

Lectures 5-6

That's all I really want to cover in Chapter One. Now I'd like to move on to Chapter Two, which deals with the first law of thermodynamics. Remember that in our first lecture I said that thermodynamics asks what can or can't happen when energy is added to a system. This statement begs the questions "How can we get energy into or out of a system?" and "How does this affect the total energy of our system?"

The first means of **transferring energy** that we'll discuss is **work**. The most common type of work, **mechanical work**, is simply defined as **force x distance**. A more formal statement of this definition is "For an infinitesimal displacement dx along the x axis, the work, $dw = -F_x dx$,

and for a finite displacement along the x -axis from x_1 to x_2 , $w = -\int_{x_1}^{x_2} F_x dx$, where F_x is the component

of the force along the x axis." It is important to understand in this definition that the force that really matters here is not the force applied to the system, but the resisting force. Thus if there is a system with little resistance to motion, the same work is done if I apply just barely enough force to displace the system as if I applied force far in excess of the resisting force. [WHICH DO YOU THINK IS THE MORE EFFICIENT USE OF FORCE? WHAT DO YOU THINK HAPPENS TO THE EXCESS FORCE IN THE LATTER CASE?]

An implication of this definition is that **if there is no displacement, no work is accomplished**. So for example, no matter how hard I push on this whiteboard, if it doesn't move no work has been done. On the other hand, if I slide this eraser across the table I have done work, because a displacement has occurred. Q: IS THERE A WAY FOR DISPLACEMENT TO OCCUR, BUT STILL HAVE NO WORK?

If forces are exerted along all **three Cartesian axes**, x , y , and z , then the work done is

$$w = -\left[\int_{x_1}^{x_2} F_x dx + \int_{y_1}^{y_2} F_y dy + \int_{z_1}^{z_2} F_z dz\right]$$

which can be more compactly written as

$$w = -\int_{r_1}^{r_2} F \cdot dr$$

where the dot indicates what is called a scalar or dot product, $r_1 = (x_1, y_1, z_1)$; $r_2 = (x_2, y_2, z_2)$ and $F = (F_x, F_y, F_z)$.

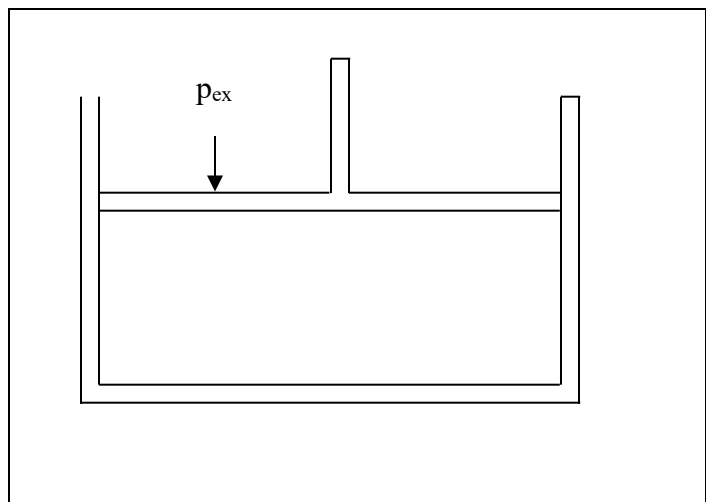
Now let's consider some examples. If I lift this eraser, I've done work on it because I've moved it against an opposing force, gravity, and as a result, I've increased its gravitational energy. The work is given by

$$w = -\int_{z_1}^{z_2} -mg dz = mg(z_2 - z_1),$$

where $-mg$, the mass of the eraser times the acceleration, is the force in the z direction.

Now let's consider the work done when a gas expands or is compressed. This is an important system that allows us to develop many of the ideas and functions of thermodynamics, which we will later exploit in our analysis of more interesting systems. We need to start by defining our system. Consider a gas in a cylindrical container, bounded at the top by a massless frictionless piston (available in all neighborhood P-Chem supply stores).

