

Lecture 16

The entropy is a lovely function because it is all we need to know in order to predict whether a process will be spontaneous. However, it is often inconvenient to use, because to predict whether a process will be spontaneous, it is necessary to know the entropy change in both the system and the surroundings. It would be convenient if we could **define functions that could predict spontaneity by referring to the system alone.**

To do this let's return to the second law. The second law says "in a reversible process the entropy of the universe is constant; in an irreversible process, the entropy of the universe increases". We can express this mathematically as  $dS + dS' \geq 0$ , where  $dS$  is the entropy change of the system,  $dS'$  is the entropy change of the surroundings and the sum equals zero only if the process is reversible. Therefore, for spontaneous processes this becomes  $dS + dS' > 0$ .

If the system and the surroundings are in thermal equilibrium at temperature  $T$ , we can write  $dS' = -dq/T$ , where  $dq$  is the heat transferred *to the system*. Thus we can write our condition for an irreversible process as  $dS - dq/T > 0$  or more generally as  $dS - dq/T \geq 0$ . This is a version of the Clausius inequality we saw earlier. Note that already this inequality refers only to the system, since the first term is the entropy change of the system and the second term contains the heat transferred to the system. But, and this is important, this is still the second law, so we are still predicting spontaneity, this time while referring only to the system.

Now consider a **constant volume system**. At constant volume, we have  $dq_v = dU$ . If we substitute this in our inequality it becomes  $dS - dU/T \geq 0$ , which with little difficulty we can rearrange to  $TdS \geq dU$  (constant  $V$ ), which becomes the condition for the spontaneity of a process at constant volume. To explore some of the consequences of this simple inequality, let's consider

the additional constraint of constant energy. Then our equation becomes  $TdS \geq 0$  (**Constant U, V**) or  $dS_{U,V} \geq 0$ .  $dS$  is only equal to zero for a reversible process, so this inequality tells us that at constant energy and volume, the entropy of the system increases for spontaneous processes. Now let's consider the situation where **entropy is constant**. The inequality now becomes  $dU_{S,V} < 0$ . In other words, if the entropy of the system and its volume are constant, the energy of the system must decrease for a process to be spontaneous. This makes sense if we remember that the entropy of the universe must increase in order for a process to be spontaneous. If the entropy change of the system is zero, then the entropy of the surroundings must increase. If  $V$  is constant so that no expansion work can be done, the only way for the entropy of the surroundings to increase is if heat flows from the system to the surroundings, which reduces the energy of the system. Hence  $dU_{S,V} \leq 0$ .

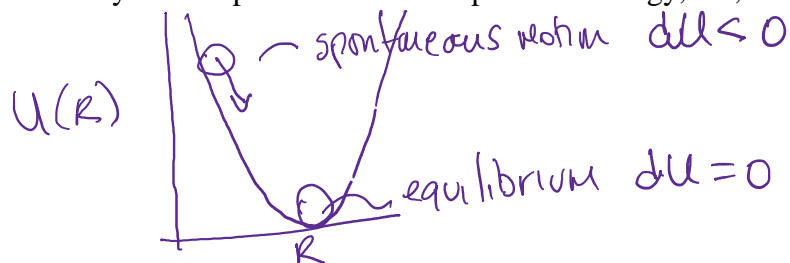
What happens to our original inequality,  $dS - dq/T \geq 0$ , if the heat is transferred at **constant pressure**? We know that  $dq_p = dH$ , so this yields  $dS - dH/T \geq 0$  or  $TdS \geq dH$  (constant  $p$ ). If we consider this inequality under conditions of constant enthalpy as well it reduces to  $dS_{H,P} \geq 0$ . In other words, at constant pressure and enthalpy the entropy of the system increases for a spontaneous process. At constant  $S$ , the inequality reduces to  $dH_{S,P} \leq 0$ . Q: CAN ANYONE EXPLAIN WHY  $dH_{S,P} < 0$  FOR A SPONTANEOUS PROCESS? [ $dS_{tot} > 0$ ,  $dS_{sys} = 0$ ,  $S_{surr}$  must be  $> 0$ ,  $q$  flows to surroundings, so  $dH$  decreases]

The essential content of these inequalities can be expressed by two new state functions. Note that our constant volume inequality can be expressed as  $dU - TdS \leq 0$ , which leads to the definition of the first of our new state functions, the **Helmholtz free energy**,  $A \equiv U - TS$ . For small changes of  $A$  its differential is  $dA = dU - d(TS)$ , which under conditions of constant  $T$  becomes

$dA = dU - TdS$ . Comparing this to our constant volume inequality we see that  $dA_{T,V} \leq 0$  is the constant V, constant T statement of the condition for spontaneity.

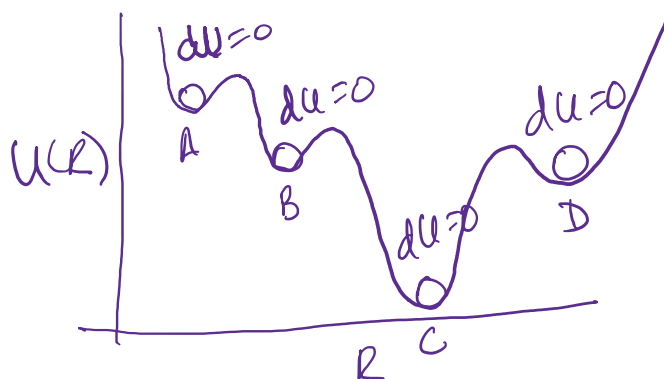
Similarly our constant pressure inequality can be rewritten as  $dH - TdS \leq 0$ , which leads to the definition of the **Gibbs free energy** as  $G = H - TS$ . Q: WHAT IS THE DIFFERENTIAL OF G? [ $dG = dH - d(TS)$ .] Under constant T this becomes  $dG = dH - TdS$ . Comparison of this equation with the constant p inequality shows that at constant p, T, the condition for spontaneity is  $dG_{p,T} \leq 0$ .

Let's discuss the Hemholtz free energy and the Gibbs free energy in more detail. We have shown that a process is spontaneous at constant volume and temperature if  $dA < 0$ . In other words in a spontaneous process at constant volume and temperature the Hemholtz free energy of the system will decrease. When does it stop decreasing? To answer this lets consider a simple physical problem, a ball moving along a potential. If we put the ball toward the top of the potential and release it, it moves spontaneously toward positions of lower potential energy, i.e.,



$dU < 0$ . If we place it at the bottom of the potential surface, and we release it, the ball will not move and  $dU = 0$ , and we say the system is in equilibrium.

This is not only the case for a simple potential like the one we've just considered. Take this more complicated potential. At positions A, B, C and D if we release a ball with no kinetic energy, it will remain stationary,  $dU$  will equal 0, and the ball will be in a mechanical equilibrium.



