

# Introduction to Physical Chemistry – Lecture 9

## I. LECTURE OVERVIEW

In this lecture, we will discuss the concept of material phases. We will also use the tools and concepts we have developed thus far and apply them to the problem of phase equilibrium.

## II. WHAT IS A PHASE?

A *phase* of matter refers to the way that the molecules of a material are organized. The particular phase of a material may change with temperature and pressure. In certain cases, several phases may exist at the same time.

### A. Solids, liquids, gases, and plasmas

There are four accepted kinds of phases of matter: (1) Solid. (2) Liquid. (3) Gas. (4) Plasma. We will discuss each of these in turn.

#### 1. Solids

In a *solid*, all of the atoms or molecules of a material are held in place by strong intermolecular attractive forces. Some atomic/molecular motion is possible, but this is largely vibrational motion. For the most part, the atoms and/or molecules stay in one place, and form an orderly, crystalline structure.

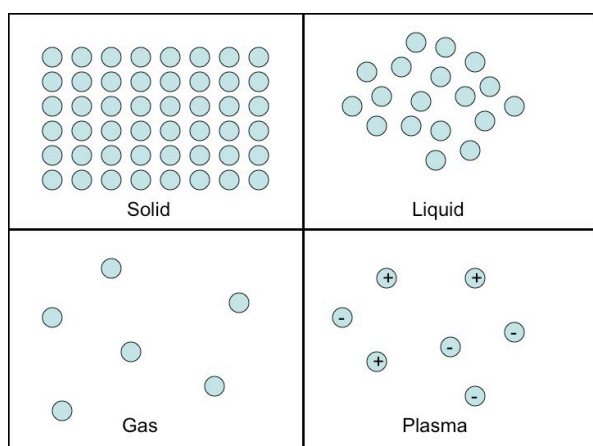


FIG. 1: Illustration of the microscopic structure of the four kinds of phases.

#### 2. Liquids

In a *liquid*, the atoms or molecules of a material are not so tightly bound that they cannot move. Thus, in a liquid, the atoms and/or molecules can slide past each other, which is why a material in a liquid state can flow. However, intermolecular attractive forces are still sufficiently strong that the atoms/molecules stay fairly close to each other. What is interesting is that for certain materials, such as water, the liquid state can be denser than the solid state. So, in a liquid, the atoms/molecules are not necessarily further apart from one another than in a solid.

Because the intermolecular interactions in a liquid are still relatively strong, a liquid tends to have a fixed volume. However, because the atoms/molecules of a liquid are fairly close to each other, any further decrease of the interparticle distances will lead to strong repulsive forces between the atoms/molecules, which is why liquids are generally relatively incompressible.

#### 3. Gases

In a *gas*, the atoms or molecules of a material are relatively far apart from each other, and so they can move freely and largely unaffected by the weak interparticle attractive forces.

Because the intermolecular interactions in a gas are weak, with large interparticle distances, gases are highly compressible, and will also occupy a volume equal to the volume of the container they are in.

#### 4. Plasmas

A *plasma* is essentially a gas that is so hot that the electrons are no longer bound to atomic nuclei. The result is a gas that consists of a mixture of free atomic nuclei and electrons.

The sun is an example of an object in a plasma phase. Plasmas are temporarily generated during lightning discharges, where the air in the region of the lightning bolt becomes so hot that the electrons are essentially stripped from the air molecules.

Plasmas are also generated in experimental nuclear fusion reactors (specifically the toroidal tokamak-type reactor). Electric current is passed through a gas to heat it and turn it into a plasma. Once the gas goes into the plasma state and is electrically conducting, it can respond to an external magnetic field. In particular, a magnetic field can be used to squeeze the plasma to densities and temperatures such that nuclear fusion is initiated.

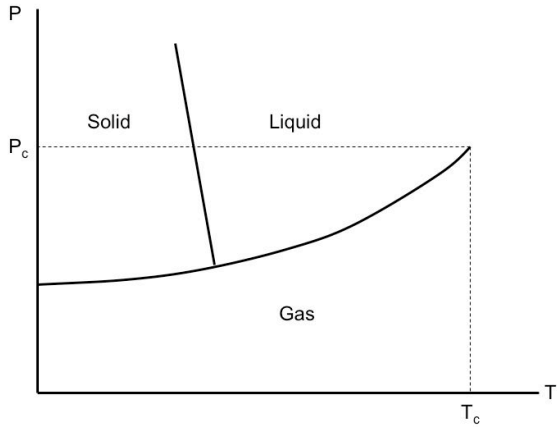


FIG. 2: Illustration of solid-liquid-gas equilibrium diagram. The point where the solid, liquid, and gas regions all meet is a point where all three phases are in equilibrium. It is called the *triple point*.

