dT}{T} = C_p \ln \left( \frac{T_f}{T_i} \right) = -C_p \ln(1+x)$$

$$\therefore \Delta S_{\text{universe}} = \Delta S_{\text{reservoir}} + \Delta S_{\text{system}} = C_p [x - \ln(1+x)]$$

c. Though the entropy of the reservoir **decreases** in this process, the overall entropy of the universe increases because the magnitude of the entropy increase in the system is **greater** than the decrease in the reservoir's entropy. The second law does not specify the behavior of the entropy for the system or reservoir alone; only that the total entropy change must be positive in a spontaneous process.

5. **Diffusion experiments obey the second law.** Consider the diffusion experiment sketched schematically below. The system is composed of two subsystems separated by a permeable membrane. The left subsystem is initially composed of a pure liquid **A**, while the right subsystem is initially a second pure liquid **B**. The membrane allows free transfer of **A** and **B** molecules between the two subsystems. The system is held at constant temperature and pressure, and is closed to its surroundings.

If the two liquids have similar modes of bonding, they may be completely miscible and mix to form an *ideal solution*. The chemical potential of a component *i* in an ideal solution is:

$$\mu_i = \mu_{i,o} + RT \ln X_i$$

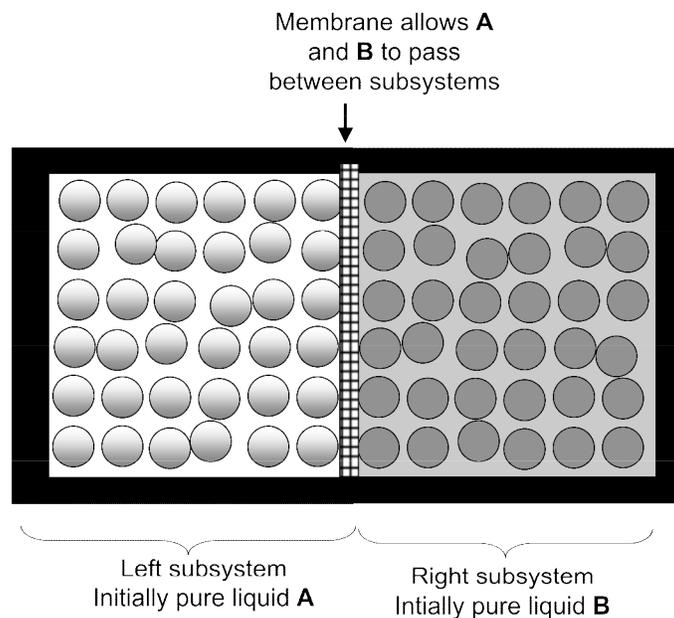
where  $\mu_{i,o}$  is a constant, R is the gas constant (8.3144 J/mole K), T is the absolute temperature, and  $X_i$  is the mole fraction of component *i* in the system:

$$X_i = \frac{n_i}{\sum_{j=1}^C n_j} \quad \text{The sum is over all of the C components of the system.}$$

The total moles of molecules of each type in the system is fixed:

$$\begin{aligned} n_A^L + n_A^R &= N_A \\ n_B^L + n_B^R &= N_B \end{aligned}$$

(The superscripts L and R refer to the left and right subsystems, respectively).  $N_A$  and  $N_B$  are constants.



- a. We showed several examples in lecture of how the condition  $dS_{\text{universe}} = 0$  can be used to define requirements for equilibrium (e.g., uniform T, uniform P, etc.). We further introduced the Gibbs free energy, which provides a simple criterion for equilibrium under conditions of constant temperature and pressure:  $dG_{\text{system}} = 0$ . Using  $dG_{\text{system}} = 0$  and the approach used in lecture for demonstrating thermal and mechanical equilibrium, show that for chemical equilibrium in the simple system described above, the following conditions must be met:

$$\mu_A^L = \mu_A^R$$

$$\mu_B^L = \mu_B^R$$

(Treat each subsystem as a separate phase- the superscript L denotes the left subsystem, the superscript R denotes the right subsystem).

- a. The differential for the Gibbs free energy of a multi-component, multi-phase system is:

$$dG = VdP - SdT + \sum_{i=1}^C \sum_{j=1}^P \mu_i^j dn_i^j$$

...which at constant temperature and pressure reduces to:

$$dG = \sum_{i=1}^C \sum_{j=1}^P \mu_i^j dn_i^j$$

For the present system, comprised of two subsystems, we can write the differential for the Gibbs free energy of the total system as:

$$dG_{\text{system}} = dG_A + dG_B = \mu_A^L dn_A^L + \mu_B^L dn_B^L + \mu_A^R dn_A^R + \mu_B^R dn_B^R$$