We specify that the external pressure is p_{ex} . Q: IF THE EXTERNAL PRESSURE IS p_{ex} AND THE AREA OF THE PISTON IS A , WHAT IS THE FORCE EXERTED ON THE PISTON? [$F = p_{ex} * A$] The gas is expanded by



moving the piston upward against the external pressure p_{ex} and is compressed by moving the piston downward with pressure p_{ex} . We require that such expansions and compressions are **quasistatic**. This just means that no turbulence is created in course of the expansion. Q: WHY IS IT IMPORTANT TO SPECIFY THAT THERE IS NO TURBULENCE? [Turbulence is existence of regions of different pressure throughout the gas. This results in two problems. First the system is not in equilibrium and second the pressure is not well defined.] Now let's say that the system expands so that the piston moves up by a distance dz . How much work is done? Remember first our definition of differential work, $dw = -F * dz$, and now our definition of pressure, $p_{\text{ex}} = F/A$, which implies, $p_{\text{ex}} * A = F$. Combining the definition of pressure with the definition of differential work we get

$$dw = -p_{\text{ex}} * A * dz$$

But for a cylinder $A * dz$ is the differential volume, dV , so this equation becomes $dw = - p_{\text{ex}} dV$.

If the volume increases, the system is doing work, its energy decreases and therefore **the work is negative**. **If instead we compress the gas**, work is done on the system, its energy increases, and so **the work is positive**. For a macroscopic displacement the work is given by the integral

$$w = - \int_{V_1}^{V_2} p_{\text{ex}} dV$$

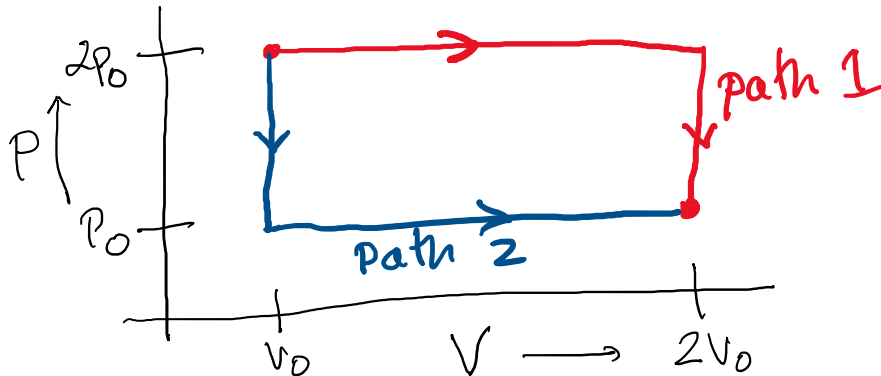
If our pressure is in Pa and our volume in m^3 then our work has units of Joules.

I need to make a very important point here. **The amount of work that's done during a given expansion depends on the way that the expansion is done**. This means that **work is not a state function**. To understand both what a state function is, and why work is not a state function, remember that the state of a system, and therefore all the state variables of a system, depends only on the values of the state variables, and not on the history of the system. Therefore, the difference

in the value of a state function when changing from one state to another depends only on the initial and final states of the system, and not on the path taken between the two states. Since the amount of work depends on the path from the initial volume to the final volume, it is not a state function. We will call work and other functions whose values are path dependent **path functions**.

An even more common example of a path function is life itself. Remember that the poet Robert Frost wrote “And I, I took the road less traveled by and that has made all the difference.” If life was a state function it wouldn't matter what road you took.

In the next few lectures you'll see several examples of different paths leading to different amounts of work, but there's a very nice example that I'd like to go over with you. We want to take a sample of gas at initial state $(2p_0, V_0)$ to a final state of $(p_0, 2V_0)$. We'll use two paths and calculate the work. The first path has two steps. First at a constant pressure of $2p_0$, we'll expand



our gas from volume V_0 to volume $2V_0$. Since p_{ex} is constant we can pull it out of the integral to get

$$w = -p_{ex} \int_{V_1}^{V_2} dV = -p_{ex}(V_2 - V_1) = -p_{ex}\Delta V = -2p_0V_0$$

In the second step, we cool the sample at constant volume, until the pressure reaches p_0 . WHAT IS THE WORK DONE IN THIS STEP? So the total work for the first path is $-2p_0V_0$.