## B. Phase Diagrams

A *phase diagram* is a graph that shows, as a function of various thermodynamic variables, the phase of a given material. One of the most common phase diagrams is a  $P, T$ -diagram, showing the phase dependence of a material as a function of temperature and pressure (see Figure 2).

## C. Other kinds of phases

While solids, liquids, gases, and plasmas are the four most commonly described phases of a material, there are other kinds of phases that may be observed. As we have mentioned previously, a phase simply refers to a distinct organizational mode of a material. In Figure 3, we illustrate two kinds of phase transitions, namely the ferromagnetic to paramagnetic transition, and Bose-Einstein condensation.

### 1. Ferromagnets

So, for example, there are materials, known as *ferromagnets*, that, in the absence of a magnetic field, will, at thermal equilibrium, have no net magnetization. More precisely, below a certain temperature, known as the *Curie temperature*, a ferromagnet is divided into distinct domains, each of which has a net magnetization (the electronic spins in a given domain point in the same direction). However, the total magnetization of all the domains sums to a value close to zero.

In the presence of a magnetic field, the magnetic domains align, producing a “permanent” magnet. However, above the Curie temperature, a ferromagnet undergoes a phase transition where the magnetic domains lose their

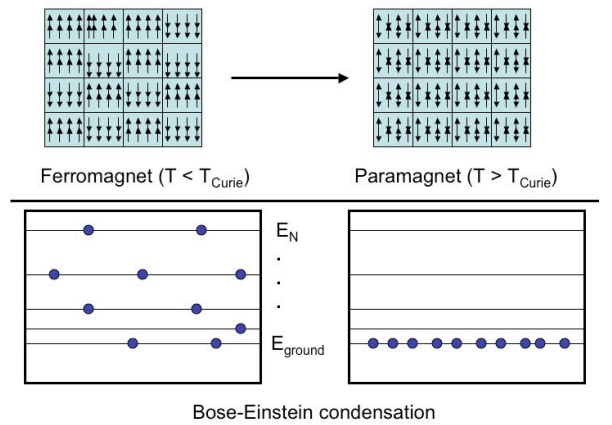


FIG. 3: Illustration of the ferromagnet to paramagnet phase transition, and Bose-Einstein condensation.

net magnetization. Therefore, above the Curie temperature, the material can no longer be magnetized. Such a material is called *paramagnetic*, because, although it will respond to an external magnetic field, it itself retains no net magnetization when the field is removed.

### 2. Bose-Einstein condensation

A particularly exotic phase transition is known as *Bose-Einstein condensation*. To fully understand the phenomenon of Bose-Einstein condensation, you first need to learn some quantum mechanics and statistical mechanics. That being said, it is possible to give a rough explanation of what happens in a Bose-Einstein condensate:

In classical mechanics, energy is continuous. That is, a particle can have any energy. In quantum mechanics, this is not generally true. Because particles have a wave-like character to them, confining the particles to a finite volume results in only certain wavelengths being allowed. Because in quantum mechanics, energy is directly tied to wavelength (the shorter the wave, the higher the energy), a particle confined to a box can only occupy certain states. The lowest energy state is known as the *ground state*.

Now, in quantum mechanics, there are two kinds of particles: (1) *bosons*, which can occupy the same state at the same time, and (2) *fermions*, which cannot occupy the same state at the same time.

At high temperatures, the distinction between bosons and fermions is generally not important. There are so many energy states available that the chances of two particles occupying the same state is very small. However, at low temperatures, the distinction between bosons and fermions is an important one.

At sufficiently low temperature, a collection of bosons can undergo a phase transition whereby they collectively all go into the ground state. The interesting aspect of this

phase transition is that it is not noticeable by a change in density of the system. The reason for this is that the phase transition is defined by a change in the collective velocity, or equivalently, momentum, of the particles.