Now let's return to the Helmholtz function. If we have a spontaneous process at constant  $V$  and  $T$ ,  $dA < 0$ . For example, we could have a vessel containing air at 1.5 atm, where the surroundings are at 1.0 atm. We allow air to leak out of the system. If we let the process continue until it naturally stops, i.e. comes to equilibrium, then the pressures are equalized at 1 atm. **WHAT IS  $dA$  AT THE POINT WHERE WE REACH EQUILIBRIUM?**

To understand more about what  $dA$  tells us, let's take our system now in equilibrium and push it in the same direction, loss of pressure. Now the internal pressure is less than 1 atm. The spontaneous process is now for air to leak back into the system, so  $dA < 0$  for increasing pressure and by induction,  $dA > 0$  for continuing to decrease the pressure. In other words if we have a system out of equilibrium, and we use some process to approach equilibrium,  $dA < 0$  for that process. If we pass equilibrium  $dA > 0$ . In other words, before equilibrium,  $dA < 0$  and beyond equilibrium  $dA > 0$ . Therefore, at equilibrium,  $dA$  must equal 0. This in turn implies that when not in equilibrium  $dA$  for the spontaneous process is  $< 0$  but as we approach equilibrium,  $dA$  approaches 0. In other words,  $A$  behaves in a way analogous to the potential energy for the motion of a mechanical object. **Because  $A$ ,  $G$ ,  $H$  and  $U$  all behave in ways analogous to the potential energy, they are all called thermodynamic potentials.**

To clarify a final time,  $dA < 0$  implies a spontaneous process at constant  $V$ ,  $T$  and  $dA = 0$  at equilibrium for constant  $V$ , and  $T$ . Remember that  $dA = dU - TdS < 0$  for a spontaneous process. Therefore, at constant  $V$  and  $T$  spontaneous processes tend toward lower energy and higher entropy. Remember, though, that in this equation,  $dU$  is a measure of spontaneity only because it

reflects the entropy change in the surroundings at constant  $V$ ,  $T$ , and that the statement  $dU - TdS < 0$  is exactly equivalent to the second law statement, “The entropy of the universe increases in a spontaneous process.”

$A$  has another meaning in addition to helping predict spontaneity under the appropriate conditions. If we know  $dA$  for some process, or  $\Delta A$  for some finite process, we know the maximum work the system can do. Therefore we can write  $dA \Rightarrow -dw_{\max}$  and  $\Delta A \Rightarrow -w_{\max}$ . To show this let's start by **proving** our earlier assertion **that a system does its maximum work under reversible conditions**. We start with the Clausius inequality,  $dS - dq/T \geq 0$ , remembering that the equality holds for a reversible process. We can rearrange this to  $T dS \geq dq$  and remembering that  $dq = dU - dw$ , this becomes  $T dS \geq dU - dw$ . We can rearrange this to  $-dw \leq -dU + TdS$  which reduces to  $-dw \leq -dA$ . Since  $-dw$ , the work done by the system, is less than or equal to  $-dA$ , it follows that the maximum work occurs when  $-dw = -dA$ , i.e.,  $-dw_{\max} = -dA$ . Remember though that  $-dw$  is only equal to  $-dA$  for a reversible process. Therefore the maximum work is only achieved for reversible processes.

Now let's return to the Gibbs free energy. Along with the enthalpy, the Gibbs free energy is the most important state function in chemistry. We determined earlier that if  $dG_{T,P} < 0$  then a process will be spontaneous. These conditions of constant pressure and temperature are clearly important for chemists, since most reactions are run under conditions of constant temperature and pressure. Using the same reasoning that we used for the Helmholtz free energy, we find that if  $dG < 0$  at constant  $T$  and  $P$ , the process will be spontaneous. If  $dG > 0$  at constant  $T$  and  $P$ , the reverse process will be spontaneous, and finally if  $dG = 0$  the system will be under equilibrium with respect to the process. Again as was the case with  $dA$ , as a process moves a system spontaneously toward

equilibrium,  $dG$  moves toward 0.

An illustration of the importance of  $\Delta G$  is the spontaneity of endothermic processes under some conditions. Since  $\Delta G = \Delta H - T\Delta S$ , if  $\Delta H > 0$ ,  $\Delta G$  can be less than 0 if  $\Delta S > 0$  and  $T$  is sufficiently high.

Using  $\Delta A$  we found that we could predict the maximum work done by a system. This leads us to ask if there is something similar that we could learn from  $\Delta G$ . We begin with our differential of  $G$  under conditions of constant  $T$ ,  $dG = dH - TdS$ . We know that  $dH = dU + d(pV) = dw + dq + d(pV)$ . The work term can be broken down into two components, expansion work, which is given by  $-p_{\text{ex}} dV$ , and nonexpansion work, which we will simply call  $dw_e$ . If we insert this in our equation for  $dG$ , and expand  $d(pV)$  we get

$$dG = -p_{\text{ex}} dV + dw_e + dq + p dV + V dp - T dS.$$

For a reversible process,  $p_{\text{ex}} = p$ , and  $dq = TdS$  and  $dw_e = dw_{e,\text{max}}$ , so this simplifies to  $dG = dw_{e,\text{max}} + V dp$ . Under conditions of constant pressure this finally simplifies to  $dG = dw_{e,\text{max}}$ . The reason for the subscript  $e$  in this case is historical – at the time Gibbs derived the properties of the Gibbs Free Energy, the most important kind of non-expansion work was electrochemical. Hence the choice of subscript. Note that as in the case of the Hemholtz free energy, if  $dG < 0$ , the implication is that  $dw_{e,\text{max}} < 0$  and the system is capable of doing non-expansion work. If on the other hand  $dG > 0$ , then  $dw_{e,\text{max}} > 0$  and for a process to occur, work must be done on the system.

Lecture 17

Remember that our definition of the Gibbs free energy is  $G = H - TS$ . The Gibbs free energy is of interest to chemists because it predicts the spontaneity of reactions under conditions of constant temperature and pressure. Of equal importance in chemistry is the condition  $dG_{p,T} = 0$ , since it allows us to relate the Gibbs free energy to conditions of equilibrium. However before we can relate  $dG$  to equilibrium in ways that are useful to us, we need to further explore the nature of  $G$ ,  $U$ ,  $H$ , and  $A$  and learn ways to relate them. This means in part a return to partial derivatives.

Let's begin by returning to our first thermodynamic potential, the energy. Our earliest definition of energy change was  $dU = dq + dw$ . In chapter 3 we showed that  $dq_{\text{rev}}/T = dS$  or  $dq_{\text{rev}} = TdS$ . For a reversible process we also have  $dw = -p dV$ . Substituting both of these in our equation for  $dU$  yields  $dU = TdS - pdV$ . This is called the fundamental relation, because it defines  $dU$  strictly in terms of basic state functions, and because our other major state functions,  $H$ ,  $G$  and  $A$  are all defined in terms of  $U$ . The fundamental equation is the first of four **Gibbs equations** we'll see, each of **which expresses the differential of a thermodynamic potential in terms of its fundamental variables**.

The equation for  $U$  shows that  **$U$  is a function of  $S$  and  $V$** , i.e.,  $U = U(S, V)$ . We can see this because in our fundamental relation  **$S$  and  $V$  are the variables contained in the differentials**. It can also be seen because  **$S$  and  $V$  are the variables that are held constant when we use  $dU$  to predict spontaneity**. As such they are called natural variables. It is possible to define  $U$  as a function of other variables, as we did earlier in defining  $U$  as a function of  $V$  and  $T$ , but as a consequence of our exploration of the second law,  $U$  allows us to predict spontaneity or equilibrium when  $S$  and  $V$  are held constant, and not when other variables are. Because  $U$  is a

function of  $S$  and  $V$ , the differential  $dU$  becomes

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

If we compare this to our fundamental relation we see that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -p$$

The first equation defines the temperature as the ratio of changes in energy and entropy in a closed volume. You can see that by delving deeper into thermodynamics we are beginning to interrelate its fundamental quantities.

The fact that the energy is an exact differential allows us to develop a new set of thermodynamic relations. Remember that our test for an exact differential is that if we have a function  $df = a dx + b dy$ , then  $(\partial a/\partial y)_x = (\partial b/\partial x)_y$ . Our fundamental equation is

$$dU = -pdV + TdS.$$

Since  $U$  is a state function,  $dU$  is an exact differential, and we can apply the equation for  $df$  to  $dU$  to get,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

This equation is one of a group of relations called **Maxwell relations**. It is not immediately obvious and cannot be derived from our other rules for the manipulation of partial derivatives.