In our second path, the first step will be to cool the sample at a constant volume of V_0 until

the pressure goes down to p_0 . WHAT IS THE WORK IN THIS STEP? The second step will be to expand the gas from V_0 to $2V_0$ at a constant pressure p_0 . WHAT IS THE WORK IN THIS STEP? $[-p_0V_0]$. So the total work in this second path is $-p_0V_0$. Two different paths - two different amounts of work done.

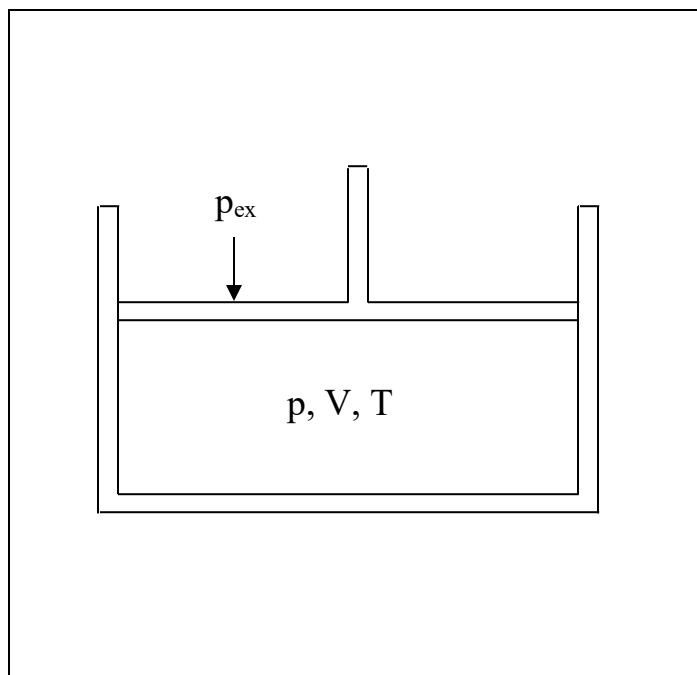
As you can see, **to evaluate the amount of work done, we need to specify the nature of the external pressure, and the way it changes with volume**, so let's consider some other specific cases. The next case we'll consider is free expansion. Free expansion means expansion into a vacuum, i.e., $p_{ex} = 0$. Therefore,

$$w = -\int p_{ex} dV = -p_{ex} \int dV = 0$$

Free expansion is just a special case of expansion against a constant external pressure, which we did a moment ago.

Our next case is called a **reversible expansion**. Once again we are faced with a word in thermodynamics that has a specific meaning beyond its everyday use. When we say that a change in thermodynamics is **reversible**, we mean that **an infinitesimal modification of a variable will reverse that process**. To help clarify this concept, let's consider an example.

Consider a cylinder enclosed on top by a massless frictionless piston. The cylinder contains a gas with internal pressure p , volume V , and temperature T . The external pressure, which is not necessarily equal to the internal pressure,



is p_{ex} . If p_{ex} is much less than p , as in a free expansion, and we allow the gas to expand, this will be an **irreversible process**. Why? Say for example that $p = 100$ Torr and $p_{\text{ex}} = 0$ Torr. Since $p > p_{\text{ex}}$, if we release the piston the gas will expand. Now suppose we increase the external pressure to 1 Torr, a very small change. p is still greater than p_{ex} , so the gas will still expand. Since a small change in the external pressure doesn't reverse our process, expansion, the process is not reversible under these conditions.

Suppose now that p_{ex} starts off equal to p and changes so slowly that the internal and external pressures are always maintained in a state of near equilibrium. Now the expansion will be reversible. A crude example of this is to let $p = 100.5$ Torr and $p_{\text{ex}} = 100$ Torr. If we release the piston the gas will expand. Now if we increase p_{ex} by one Torr to 101 Torr, the gas compresses. According to our definition the process is reversible. The important feature of a **reversible expansion** is that during such a process the **system is always in mechanical equilibrium with its surroundings**. [What variable would be in equilibrium if the reversible process was heating rather than expansion?]