In a Bose-Einstein condensate, all the particles are in the ground state. As a result, these exotic objects exhibit strongly quantum mechanical behavior. Essentially, a Bose-Einstein condensate behaves like a single quantum-mechanical object with a well-defined wavelength. As a result, one of the current forefronts of research in low-temperature physics is to use Bose-Einstein condensates to construct a *matter laser*.

Another phenomenon associated with Bose-Einstein condensation is the phenomenon of *superfluidity*. A *superfluid* is a liquid that flows without friction. The reason why a Bose-Einstein condensate is capable of exhibiting this behavior is precisely because all of the atoms are already in the ground state. Therefore, they are simply incapable of dissipating further energy due to friction.

It should be noted that low-temperature superconductors are based on this principle. An individual electron is a fermion. However, electrons may pair up with each other to form what is known as a *Cooper pair*. This pair behaves like a boson, which may undergo Bose-Einstein condensation at low temperatures and behave as a superfluid. So, low-temperature superconductivity arises from the nearly frictionless flow of Cooper pairs through a metal (high temperature superconductivity is still a largely poorly understood phenomenon. It is currently one of the hottest topics in theoretical condensed matter physics).

### III. PHASE EQUILIBRIUM

At a given temperature and pressure, a material at thermodynamic equilibrium will generally exist in one phase. However, at specific values of temperature and pressure, a material will change from one phase to another. This is known as a *phase transition*. During the temperature and pressure at which a phase transition occurs, the two phases are in equilibrium with each other. Therefore, to understand phase transitions, we must understand phase equilibrium.

#### A. Criteria for phase equilibrium

Consider two phases, denoted  $A$  and  $B$ , that come to equilibrium at some temperature  $T$  and  $P$ . These phases may be gas-liquid, gas-plasma, gas-solid, liquid-solid, bose condensate - non-bose-condensate, etc. Because  $A$  and  $B$  are in equilibrium with each other at temperature  $T$  and  $P$ , then we may reversibly transfer material from  $A$  to  $B$ , or from  $B$  to  $A$  (because if we can't, then there's a preferred direction of material flow, which means that only one phase can exist at equilibrium).

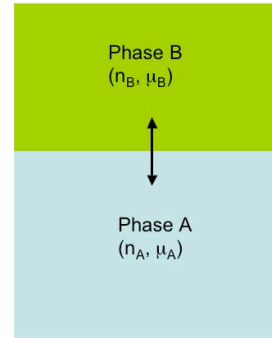


FIG. 4: Illustration of phase equilibrium.

So, let us assume that there are  $n_A$  moles of material in phase  $A$ , and  $n_B$  moles of material in phase  $B$ . Furthermore, let us reversibly transfer  $dn_{AB}$  moles from  $A$  to  $B$  at constant  $T$  and  $P$ .

If we regard phases  $A$  and  $B$  combined as one system, then the transfer of material from  $A$  to  $B$  does not involve any material flows into and out of the system. Therefore, for our purposes, the combined system is closed. Now, for a reversible process occurring on a closed system, we have,

$$dG = -SdT + VdP \quad (1)$$

If this reversible process occurs at constant temperature and pressure, then  $dT = 0$ , and  $dP = 0$ , and so,

$$dG = 0 \quad (2)$$

However, if  $G_A$  and  $G_B$  denote the Gibbs free energies of systems  $A$  and  $B$  at the temperature  $T$  and pressure  $P$ , then we have  $G = G_A + G_B$ , and so

$$0 = dG = dG_A + dG_B \quad (3)$$

Now, if  $\mu_A$  denotes the free energy per mole of material in phase  $A$  at the temperature  $T$  and  $P$ , then note that  $G_A = n_A\mu_A$ . Similarly, if  $\mu_B$  denotes the free energy per mole of material in phase  $B$  at the temperature  $T$  and  $P$ , then note that  $G_B = n_B\mu_B$ . Therefore, at constant temperature and pressure,

$$\begin{aligned} dG_A &= \mu_A dn_A = -\mu_A dn_{AB} \\ dG_B &= \mu_B dn_B = \mu_B dn_{AB} \end{aligned} \quad (4)$$

Therefore,

$$0 = dn_{AB}(\mu_B - \mu_A) \Rightarrow \mu_A = \mu_B \quad (5)$$

This is the criterion we have been looking for: *Two phases are in thermodynamic equilibrium if and only if the molar free energy  $\mu$  of the material is identical in the two phases. That is,  $\mu_{Phase 1} = \mu_{Phase 2}$ .*

We will put this concept to good use in the remaining subsections.