An alternative approach to deriving this Maxwell relation is as follows. We've already shown that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -p$$



We know from our earlier discussion of partial derivatives that the mixed second derivatives,

$$\left(\frac{\partial^2 U}{\partial x \partial y}\right) \text{ and } \left(\frac{\partial^2 U}{\partial y \partial x}\right)$$

are equal. Therefore

$$\left(\frac{\partial^2 U}{\partial V \partial S}\right) = \left(\frac{\partial^2 U}{\partial S \partial V}\right) \text{ and } \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

Because dH, dA and dG are all also perfect differentials, we can generate Maxwell relations for them as well. Let's start with the enthalpy. Q: WHAT IS THE DEFINITION OF THE ENTHALPY? [H = U + PV] Q: WHAT IS THE DIFFERENTIAL OF H, dH? [dH = dU + d(pV)] If we substitute our fundamental equation for dU, and expand d(pV) we obtain dH = TdS - pdV + pdV + Vdp = TdS + VdP. This is the Gibbs equation for the change in enthalpy. Q: THIS TELLS US THAT H IS A FUNCTION OF WHICH VARIABLES? [H = H(S,p)] We write down our test for a perfect differential,

$$\text{if } df = adx + bdy \text{ then } \left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y$$

and recognize that since dH is a perfect differential we can write

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p,$$

our second Maxwell relation. Now let's do the remaining two. Q: WHAT IS THE DEFINITION OF G? [G = H - TS = U + PV - TS] Q: WHAT IS THE DIFFERENTIAL OF G, dG? [dG = dU + d(pV) - d(TS)] = TdS - pdV + pdV + Vdp - TdS - SdT and therefore, dG = VdP - SdT, the Gibbs equation for the Gibbs Free Energy. The natural variables for G are therefore p and T since small changes in p and T lead to changes in G, i.e., G = G(p, T). Q: WHAT IS THE DIFFERENTIAL OF G(p,T)?

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

If we compare this equation with our other equation for  $dG$  we find that  $(\partial G/\partial T)_p = -S$  and  $(\partial G/\partial p)_T$

$= V$ . Q: WHAT IS THE MAXWELL RELATION FOR  $G$ ?

$$\left(\frac{\partial^2 G}{\partial p \partial T}\right) = \left(\frac{\partial^2 G}{\partial T \partial p}\right) \text{ or } -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

Finally lets calculate the Maxwell relation for  $A$ . Q: WHAT IS THE DEFINITION OF  $A$ ? [ $A = U -$

$TS$ ] WHAT IS THE DIFFERENTIAL OF  $A$ ? [ $dA = dU - d(TS) = TdS - pdV - TdS - SdT$  and therefore

$dA = -pdV - SdT$ .] Q: WHAT ARE THE NATURAL VARIABLES OF  $A$ ? [ $A = A(V,T)$ ] Q: WHAT IS THE

MAXWELL RELATION FOR  $A$ ? [ $(\partial p/\partial T)_V = (\partial S/\partial V)_T$ .] This yields us four Gibbs equations and four

Maxwell relations. The Gibbs equations are:

$$dU = -pdV + TdS$$

$$dH = VdP + TdS$$

$$dA = -pdV - SdT$$

$$dG = Vdp - SdT$$

And the four Maxwell relations are:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

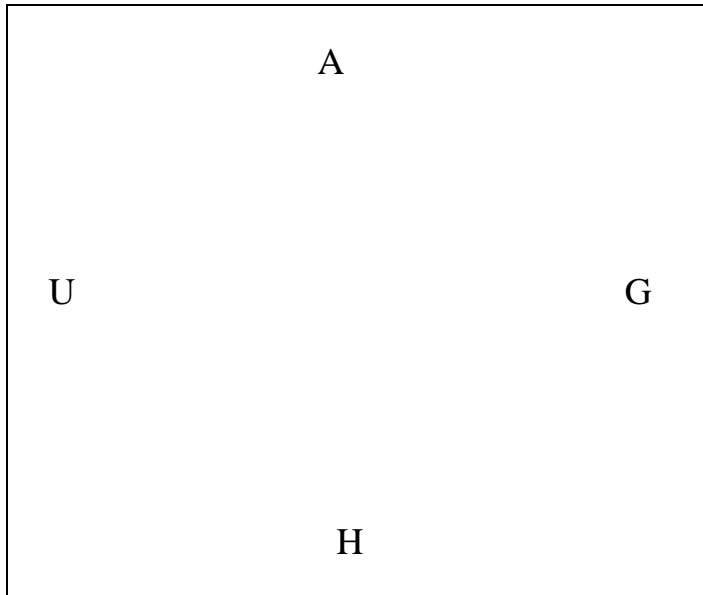
$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

You can see that these last two of the Maxwell relations look particularly useful since they

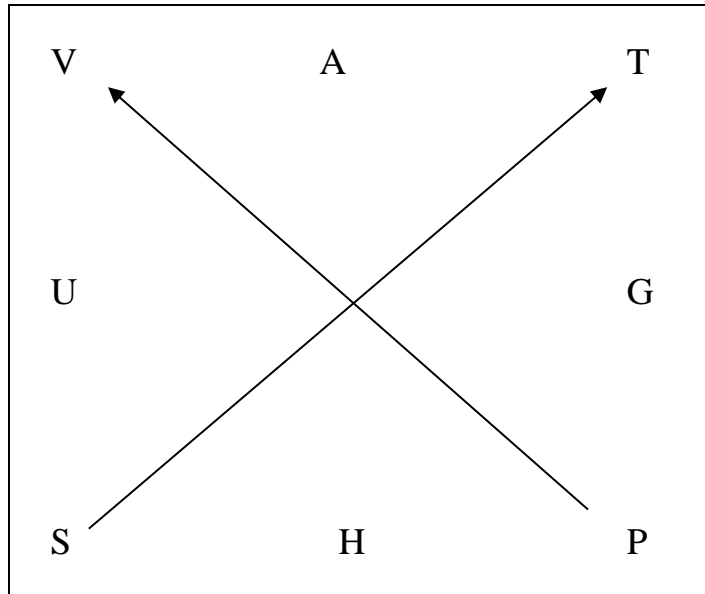
express the difficult to measure  $(\partial S/\partial V)_T$  in terms of the easy to measure  $(\partial p/\partial T)_V$ , and the difficult to measure  $-(\partial S/\partial p)_T$  in terms of the easy to measure  $(\partial V/\partial T)_p$ . These Maxwell relations are important enough that I would expect you to be able to easily derive them.

While both the Gibbs equations and Maxwell relations are very useful, and fairly easy to derive, they are hard to remember. There is a simple mnemonic device called the **thermodynamic square** which makes it very simple to remember the Maxwell relations and the Gibbs equations for the thermodynamic potentials. To construct the



thermodynamic square we draw a square. At the top of the square we put A, the first of the thermodynamic potentials alphabetically, and then proceed both alphabetically and clockwise with the rest of the potentials.

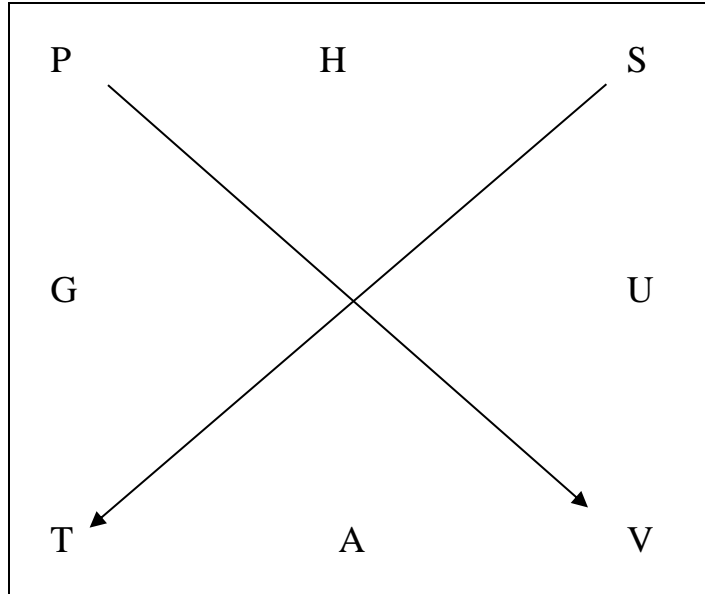
Now in the corners we put the variables common to the potentials on either side. A and G are both functions of T, G and H are both functions of p, U and H are both functions of S and U and A are both functions of V. Finally we draw an arrow from S to T and from p to V.