The first implication of the concept of reversibility is that during a reversible expansion, the internal and external pressures are equal, i.e., $p_{\text{ex}} = p$. So for a reversible expansion or compression,

$$w_{\text{rev}} = -\int_{V_1}^{V_2} p dV$$

This is the first instance of an important concept. **Variables describing systems are more powerful than variables describing the surroundings, since in principle we can know everything about a system, and therefore can know the state of the system, and can know equations of state describing the relationship between state variables.** Thus, once we know

how p and V are related for a given system we can evaluate the integral. In contrast, **we can never know the surroundings with the same degree of completeness since they are so large.**

Let's illustrate this with the case of an **isothermal reversible expansion in a closed system. We will consider the case where our gas is ideal.** In these derivations, it's always best to begin with your fundamental equation, and then add the conditions that apply to the problem. For expansion of a gas, the most general equation is

$$w = -\int_{V_1}^{V_2} p_{\text{ex}} dV$$

Now we add the condition of reversibility. [What change do we make in this equation because the expansion is reversible?]

$$w_{\text{rev}} = -\int_{V_1}^{V_2} p dV$$

In order to evaluate this integral, since p is a function of V , we need to know how p changes when V changes. Since for an ideal gas $p = nRT/V$, this becomes

$$w_{\text{rev}} = -\int_{V_1}^{V_2} nRT \frac{dV}{V}$$

Now we add the constraint that the expansion is isothermal, which means that T is constant. The constraint of a closed system ensures that n is constant, so we can pull both n and T out of the integral to obtain

$$w_{\text{rev}} = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

and finally

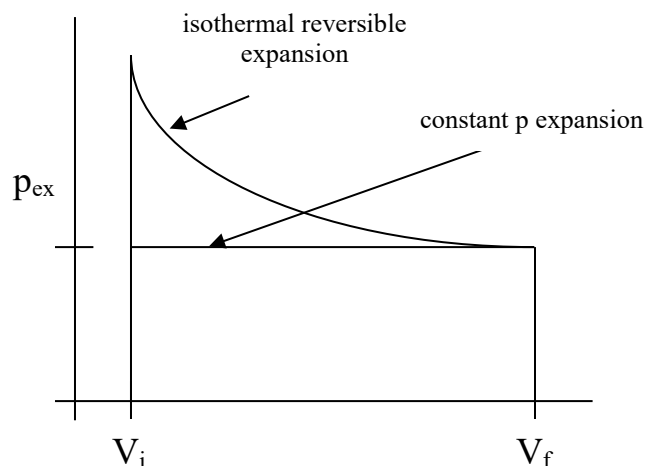
$$w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1}$$

We can illustrate the amount of work in a process graphically by remembering that

$$\int f(x) = \text{area under } f(x).$$

Let's look graphically at the work of an expansion from V_i to V_f under conditions of constant external pressure, and in an isothermal reversible expansion, where p_f is the same in both cases. For the constant pressure expansion, since p_{ex} is constant, the work is

simply $-p_{\text{ex}} (V_f - V_i)$. The reversible expansion, for which p_i is much higher, has a much larger area. Therefore we find that $w_{\text{rev}} > w_{\text{irrev}}$. We will find later that this result is even stronger, that in fact, the reversible work is the maximum work which can be done by the system; $w_{\text{rev}} = w_{\text{max}}$. In addition, we will show later that this result is valid not just for perfect gases, but for all systems.



In many problems where we calculate work due to the expansion of a gas, the pressure is expressed in atmospheres and the volumes in liters. This leads to the problem that the work is expressed in an unfamiliar unit of energy, the liter-atmosphere. How do we convert it to something more familiar like joules? WHAT CONSTANT DO WE KNOW THAT HAS L - ATM IN IT? [R, gas constant, $0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$] R is also tabulated with units which include joules, with a value of $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. If we divide these two constants the K and mol cancel and we have our conversion factor, 101 J/L-atm. This will be useful for many problems.