## B. Variation of boiling point with pressure

Our first application of the equilibrium criterion  $\mu_A = \mu_B$  will be to vapor-liquid equilibrium. Specifically, we wish to determine how the boiling point varies with pressure.

So, suppose that at some temperature  $T$  and pressure  $P$ , the liquid and gas phases of a material are in thermodynamic equilibrium. This means that,

$$\mu_{liquid}(T, P) = \mu_{gas}(T, P) \quad (6)$$

Now suppose that we change the pressure slightly, from  $P$  to  $P + dP$ . We wish to determine the new temperature  $T + dT$  at which the liquid and gas phases will be in equilibrium. Note that the condition for equilibrium at the new temperature and pressure is given by,

$$\mu_{liquid}(T + dT, P + dP) = \mu_{gas}(T + dT, P + dP) \quad (7)$$

and so, we have,

$$\begin{aligned} & \mu_{liquid}(T + dT, P + dP) - \mu_{liquid}(T, P) \\ &= \mu_{gas}(T + dT, P + dP) - \mu_{gas}(T, P) \\ &\Rightarrow -\bar{S}_{liquid}(T, P)dT + \bar{V}_{liquid}dP \\ &= -\bar{S}_{gas}(T, P)dT + \bar{V}_{gas}dP \\ &\Rightarrow (\bar{S}_{gas}(T, P) - \bar{S}_{liquid}(T, P))dT = (\bar{V}_{gas} - \bar{V}_{liquid})dP \\ &\Rightarrow \frac{dP}{dT} = \frac{\Delta\bar{S}_{vap}(T, P)}{\Delta\bar{V}_{vap}(T, P)} \end{aligned} \quad (8)$$

and so,

$$\frac{dP_{boil}}{dT} = \frac{\Delta\bar{S}_{vap}(T, P)}{\Delta\bar{V}_{vap}(T, P)} \quad (9)$$

To make this equation more useful, note first that, if we reversibly convert one mole of liquid to gas at the equilibrium temperature  $T$  and pressure  $P$ , we obtain,

$$\Delta\bar{S}_{vap}(T, P) = \frac{Q_{vap}}{T} = \frac{\Delta\bar{H}_{vap}(T, P)}{T} \quad (10)$$

since, for a process that occurs at constant pressure, the heat added is equal to the enthalpy change. Therefore,

$$\frac{dP_{boil}}{dT} = \frac{\Delta\bar{H}_{vap}(T, P)}{T\Delta\bar{V}_{vap}(T, P)} \quad (11)$$

Now, let us make the following, reasonable two approximations: (1)  $\bar{V}_{gas} \gg \bar{V}_{liquid}$ , that is, the molar volume of the gas is much, much larger than the molar volume of the liquid. This will only hold, of course, if we are far away from the critical temperature and pressure. (2) The vapor in the gas phase of the material behaves like an ideal gas.

The first approximation allows us to write,

$$\frac{dP_{boil}}{dT} = \frac{\Delta\bar{H}_{vap}(T, P)}{T\bar{V}_{gas}(T, P)} \quad (12)$$

while the ideal gas relation  $\bar{V}_{gas} = RT/P$  gives,

$$\frac{dP_{boil}}{dT} = P \frac{\Delta\bar{H}_{vap}(T, P)}{RT^2} \quad (13)$$

Dropping the ‘‘boil’’ subscript for the moment, and assuming that  $\Delta\bar{H}_{vap}$  has only a weak temperature and pressure dependence, we have,

$$\begin{aligned} \frac{dP}{P} &= \frac{\Delta\bar{H}_{vap}(T, P)}{R} \frac{dT}{T^2} \\ \Rightarrow \int_{P_1}^{P_2} \frac{dP}{P} &= \frac{\Delta\bar{H}_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \\ \Rightarrow \ln P_2 - \ln P_1 &= \frac{\Delta\bar{H}_{vap}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \end{aligned} \quad (14)$$

An equivalent formulation of this formula is that  $\ln P + \Delta\bar{H}_{vap}/(RT)$  is a constant along the vapor-liquid equilibrium curve (that is, along  $(T, P) = (T, P_v(T))$ , where  $P_v(T)$  denotes the vapor pressure of the liquid at temperature  $T$ ).