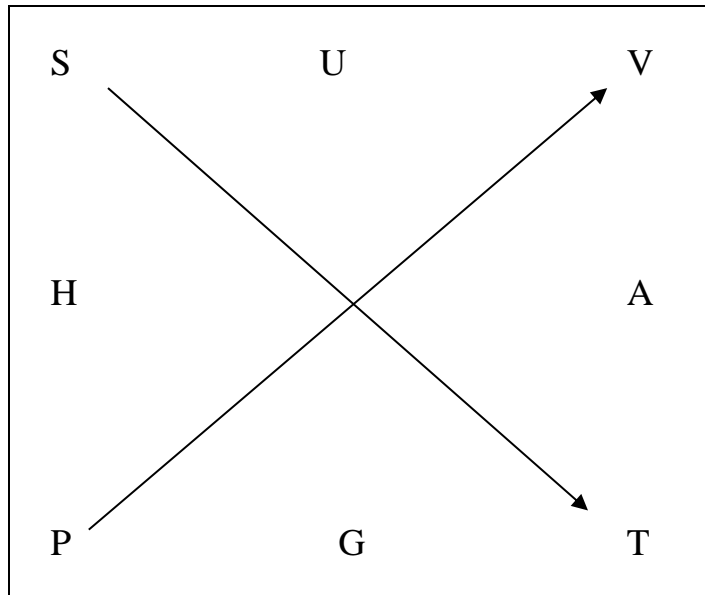
We can use the square two ways, to remember the Gibbs equations, the

differential forms for changes in the potentials, and to remember the Maxwell relations. To find the Gibbs equation for a potential, rotate the square until the potential you want to find is on the bottom of the square. In this case we'll use H. The differential form of a potential is the sum of two terms, each of which is a differential multiplied by another variable. When we place a potential on the bottom of the square, the differential (independent) variables will be the ones flanking it. For the example of dH, the differentials are dS and dp. Each of these differentials is multiplied by the variable diagonally across from it. Thus the two terms in dH are Vdp and TdS. Now all we need are the signs of the two terms. For the signs we just look at the direction of the arrows. If the arrow connecting two variables points up, the sign on the term will be positive, and if the arrow connecting the two variables points down, the sign on the term will be negative. The pV arrow points up so we have +pdV and the TS arrow points up so we have +TdS, which finally yields,  $dH = pdV + TdS$ .

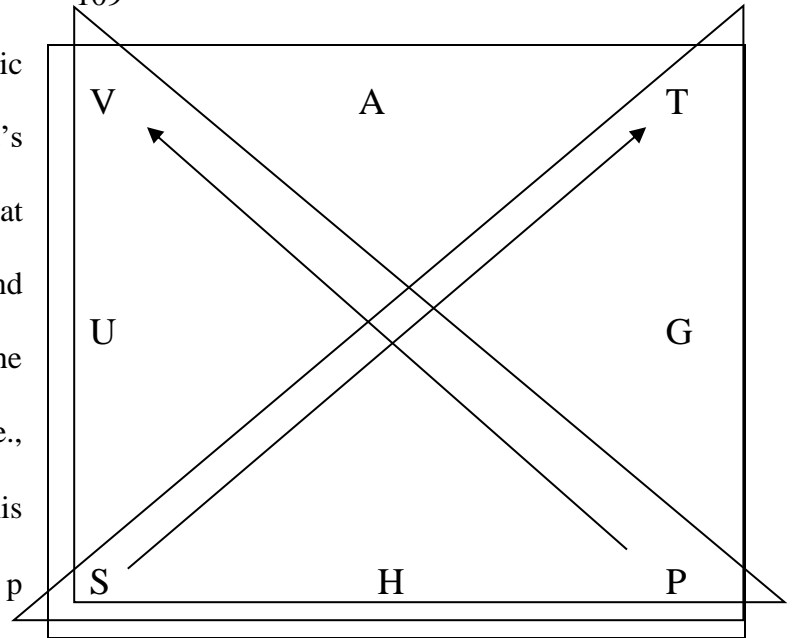
To do a different thermodynamic potential we just turn the thermodynamic square so the potential we are interested in is on the bottom. Let's use the square to get the differential of  $A$ . First we turn the square so  $A$  is on the bottom. The differential terms are  $dT$  and  $dV$ . The two terms,  $pdV$  and  $SdT$  are both negative because for both of these the arrows point down. Therefore  $dA = -pdV - SdT$ .



Let's do one last example,  $dG$ . First we turn the square so that the  $G$  is on the bottom. Q: Which variables are the differentials? [ $dp$ ,  $dT$ ] Q: What are the pairs of variables for the two terms? [ $VP, TS$ ] Therefore the two terms are  $Vdp$  and  $SdT$ . Q: What is the sign for  $Vdp$ ? [Arrow up, +] Q: What is the sign for  $SdT$ ? [arrow down, -] So  $dG = Vdp - SdT$ .

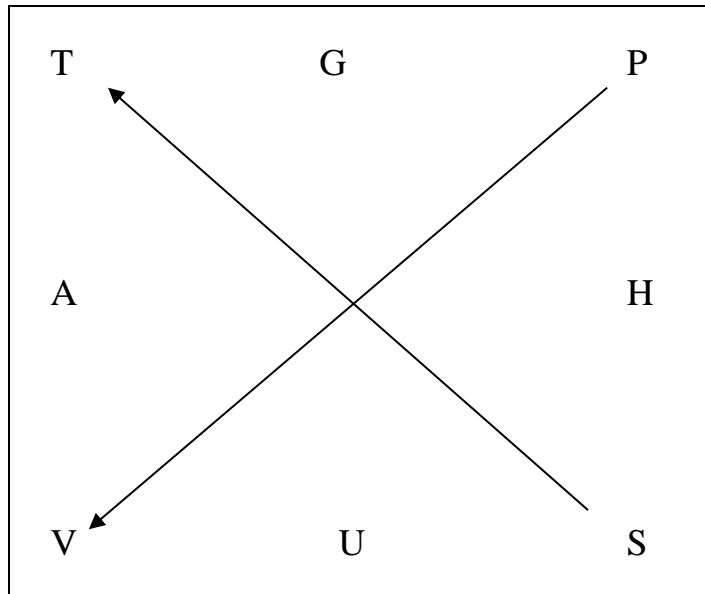


Now let's use the thermodynamic square to find Maxwell relations. First let's turn it right side up again. You can see that the pV arrow makes a triangle with p, V and S. The partial from this corner has the variables in the same positions, i.e.,  $(\partial V/\partial S)_p$ . The other triangle from this orientation of the square is made with T, p and S, which gives us the partial  $(\partial T/\partial p)_s$ .



Once again the direction of the arrow gives the direction for each term. Since both arrows go up both terms are positive. So the Maxwell relation for this side is  $(\partial V/\partial S)_p = (\partial T/\partial p)_s$ . To find other Maxwell relations just turn the square on its side.