In discussing work, we were only discussing one mode of increasing or decreasing energy. Our next questions are: “Are there other forms of energy transfer?” and “Are the forms of energy transfer independent of each other, or are they somehow related?”

Work is a form of **energy transfer**. By definition, if I do work on a system, its energy increases. If a system performs work, its energy decreases. Now let's consider some cases where I do work. If I lift an eraser, I do work and if I push this door I do work as well. Now I'm going to push against this wall. AM I DOING WORK? [No. $dz = 0$] WELL, AM I EXPENDING ENERGY? [Sure feels like it to me] IF I'M EXPENDING ENERGY AND NOT DOING WORK, WHERE IS THE ENERGY GOING? [Heat] Now consider what happens when I slide an eraser. At first I do work on it and get it to slide. But then it stops. What happened to the energy I put into it? [Friction converts kinetic energy to heat]. This suggests that **heat is another form of energy transfer**.

These types of considerations led to the **First Law of Thermodynamics**. A qualitative statement of this law is "**energy is conserved**". In other words, energy can be converted from one form to another, but it cannot be destroyed. A more formal statement of the first law is "**The work needed to change an adiabatic system from one state to another is independent of the path.**" What this implies is that the adiabatic work, w_{ad} , **is a state function**, since state functions are functions that are path independent. Note that **in general work is *not* a state function**. It is specifically the adiabatic work that is a state function. In addition, this implies that the adiabatic work will be the same as the energy difference. Why is the adiabatic work equal to the energy added? Remember that adiabatic means that there is no thermal interaction between the system and the surroundings, i.e., there is no heat loss. In the case of our eraser, we did work to put energy into our system, but it was all lost to heat. If we hadn't lost energy to heat all our energy would still have been in the system. So in an adiabatic system if we transfer energy into the system as work, there's no way for the energy to get out, and it's trapped in the system.

To formalize this relation between energy and adiabatic work, and to ease some possible confusion arising from w_{ad} being a state function while w is not, we define the energy difference,

$$\Delta U = U_2 - U_1 = w_{\text{ad}}.$$

In other words, when we do work on an adiabatic system, one in which no heat transfer is allowed, all of the work goes to increasing the energy of the system.

Lectures 7-8

At this point we have quantitative definitions for work, $-\int F \cdot dr$, and change in energy, $\Delta U = w_{ad}$. We have no such quantitative definition for heat. WHAT ARE SOME OF THE CHARACTERISTICS OF HEAT? [Energy transfer, distinct from work, associated with temperature differences]

We can use the first law to help define heat quantitatively. Suppose that we have taken some **adiabatic system** from state 1 to state 2. The energy change will be $\Delta E = w_{ad}$. Now suppose we strip away the insulation to make this a **diathermal** system, one in which there is no barrier to heat flow. Now once again we go between state one and state two, but since work is in general not a state function, the work for this path will be different, $w_{ad} \neq w_{dia}$. For example, the work needed to increase the temperature of 1 gram of water 10K adiabatically is 42 J. The work to increase the temperature of the same system 10K by diathermal processes could be 6 J, 60 J, 600 J or even 6000 J depending on the conditions we choose. The difference between the work done in the two cases is defined as the heat, q .

$$w_{ad} - w \equiv q$$

Since we know how to measure the work in either case, we now have a definition of heat that is both quantitative and quantifiable. Like work, **heat is path dependent and is therefore not a state function.**

Note that if we substitute ΔU for w_{ad} in the definition of heat we obtain

$$q = \Delta U - w \text{ or}$$

$$\Delta U = q + w,$$

a more familiar statement of the first law. [WHY IS THIS EQUIVALENT TO THE STATEMENT "ENERGY

IS CONSERVED?] For an infinitesimal change of energy this becomes

$$dU = dq + dw.$$

There are many different kinds of work. We have mentioned two, the work of expansion of a gas ($dw = -p dV$) and moving an object against gravity. ($dw = mgdh$). There are other kinds of work that are of interest to a chemist. The three most important are the work involved in moving a charge against an electric field, the work involved in expanding a surface, and for polymer chemists, the work involved in stretching an elastic object, like a rubber band.