The expression we have just derived is known as the *Clausius-Clapeyron relation*. It relates the variation of boiling point to pressure, or equivalently, it relates the variation of the vapor pressure of a liquid to temperature. Note that, as  $T$  increases, the vapor pressure  $P_v(T)$  must increase. Therefore, as the pressure increases, the boiling point increases as well.

The Clausius-Clapeyron relation is generally accurate over fairly small temperature ranges (so that  $\Delta\bar{H}_{vap}$  doesn't vary too much), and at relatively low pressures (so that we can assume that  $\bar{V}_{gas} \gg \bar{V}_{liquid}$ , and that the gas is ideal).

## C. Variation of freezing point with pressure

We now turn our attention to solid-liquid equilibrium. Proceeding similarly as with the vapor-liquid equilibrium, we obtain,

$$\frac{dP_{melt}}{dT} = \frac{\Delta\bar{H}_{fus}}{T\Delta\bar{V}_{fus}} \quad (15)$$

where  $\Delta\bar{H}_{fus} = \bar{H}_{liquid} - \bar{H}_{solid}$ , and  $\Delta\bar{V}_{fus} = \bar{V}_{liquid} - \bar{V}_{solid}$ .

Integrating, we get,

$$P_2 - P_1 = \frac{\Delta\bar{H}_{fus}}{\Delta\bar{V}_{fus}} \ln \frac{T_2}{T_1} \quad (16)$$

which may be re-written as,

$$\frac{T_2}{T_1} = \exp\left[\frac{\Delta\bar{V}_{fus}}{\Delta\bar{H}_{fus}}(P_2 - P_1)\right] \quad (17)$$

Now, because  $\Delta\bar{V}_{fus}$  is generally very small, a given change in pressure will lead to a very small change in melting temperature. Writing  $\Delta P = P_2 - P_1$ , and  $\Delta T =$

$T_2 - T_1$ , and expanding the exponential to first-order, we get,

$$\begin{aligned} 1 + \frac{\Delta T}{T_1} &= 1 + \frac{\Delta \bar{V}_{fus}}{\Delta \bar{H}_{fus}} \Delta P \\ \Rightarrow \frac{\Delta T}{T_1} &= \frac{\Delta \bar{V}_{fus}}{\Delta \bar{H}_{fus}} \Delta P \end{aligned} \quad (18)$$

giving us our final formula for the change in melting temperature,

$$\frac{\Delta T}{T} = \frac{\Delta \bar{V}_{fus}}{\Delta \bar{H}_{fus}} \Delta P \quad (19)$$

This formula is valid over relatively small temperature changes.

Note that if  $\bar{V}_{fus} > 0$ , then increasing the pressure will increase the melting temperature. This makes sense, since, if the liquid is less dense than the solid, then, if we are squeezing the solid more strongly, the solid will need to be heated more to get the kinetic motions of the molecules strong enough to overcome the increased pressure holding them together.

However, if  $\bar{V}_{fus} < 0$ , then increasing the pressure will actually *decrease* the melting temperature. An example of a material that exhibits this phenomenon is water.

#### IV. A NOTE ON SPONTANEITY

We have already discussed the concept of reversibility and irreversibility, and the equivalence between reversibility and thermodynamic equilibrium. Regarding irreversible processes, another term for a process that is irreversible is *spontaneous*. A spontaneous process is one that happens without any external influence on the system. So, for example, the flow of heat from a high temperature to a low temperature region is a spontaneous process. The flow of gas from a high pressure to a low pressure region is also a spontaneous process.

When it comes to matter flows, we wish to determine when we can tell in what direction an irreversible, i.e. spontaneous, process will occur. This is a conceptually difficult question to work out, so we will proceed slowly.

The concept of  $\mu$  introduced is in fact a much more subtle concept than may appear at first glance. To see why, note that, if we consider an open system instead of a closed system, then the internal energy  $U$  can be changed by matter flows. For a closed system, we have  $U = TdS - PdV$ . In this case, for a single-component system, the total number of moles is fixed, and so we do not need to explicitly consider the dependence of  $U$  on the number of moles  $n$ .