Let's look at the Maxwell relation for the U side. Once again, we turn our square so the potential of interest is on the bottom. The first triangle is made by T, V and S. Q: WHAT IS THE CORRESPONDING PARTIAL?  $[(\partial T/\partial V)_S]$  The second triangle is made by p, S, and V. Q: WHAT IS THE PARTIAL?  $[-(\partial p/\partial S)_V]$  So this second Maxwell relation is  $(\partial T/\partial V)_S = -(\partial p/\partial S)_V$



Lecture 18

Let's see how we might use these Maxwell relations. Remember we said that for an ideal gas the energy is independent of volume at constant temperature. This is equivalent to saying that

$(\frac{\partial U}{\partial V})_T = 0$  for an ideal gas. Let's prove this, but instead of evaluating this directly for an ideal

gas, let's find an equation for  $(\frac{\partial U}{\partial V})_T$  which is true for any substance, and then apply that to the

ideal gas law. Such an equation is called a **Thermodynamic Equation of State**. In developing a

thermodynamic equation of state, we want to express  $(\frac{\partial U}{\partial V})_T$  in terms of our observables, p, V,

T, S, n,  $\alpha$ ,  $\kappa$ , and  $C_p$ . Before we start let's write down our definitions for T, p, S and V.

$$T = (\frac{\partial U}{\partial S})_V \quad p = -(\frac{\partial U}{\partial V})_S \quad V = (\frac{\partial G}{\partial p})_T \quad S = -(\frac{\partial G}{\partial T})_p$$

Let's try relating  $(\frac{\partial U}{\partial V})_T$  to temperature. To do this we need to use a version of the chain rule of partial differentiation.

$$(\frac{\partial f}{\partial x})_z = (\frac{\partial f}{\partial x})_y + (\frac{\partial f}{\partial y})_x (\frac{\partial y}{\partial x})_z$$

We are going to use this equation to find a starting point in our relation of  $(\frac{\partial U}{\partial V})_T$  to T. We do

this by first setting  $(\frac{\partial U}{\partial V})_T$  equal to  $(\frac{\partial f}{\partial x})_z$  which fixes the values of f, x and z in our new chain

rule. This sets f, x and z equal to  $U = f$ ,  $V = x$ , and  $T = z$ . Since we're relating this to temperature,

$(\frac{\partial U}{\partial S})_V$ , and since U and V are already fixed,  $(\frac{\partial U}{\partial S})_V$  has to be equal to  $(\frac{\partial f}{\partial y})_x$  which means that

S has to equal y. This means that we can write

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_S + \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T$$

Comparing this with our thermodynamic definitions of p and T we see that

$$\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial S}{\partial V}\right)_T$$

Unfortunately,  $\left(\frac{\partial S}{\partial V}\right)_T$  is inconvenient to measure, and also means that to calculate the change of

internal energy with volume we have to keep track of four variables, p, T, S and V. It would be

convenient if we could find a more useful equivalent of  $\left(\frac{\partial S}{\partial V}\right)_T$ . Examining our list of Maxwell

relations we see that  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ . So this equation now becomes

$$\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V$$

an equation which relates the change of energy with volume to easily measured observable quantities.

Earlier we had argued that  $\left(\frac{\partial U}{\partial V}\right)_T = 0$  for an ideal gas. This conclusion was based on discussions of transfer of energy from kinetic energy, the energy of heat, to potential energy, as the molecules were separated against an external force. It was a sensible argument, but by no means a proof. With our result above we can prove this assertion. We begin with

$$\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V$$

Since for an ideal gas  $p = nRT/V$ , this becomes



$$\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{nR}{V}\right) = -p + p = 0$$

This simple result shows one of the strengths of thermodynamics. It is able to obtain results that can either be applied generally, as in our thermodynamic equation, or be applied to specific models, as we have just done for the ideal gas law.

Let's use this equation to calculate the value of  $\left(\frac{\partial U}{\partial V}\right)_T$  for a van der Waals gas.

Remember that for a van der Waals gas

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Substituting into our equation for  $(\partial U/\partial V)_T$  yields

$$\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V = -p + \frac{nRT}{V - nb} = -\frac{nRT}{V - nb} + \frac{an^2}{V^2} - \frac{nRT}{V - nb} = \frac{an^2}{V^2}$$

so we see that for a gas with any kind of real properties, the energy will change with volume at constant temperature. We see also, that since the term which represents the effect of the attractive potential is the one which makes  $\left(\frac{\partial U}{\partial V}\right)_T$  non zero, that it is indeed the presence of attractive forces that makes energy change when van der Waals gasses are expanded under constant temperature conditions.

Now that we've increased our arsenal for manipulating partial derivatives, let's return to the Gibbs Free Energy. Since we often want to control a chemical reaction by changing the ambient temperature, and the Gibbs Free Energy predicts spontaneity under chemically useful conditions, let's look at **the way  $\Delta G$  changes with temperature**. Remember that

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp = -SdT + Vdp$$

and therefore  $(\partial G/\partial T)_p = -S$ . This is a useful equation as long as we know the entropy of our system (and ideally, the entropy as a function of temperature).

What if we don't know the entropy? We can derive a new relation to give us a second way to calculate the change in Gibbs Free Energy with temperature. Our definition of G was  $G = H - TS$  which can be rearranged to yield  $(G - H)/T = -S$  and therefore  $(\partial G/\partial T)_p = (G - H)/T$ . If we collect the G's on one side of the equation we get  $(\partial G/\partial T)_p - G/T = -H/T$ . This expression is difficult to integrate. However, if we recognize that because of the product rule,

$$\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = T\left(\frac{\partial}{\partial T} \frac{G}{T}\right)_p$$

This becomes

$$\left(\frac{\partial}{\partial T} \frac{G}{T}\right)_p = -\frac{H}{T^2}$$

This is known as the **Gibbs-Hemholtz equation** and relates the enthalpy to the temperature dependence of G/T. This is not a critically important equation, but the form can be useful for some types of calculations. Note that the forms

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T}$$

and

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

are of equal importance. The Gibbs-Hemholtz equation is particularly useful in calculating the change of  $\Delta G$  for a process as the temperature changes. In this case the equation becomes

$$\left(\frac{\partial}{\partial T} \frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2}$$

Note that to solve this equation for a new  $\Delta G$ , we multiply both sides by  $\partial T$  to get

$$\partial\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2} \partial T$$

We integrate the left side from  $\frac{\Delta G_1}{T_1}$  to  $\frac{\Delta G_2}{T_2}$  and the right side from  $T_1$  to  $T_2$  to obtain

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H}{T^2} \partial T .$$

Let's look now at how the **Gibbs function varies with pressure**. We begin with our differential of G,  $dG = Vdp - SdT$ . If we change pressure at constant T from  $p_1$  to  $p_2$  we get

$$\int dG = \int Vdp ,$$

and therefore,

$$G_f = G_i + \int_{p_1}^{p_2} Vdp$$

For liquids and solids, V is almost constant so this can be approximated as

$$G_f = G_i + V\Delta p$$

or for molar quantities,

$$\bar{G}_f = \bar{G}_i + \bar{V}\Delta p .$$

For gases,  $\bar{V}$  is dependent on pressure so we cannot take it out of the integral. For an ideal gas we have

$$\bar{G}_f = \bar{G}_i + \int \frac{RT}{p} dp = \bar{G}_i + RT \ln \frac{p_f}{p_i} .$$

This equation is important in showing the **pressure dependence of the Gibbs Function**, but is particularly important in the way it allows us to begin to relate  $G$  to chemical equilibria.