At equilibrium:

$$dG_{\text{system}} = 0$$

$$\mu_A^L dn_A^L + \mu_B^L dn_B^L + \mu_A^R dn_A^R + \mu_B^R dn_B^R = 0$$

The constraint that the total number of **A** and **B** molecules present is fixed gives:

$$dn_A^L + dn_A^R = 0$$

$$n_A^L + n_A^R = N_A \quad dn_A^L = -dn_A^R$$

$$n_B^L + n_B^R = N_B \quad dn_B^L + dn_B^R = 0$$

$$dn_B^L = -dn_B^R$$

Applying this constraint in the equilibrium equation:

$$(i) \quad (\mu_A^L - \mu_A^R)dn_A^L + (\mu_B^L - \mu_B^R)dn_B^L = 0$$

Equilibrium is achieved when the free energy differential is 0 for any fluctuation  $dn_A^L$  or  $dn_B^L$ . This requires:

$$(\mu_A^L - \mu_A^R) = 0$$

$$(\mu_B^L - \mu_B^R) = 0$$

which gives:

$$\mu_A^L = \mu_A^R$$

$$\mu_B^L = \mu_B^R$$

- b. Suppose the total number of molecules on either side of the membrane is initially equal and must remain equal (e.g., due to the liquids being approximately incompressible and having similar molecular volumes):

$$n_A^L + n_B^L = N^L$$

$$n_A^R + n_B^R = N^R$$

$$N^L = N^R = N_A = N_B$$

In addition, the chemical potential constants  $\mu_{i,0}$  for each species can be taken as equal on either side of the membrane:

$$\mu_{A,0}^L = \mu_{A,0}^R$$

$$\mu_{B,0}^L = \mu_{B,0}^R$$

Given these constraints, calculate the values of  $n_A^L$ ,  $n_A^R$ ,  $n_B^L$ , and  $n_B^R$  at equilibrium in terms of the given constants if **A** and **B** form an ideal solution on either side of the membrane.

- b. If the number of molecules on either side of the membrane is fixed, this constraint provides:

$$n_A^L + n_B^L = N^L$$

$$n_A^R + n_B^R = N^R$$

$$N^L = N^R$$

$$dn_A^L = -dn_B^L$$

$$dn_A^R = -dn_B^R$$

Applying this additional constraint into the equilibrium condition (i) above:

$$(\mu_A^L - \mu_A^R)dn_A^L + (\mu_B^L - \mu_B^R)dn_B^L = 0$$

$$\begin{aligned}(\mu_A^L - \mu_A^R)dn_A^L - (\mu_B^L - \mu_B^R)dn_A^L &= 0 \\(\mu_A^L - \mu_A^R - \mu_B^L + \mu_B^R)dn_A^L &= 0\end{aligned}$$

For equilibrium, we must have:

$$\mu_A^L - \mu_A^R - \mu_B^L + \mu_B^R = 0$$

If the liquids and **A** and **B** form an ideal solution, we can expand the chemical potentials as:

$$\mu_{A,o}^L + RT \ln X_A^L - \mu_{A,o}^R - RT \ln X_A^R - \mu_{B,o}^L - RT \ln X_B^L + \mu_{B,o}^R + RT \ln X_B^R = 0$$

The chemical potential constants for each species are equal, which simplifies this expression:

$$\begin{aligned}\mu_{B,o}^L &= \mu_{B,o}^R \\ \mu_{A,o}^L &= \mu_{A,o}^R \\ RT \ln X_A^L - RT \ln X_A^R - RT \ln X_B^L + RT \ln X_B^R &= 0 \\ \ln \frac{X_A^L}{X_A^R} &= \ln \frac{X_B^L}{X_B^R} \\ \frac{X_A^L}{X_A^R} &= \frac{X_B^L}{X_B^R} \\ \frac{n_A^L}{n_A^R} &= \frac{n_B^L}{n_B^R} \\ n_A^L (N_B - n_B^L) &= n_B^L (N_A - n_A^L) \\ \frac{(N_B - n_B^L)}{n_B^L} &= \frac{(N_A - n_A^L)}{n_A^L} \\ \frac{N_B}{n_B^L} - 1 &= \frac{N_A}{n_A^L} - 1 \\ \frac{N_B}{n_B^L} &= \frac{N_A}{n_A^L} \\ n_A^L &= \frac{N_A}{N_B} n_B^L\end{aligned}$$

If the number of moles of  $N_A = N_B$ , then we have at equilibrium:

$$n_A^L = n_B^L$$

Looking back at our other constraints, this means:

$$n_A^L = n_B^L = n_A^R = n_B^R = \frac{N^L}{2}$$

...thus, as your intuition hopefully suggests, this free diffusion experiment ends with the a uniform concentration of molecules throughout the left and right subsystems. Note that this problem would become more interesting if the chemical potentials had a different form- this is where the chemistry of specific molecules comes into play in real systems. We will examine the effects of more complicated chemical potentials later in the term.