For an open system, we need to incorporate an explicit dependence on  $n$ . Note that, in the formulation of the First Law for closed systems, we regard  $U$  as a function of  $S$  and  $V$ . For an open system, we regard  $U$  as a function

of  $S$ ,  $V$ , and  $n$ , so that  $U = U(S, V, n)$ . We then have,

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn \\ &= TdS - PdV + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn \end{aligned} \quad (20)$$

Regarding  $H$  as a function of  $S$ ,  $P$ , and  $n$ , we obtain,

$$dH = TdS + VdP + \left(\frac{\partial H}{\partial n}\right)_{S,P} dn \quad (21)$$

while from  $H = U + PV$  we also have,

$$dH = TdS + VdP + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn \quad (22)$$

and so,

$$\left(\frac{\partial H}{\partial n}\right)_{S,P} = \left(\frac{\partial U}{\partial n}\right)_{S,V} \quad (23)$$

Proceeding similarly with  $A$  and  $G$ , we get, finally, that,

$$\begin{aligned} \mu &\equiv \left(\frac{\partial G}{\partial n}\right)_{T,P} \\ &= \left(\frac{\partial A}{\partial n}\right)_{T,V} \\ &= \left(\frac{\partial H}{\partial n}\right)_{S,P} \\ &= \left(\frac{\partial U}{\partial n}\right)_{S,V} \end{aligned} \quad (24)$$

These relations will be important in determining the direction of matter flows.

Turning our attention to this problem, let us consider two phases,  $A$  and  $B$ , at a given temperature  $T$  and pressure  $P$ , with molar free energies  $\mu_A$  and  $\mu_B$ , respectively. If the two phases are in contact, such that matter can flow between  $A$  and  $B$ , and assuming  $\mu_A < \mu_B$ , which way will matter flow?

To answer this question, note that phase  $A$  has some internal energy  $U_A$ , entropy  $S_A$ , and volume  $V_A$ , while phase  $B$  has some internal energy  $U_B$ , entropy  $S_B$ , and volume  $V_B$ .

At this stage, let us seal off the two phases from the rest of the environment, so that the combined system is now isolated from the rest of the environment. Since we haven't changed any thermodynamic variables by this, it makes sense that the direction of matter flows should remain the same.

However, with an isolated system, we know from Lecture 6 that such a system will seek a state of maximal entropy. Therefore, the direction of matter flows must be such to increase the total entropy of the combined system.

So, suppose in phase  $A$ , we have a set of infinitesimal entropy, volume, and mole number changes  $dS_A$ ,  $dV_A$ , and  $dn_A$ , while in phase  $B$ , we have a set of infinitesimal entropy, volume, and mole number changes

$dS_B$ ,  $dV_B$ , and  $dn_B$ . Since the system is isolated with a fixed volume, we have  $dV_B = -dV_A$ , while mass conservation gives,  $dn_B = -dn_A$ . Energy conservation gives  $dU_B = -dU_A$ , and so,

$$\begin{aligned} dU_A &= TdS_A - PdV_A + \mu_A dn_A \\ dU_B &= -dU_A = TdS_B - P(-dV_A) + \mu_B(-dn_A) \end{aligned} \quad (25)$$

Adding the two equations together gives,

$$\begin{aligned} 0 &= Td(S_A + S_B) - (\mu_B - \mu_A)dn_A \\ \Rightarrow Td(S_A + S_B) &= (\mu_B - \mu_A)dn_A \end{aligned} \quad (26)$$

Because the entropy of an isolated system always tends

to a maximum, we must have  $d(S_A + S_B) > 0$  unless  $S_A + S_B$  is already at its maximal value.

Note that for  $dn_A > 0$ , we have, since  $\mu_B > \mu_A$ , that  $(\mu_B - \mu_A)dn_A > 0$ , hence the total entropy will increase if we transfer matter from phase  $B$  to phase  $A$ . Note that the change in the Gibbs free energy in moving from phase  $B$  to phase  $A$  is given by  $\Delta\bar{G} = \mu_A - \mu_B < 0$ . This is therefore the direction of matter flow, and brings us to our criterion for determining spontaneity:

*Matter will always flow from a region of higher  $\mu$  to a region of lower  $\mu$ . Therefore, a process is spontaneous if and only if the  $\Delta\bar{G}$  associated with that process is negative.*