Before we can develop relationships involving equilibria, we have to introduce a new concept, that of the **chemical potential,  $\mu$** . The concept of the chemical potential,  $\mu$ , is developed in the following way. Remember that in our earliest discussions of energy we talked about extensive properties, properties whose values depend on the amount of material. Energy is one example of an extensive variable. This should make basic sense. For example, 2 gallons of gasoline will take you twice as far as 1 gallon of gasoline, and therefore will do twice as much work. Up to now we've only considered thermodynamic processes in which mole number is constant, in other words, closed systems. For these processes we've said that  $U = U(S,V)$ . If we allow mass transfer, i.e., **if we consider open systems, the mole number affects the energy as well**. In this case we have to write  $U = U(S,V,n)$ . If we had a system with two chemical components, then  $U$  will depend on the mole number of each of them and  $U = U(S,V,n_1,n_2)$ . **For a system of  $j$  components this becomes  $U = U(S,V,n_1,n_2,\dots,n_j)$ .**

When we wanted to describe the change in energy for a system with no mass transfer, we wrote down the differential,

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

where we have already shown that  $(\partial U/\partial S)_V = T$  and  $(\partial U/\partial V)_S = -p$ . For a one component system in which we consider mass transfer this becomes

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn$$

We call  $(\partial U/\partial n)_{S,V}$ , **the change in energy with mole number, the chemical potential,  $\mu$** . We

can thus write  $dU = TdS - pdV + \mu dn$ . For a  $j$  component system this becomes

$$dU = TdS - pdV + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_j dn_j,$$

where

$$\mu_j = \left( \frac{\partial U}{\partial n_j} \right)$$

Remember that  $G$  is defined by  $G = H - TS = U + PV - TS$ . Substituting our explicit equation for  $dU$  we get

$$dG = -SdT + Vdp + \sum_j \mu_j dn_j$$

This means that we can now define the chemical potential in terms of the free energy:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}}.$$

This is the most common definition of the chemical potential. As we will discuss in more detail later, for a given extensive quantity  $Y$ , partial derivatives of the form

$$Y_i = \left( \frac{\partial Y}{\partial n_i} \right)$$

are called partial molar quantities. Thus, the chemical potential of the  $i$ th component of a mixture is the partial molar free energy of that component, i.e.

$$\mu_i = \bar{G}_i.$$

Qualitatively, the chemical potential is the change in free energy of a system when a mole of the substance is added to a mixture of a given composition at a given temperature and pressure.

Thus, the chemical potential is a function of the composition, temperature and pressure, i.e.,

$$\mu_i = \mu_i(T, p, n_j),$$

where  $n_j$  represents the mole number of each of the components in the mixture.

An interesting line of reasoning that follows from these definitions is that if the chemical potential is the partial molar free energy of a component in a mixture, that we could figure out the free energy  $G$  for a given component by multiplying the chemical potential of the component by its mole number, i.e.,

$$G_i = n_i \mu_i = n_i \bar{G}_i,$$

and the free energy  $G$  for the whole mixture by adding up the free energies of all the components,

$$G = \sum_i G_i = \sum_i \mu_i n_i.$$

This is an exciting result. **In a system in which mass can be transferred, the Gibbs free energy is the sum of the products of the chemical potentials of the components of the system with their mole numbers.**

Let's look at this definition for a one component system again. We have  $\mu = \left( \frac{\partial G}{\partial n} \right)_{p,T}$ .

We can write  $G = n\bar{G}$ . Therefore for a one component system we have  $\mu = \left( \frac{\partial (n\bar{G})}{\partial n} \right)_{p,T} = \bar{G}$ , and

we see that for a one component system the chemical potential is equal to the molar Gibbs Free Energy.

As is our habit, let's begin our investigation of the chemical potential by considering the case of an ideal gas. First though, we'll use our result on the pressure dependence of the free

energy to relate  $\Delta G^\circ$ , the Standard Gibbs function, to  $\Delta G$  at other pressures. For ideal gases and other gases, we can use  $p$ , easily measured, as a measure of  $n$  since for an ideal gas we have

$$p = \frac{nRT}{V} \text{ and for a real gas } n \text{ and } p \text{ are related by } p = \frac{nRT}{V} \left( 1 + \frac{Bn}{V} + \frac{Cn}{V^2} + \dots \right), \text{ while for mixtures}$$

of real gases  $p$  and  $n$  are related by  $p_i = p \frac{n_i}{\sum_{j=1}^n n_j} = pX_i$ .

The  $\Delta G$ 's usually available in reference books are standard molar Gibbs free energies,  $\Delta \bar{G}^0$ . If we want to find  $\Delta G$  at some other pressure, we just use the ideal gas results we've obtained for the pressure dependence of  $\Delta G$ ,  $\Delta \bar{G}(p) = \Delta \bar{G}^0 + RT \ln \frac{p}{p^0}$ . But for a one component system,  $\Delta \bar{G}$

is  $\mu$  so this becomes  $\mu(p) = \mu^0 + RT \ln \frac{p}{p^0}$ . This relation of  $\mu$  to  $G$  leads us to the one component

version of the Gibbs-Duhem equation. Since  $dG = Vdp - SdT$  and  $d\bar{G} = d\left(\frac{G}{n}\right) = \frac{V}{n}dp - \frac{S}{n}dT$ ,

we can write  $d\mu = \frac{V}{n}dp - \frac{S}{n}dT$ .

Lecture 19

Having developed a substantial arsenal of thermodynamic functions, I'd like to return to the subject of thermodynamic equations of state. When I was an undergraduate, deriving these equations was the greatest pain of anything I was asked to do in P-Chem. When I got to grad school though, I was taught a simple sequence of steps that made most of these derivations simple. I'd like to share this with you to spare you some of the frustration that I went through.

A key concept is that most of the things we might want to measure or calculate in thermodynamics can be or must be expressed as a partial derivative. The algorithm I'm going to teach you is for reduction of any partial derivative to a function of  $S$ ,  $V$ ,  $p$ ,  $T$ ,  $\alpha$ ,  $\kappa_T$  and  $C_p$ , all of which are either easy to measure or commonly tabulated. The algorithm consists of the following sequence of steps.

Step 1) Eliminate the potentials from the partial derivative (i.e.  $U$ ,  $H$ ,  $G$ ,  $A$ )

a) Bring to numerator

b) Eliminate by using Gibbs equations (the differentials of  $H$ ,  $U$ , etc.) from the thermodynamic square.

Examples

A) Eliminate the potential from the partial derivative  $\left(\frac{\partial T}{\partial H}\right)_p$

In this case, the potential,  $H$ , is in the denominator of our derivative, so the tool we need to use to bring it to the numerator is the inverter, so

$$\left(\frac{\partial T}{\partial H}\right)_p = \frac{1}{\left(\frac{\partial H}{\partial T}\right)_p}$$



Now we eliminate the potential by substituting the Gibbs equation for dH,  $dH = TdS + Vdp$

$$\left(\frac{\partial T}{\partial H}\right)_p = \frac{1}{\left(\frac{TdS + Vdp}{dT}\right)_p} = \frac{1}{T\left(\frac{\partial S}{\partial T}\right)_p + V\left(\frac{\partial p}{\partial T}\right)_p}$$

B) Eliminate the potential from  $\left(\frac{\partial T}{\partial p}\right)_H$ . In this case, the potential is being held constant. In

cases like this the tools that we use to bring the potential into the numerator is the cyclic rule, followed by the inverter:

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{\left(\frac{\partial p}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_p} = \frac{-\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p}$$

and now proceed as in our first example.

Step 2) Eliminate  $\mu$

a) Bring it to the numerator

b) Eliminate it using the Gibbs-Duhem equation,  $d\mu = -\frac{S}{n}dT + \frac{V}{n}dp$

Example:

$$\left(\frac{\partial \mu}{\partial V}\right)_{S,n} = \left(\frac{-\frac{S}{n}dT + \frac{V}{n}dP}{dV}\right)_{S,n} = -\frac{S}{n}\left(\frac{\partial T}{\partial V}\right)_{S,n} + \frac{V}{n}\left(\frac{\partial p}{\partial V}\right)_{S,n}$$

Step 3) Eliminate S from the partial derivative

a) Bring it to the numerator

b) Use a Maxwell relation if possible

c) Use the chain rule to insert  $\partial T$  under  $\partial S$ , and replace by the appropriate heat

capacity.

### Examples

A.  $(\partial T/\partial p)_{S,n}$ . We use the Euler cyclic rule to bring S to the numerator.

$$\left(\frac{\partial T}{\partial p}\right)_S = -\frac{1}{\left(\frac{\partial p}{\partial S}\right)_T \left(\frac{\partial T}{\partial p}\right)_p} = \frac{-\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p}$$

We can use a Maxwell relation to obtain

$$\left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial T}\right)_p / \left(\frac{\partial S}{\partial T}\right)_p$$

Now  $(\partial S/\partial T)_p$  can be related to  $C_p$  by  $C_p = T(\partial S/\partial T)_p$  since  $q_p = TdS$  at constant p. Similarly we can show that  $C_v = T(\partial S/\partial T)_v$ . So finally we obtain,

$$\left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial T}\right)_p / \frac{1}{T} C_p$$

For our second example, let's look at a case where we insert  $\partial T$  under  $\partial S$ . When will we have to do this? When we can't find a Maxwell relation that fits!

$$\left(\frac{\partial S}{\partial p}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial p}\right)_V = \frac{1}{T} C_v \left(\frac{\partial T}{\partial p}\right)_V$$

Step 4) Bring V to numerator, then use

a)  $(\partial V/\partial T)_p = V\alpha$

b)  $(\partial V/\partial p)_T = -V\kappa_T$

Example:  $(\partial T/\partial p)_V = ?$  Q: What do we use to move V into the numerator? [Euler cyclic rule]

$$\left(\frac{\partial T}{\partial p}\right)_V = \frac{-1}{\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p} = \frac{-\left(\frac{\partial V}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_p} = \frac{-\kappa_T V}{-V\alpha} = \frac{\kappa_T}{\alpha}$$

And finally

Step 5) Get rid of  $C_v$  using  $C_p = C_v + TV\alpha^2/\kappa_T$ .

Now let's do a multistep example. Let's calculate the change of temperature with pressure under conditions of constant entropy,  $(\partial T/\partial p)_s$ . Since there are neither thermodynamic potentials nor a chemical potential in this partial, we can move directly to step three. First we use the cyclic rule:

$$\left(\frac{\partial T}{\partial p}\right)_s \left(\frac{\partial p}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_p = -1$$

which yields

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{-1}{\left(\frac{\partial p}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_p}$$

Now we bring S to the numerator using the inverter.

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{-\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p}$$

The lower term is simply  $C_p/T$  so we now have

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{-T\left(\frac{\partial S}{\partial p}\right)_T}{C_p}$$

Looking at our thermodynamic square we find a Maxwell Relation

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p,$$

which when inserted into our equation yields

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{T\left(\frac{\partial V}{\partial T}\right)_p}{C_p}$$

Noting that our partial derivative is equal to  $V\alpha$ , we get as our final result

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{TV\alpha}{C_p}$$

As a second example let's use the same method to calculate the change in energy for a real gas during an isothermal compression,  $dU = (\partial U/\partial p)_{T,n} dp$ . For this calculation we need to eliminate  $(\partial U/\partial p)_{T,n}$ . First we eliminate  $dU$  using  $dU = TdS - pdV$ .

$$\left(\frac{\partial U}{\partial p}\right)_T = \left(\frac{T\partial S - p\partial V}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T$$

Now we eliminate  $\partial S$ . First we turn to the thermodynamic square to get  $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$ , so

$$\left(\frac{\partial U}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T = -TV\alpha + p\kappa_T V$$

This simple result is an example of the power of thermodynamics. In order to obtain our earlier result about the isothermal change of energy for an ideal gas,  $dU = C_v dT$ , we had to make certain assumptions about the gas, i.e., that there were no intermolecular potentials and that therefore  $\left(\frac{\partial U}{\partial V}\right)_T = 0$ . But here we have a completely general result with no reference to a model for the structure of our system and no approximations.

As a final example lets derive the result we use in step 5,

$$C_p - C_v = \frac{TV\alpha^2}{\kappa}.$$

This is a more challenging reduction of partial derivatives since our algorithm by itself is not enough – attempts to solve this problem by using the algorithm alone simply yield the equation

$$C_p - C_v = C_p - C_v.$$

We start simply enough using the definitions of  $C_p$  and  $C_v$ ,

$$C_p - C_v = \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_v.$$

We now proceed by expressing H in terms of U using the definition

$$H = U + pV.$$

$$\begin{aligned} C_p - C_v &= \left( \frac{\partial(U + pV)}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_v \\ &= \left( \frac{\partial U}{\partial T} \right)_p + \left( \frac{\partial(pV)}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_v \\ &= \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_v \end{aligned}$$

It is at this point that our algorithm fails. When we run into a roadblock of this sort, the solution is to try a different approach. The only one of our tools for manipulating partial derivatives that is not used in our algorithm is the chain rule for partial differentiation. We use it here to relate

the partials  $\left( \frac{\partial U}{\partial T} \right)_p$  and  $\left( \frac{\partial U}{\partial T} \right)_v$ .

Remember that our chain rule for partial differentials is

$$\left(\frac{\partial f}{\partial x_1}\right)_{x_2} = \left(\frac{\partial f}{\partial y_1}\right)_{y_2} \left(\frac{\partial y_1}{\partial x_1}\right)_{x_2} + \left(\frac{\partial f}{\partial y_2}\right)_{y_1} \left(\frac{\partial y_2}{\partial x_1}\right)_{x_2}.$$

If we choose  $\left(\frac{\partial U}{\partial T}\right)_p$  to be  $\left(\frac{\partial f}{\partial x_1}\right)_{x_2}$  and  $\left(\frac{\partial U}{\partial T}\right)_v$  to be  $\left(\frac{\partial f}{\partial y_1}\right)_{y_2}$ , this fixes all our variables, with f

= U,  $x_1 = T$ ,  $x_2 = p$ ,  $y_1 = T$  and  $y_2 = V$ . Plugging these into the chain rule we get

$$\begin{aligned} \left(\frac{\partial U}{\partial T}\right)_p &= \left(\frac{\partial U}{\partial T}\right)_v \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \\ &= \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \end{aligned}$$

Substituting this into our equation for  $C_p - C_v$  we get

$$\begin{aligned} C_p - C_v &= \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v \\ &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p \\ &= \left( \left(\frac{\partial U}{\partial V}\right)_T + p \right) \left(\frac{\partial V}{\partial T}\right)_p \end{aligned}$$

We now proceed as usual with our algorithm, substituting the Gibbs equation for U, and yielding

$$\begin{aligned} C_p - C_v &= \left( \left( \frac{-pdV + TdS}{\partial V} \right)_T + p \right) \left(\frac{\partial V}{\partial T}\right)_p \\ &= \left( -p + T \left(\frac{dS}{\partial V}\right)_T + p \right) \left(\frac{\partial V}{\partial T}\right)_p \\ &= T \left(\frac{dS}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \end{aligned}$$

We next get rid of S. We look at our thermodynamic square and find that we have a useful

Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V.$$

Substituting this in our equation yields

$$C_p - C_v = T \left(\frac{dp}{dT}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

We now move the  $V$  into the numerator using the cyclic rule.

$$\begin{aligned} C_p - C_v &= T \frac{-1}{\left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial p}{\partial T}\right)_T} \left(\frac{\partial V}{\partial T}\right)_p \\ &= T \frac{-\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \left(\frac{\partial V}{\partial T}\right)_p \end{aligned}$$

Finally, using the relations  $\left(\frac{\partial V}{\partial T}\right)_p = V\alpha$  and  $-\left(\frac{\partial V}{\partial p}\right)_T = V\kappa$ , we get

$$C_p - C_v = \frac{TV\alpha^2}{\kappa}$$

Lecture 20

Let's return now to our discussion of the **chemical potential**. We showed that for a perfect gas,  $\mu = \mu^0 + RT \ln \frac{P}{P^0}$ . However, if, as we want, we relate  $\mu$  to real chemical systems, we will have to deal with **real gases**. We could deal with this situation by going back to our definition of  $\mu$  for a one component system,  $\mu = \bar{G}$ , and recalculate its pressure dependence by inserting the virial equation,

$$\bar{G}_f - \bar{G}_i = \int_{p_i}^{p_f} \bar{V} dp$$

$$\bar{V} = \frac{RT}{p} (1 + B'p + C'p^2)$$

and integrating to yield

$$\bar{G}_f = \bar{G}^0 + RT \int \left( \frac{1}{p} + B' + C'p \right) dp = \bar{G}^0 + RT \left( \ln \frac{p}{p^0} + B'(p - p^0) + \frac{C'}{2} (p^2 - p^{02}) \right)$$

which gives us for  $\mu$  for a real gas,

$$\mu = \mu^0 + RT \left( \ln \frac{p}{p^0} + B'(p - p^0) + \frac{C'}{2} (p^2 - p^{02}) + \dots \right)$$

This equation is far more accurate for real gases than our ideal gas version, but it has the disadvantage that it is awkward to handle with all its terms, and that we need a set of coefficients not just for each gas, but for each gas at each temperature. These considerations led G.N. Lewis to suggest the following equation for the pressure dependence of  $\mu$  for real gases:

$$\mu = \mu^0 + RT \ln \frac{f}{p^0},$$

where  $f$  is called the **fugacity** and has units of pressure. Remember that for an ideal gas, the term



$RT \ln p/p^0$  comes from integration of  $\int V dp$ . Replacing the pressure with the fugacity is a reflection that the pressure dependence of the volume for a real gas is different than that for an ideal gas.

**Fugacity is related to pressure by the definition  $f = \gamma p$** , where  $\gamma$  is called the **fugacity coefficient**, is a function of  $p$  and  $T$ , and is different for each substance. As with any real gas property, we want the fugacity to reduce to the pressure in the limit of low pressure, since real gases behave like ideal gases in the limit of low pressure, i.e.,

$$\lim_{p \rightarrow 0} f = p$$

Since  $f = \gamma p$ , we can also say,

$$\lim_{p \rightarrow 0} \gamma = 1.$$

It is important to note that like the virial coefficients that we use to calculate the  $p$ ,  $V$ ,  $T$  dependence of real gases, **the fugacity coefficient is an empirical quantity**, which has to be measured or calculated from other empirical quantities. To see how we can calculate this let's insert our definition of fugacity into our equation for  $\mu$  as a function of  $p$ .

$$\mu = \mu^0 + RT \ln \frac{f}{p^0} = \mu^0 + RT \ln \frac{\gamma p}{p^0} = \mu^0 + RT \ln \frac{p}{p^0} + RT \ln \gamma$$

It is interesting to note here that in this last form, our first two terms are the same as our expression for the chemical potential of an ideal gas. Remember that an ideal gas is distinguished from a real gas because its intermolecular forces are negligible. Since our expression for  $\mu$  for a real gas is identical to the expression for an ideal gas except for the term  $RT \ln \gamma$ ,  $RT \ln \gamma$  must contain all the information about the effect of the intermolecular forces of a substance on the chemical potential.

To calculate the value of  $\gamma$ , begin with  $d\mu = d\bar{G} = \bar{V}dp$  (constant T). Then

$$\int_{p'}^p V_m dp = \mu - \mu' = RT \ln \frac{f}{p^0} - RT \ln \frac{f'}{p^0} = RT \ln \frac{f}{f'}$$

For a perfect gas the difference between  $\mu$  at two different pressures is

$$\int_{p'}^p V_m^0 dp = \mu^0 - \mu'^0 = RT \ln \frac{p}{p'}$$

where here the superscript  $^0$  indicates an ideal gas. If we subtract the ideal gas value from the real gas value we will get

$$\int_{p'}^p (V_m - V_m^0) dp = RT \left[ \ln \frac{f}{f'} - \ln \frac{p}{p'} \right]$$

which rearranges to

$$\ln \left( \frac{fp'}{f'p} \right) = \frac{1}{RT} \int_{p'}^p (V_m - V_m^0) dp.$$

We can simplify this equation by taking its limit as  $p' \rightarrow 0$  and noting that

$$\lim_{p' \rightarrow 0} f' = p'$$

Therefore in the limit of low pressures, our equation becomes

$$\ln \left( \frac{f}{p} \right) = \frac{1}{RT} \int_0^p (V_m - V_m^0) dp$$

But  $f = \gamma p$  so this becomes

$$\ln \gamma = \frac{1}{RT} \int_0^p (V_m - V_m^0) dp$$

For an ideal gas  $V_m = RT/p$ . Now remember we defined a property of gases called the compression factor  $Z$ , where  $Z = pV_m/RT$ . For ideal gases  $Z = 1$ , but for real gases we can write  $V_m = RTZ/p$ .

Therefore, we can write

$$\ln \gamma = \frac{1}{RT} \int_0^p \left( \frac{RTZ}{p} - \frac{RT}{p} \right) dp = \int_0^p \left( \frac{Z-1}{p} \right) dp.$$

Note that if we return to our virial description of a real gas we have

$$Z = \frac{pV_m}{RT} = (1 + B'p + C'p^2 + \dots),$$

so

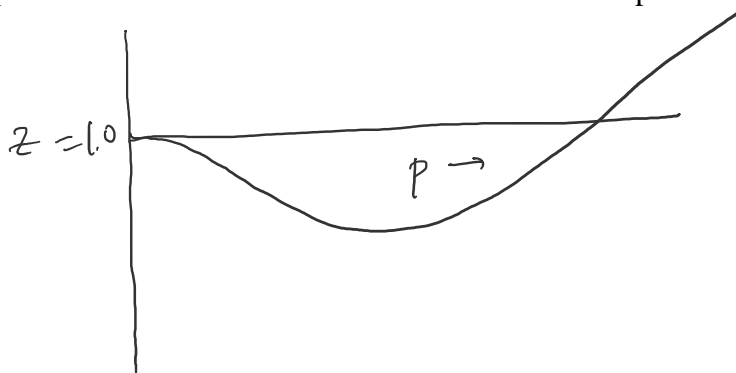
$$\ln \gamma = \int_0^p (B' + C'p + \dots) dp = B'p + \frac{1}{2}C'p^2 + \dots$$

This result is consistent with our understanding of  $\ln \gamma$  as the component of the fugacity corresponding to the intermolecular forces.

Now let's look at the implications of this result. Our equation for the chemical potential of a real gas is

$$\mu = \mu^0 + RT \ln \frac{p}{p^0} + RT \ln \gamma$$

The first two terms correspond to the chemical potential of an ideal gas so this third term with  $\ln \gamma$  will tell us how the real gas differs from an ideal gas. Since our equation for  $\gamma$  is in terms of the compression factor lets remind ourselves how the compression factor varies with pressure.



At pressures close to 0, the compression factor is close to the ideal gas value of one. As we increase the pressure, the attractive forces come into play and  $z$  drops below one. For most

gases, at pressures somewhere between 200 and 400 atm, the repulsive forces begin to dominate and  $z$  becomes greater than one.

We see from this that at pressures less than 200 atm, since  $Z < 1$ ,  $RT \ln \gamma$  is less than one and therefore  $\mu_{\text{real}} < \mu_{\text{ideal}}$ . If we have a gas at high pressure, where the repulsive forces dominate and  $Z > 1$ ,  $\ln \gamma > 0$  and therefore at high pressures  $\mu_{\text{real}} > \mu_{\text{ideal}}$ .