The last case is the simplest, with the work given simply by $dw = f dl$ where f is the force necessary to stretch the sample, and dl is the amount the sample lengthens. This follows directly from our definition of work as $dw = \mathbf{f} \cdot d\mathbf{r}$.

Our next case is also one that you should be familiar with, the case of moving a charge against a potential difference or electric field. This form of work is necessary when we consider the thermodynamics of charged systems in solution, or of electrochemistry. In this case we know from physics that the work required to move a charge against an electric field is given by $dw = -\Phi dQ$, where Φ is the potential difference or voltage against which the particle is moving and dQ is the total charge that is moved.

The third case is the one that is probably least familiar to you, and is the case of an expanding surface. In this case the differential work is given by $dw = \gamma^{\alpha\beta} dA$, where $\gamma^{\alpha\beta}$ is called the surface tension, and A is the surface area.

Notice that certain variables seem to be naturally paired in our discussion of work, like p and V , f and l , $\gamma^{\alpha\beta}$ and A . Note that all these pairs of variables have two things in common. First each pair is the product of an extensive and an intensive variable. Pressure, force, electric potential

and surface tension are all intensive variables, while volume, length, surface area and charge are all extensive. The second common feature is that the product of each of these pairs of variables is energy. Pairs of variables whose product is energy are called **canonical variables**. We will see other examples of canonical variables as our discussion of thermodynamics develops.

Since energy = $dq + dw$, **when pV work is the only kind that we can do, our energy change is $dq - pdV$** and we can write that $U = U(q, V)$, a function of two variables. But **when we have more complex systems which can also do all of these other kinds of work, then the work term contains all of these expressions**, $dU = q - p_{\text{ex}}dV - \Phi dQ + f dl + \gamma^{\alpha\beta} dA$, and we write $U = U(q, V, Q, l, A)$. The net result is that **as we increase the complexity of the system, the number of variables we have to consider increases**. Notice that the independent variables are the ones represented in the differentials.

At this point I'd like to introduce a **rigorous and objective standard** with which to define a **state function**. Remember that we defined a state function as one that depends only on the value of its state variables and not on its history. While a useful characteristic of state functions, this hardly helps us to identify which functions are state functions and which are not. Developing a tool to allow us to unambiguously identify state functions can simplify life for us.

Suppose we are interested in knowing the change in some state function X when we go from state i to state f . In state i , X has the value X_i and in state f , X has the value X_f . Since the value of X in each state is independent of how we got there, the **change in X** will also be independent of path, and will be given by $X_2 - X_1$, the difference between the values of X in the initial and final states. This can be expressed mathematically as

$$\int_1^2 dX = X_2 - X_1 = \Delta X$$

When we have a function like dU whose integral is path independent we say that dU is an exact differential. Therefore our formal definition of a state function will be that **a state function is a function whose differential is exact.**

In order to calculate **work** and **heat** we **must specify the path in our integral.** In fact, this is what we were doing when we calculated work and had to state that the conditions were either isothermal or constant pressure, for example. The isothermal and constant pressure conditions are two examples of paths. We write this formally as

$$\int_1^2 dw = w$$

Note that because the work is path dependent, we cannot write the definite integral simply as the difference between a final value of the function w and an initial value of the same function.

If we have a function like work or life which is path dependent, we say that it's differential, dw or $d\text{life}$, is an inexact differential. Inexact differentials are sometimes symbolized by a slash through the d . These new definitions of state and path functions lead to an obvious question: What in the ever-loving-blue-eyed-world is a differential?

Suppose you have a function F that is evaluated at some point x_1 . If you want to know the change in F going from x_1 to some new point $x_1 + \Delta x$, you can estimate it by calculating the slope at x_1 and multiplying it by Δx . This slope is the same as the slope of the tangent at x_1 , which is equal to the change in height of the tangent going from x_1 to $x_1 + \Delta x$, divided by Δx ,

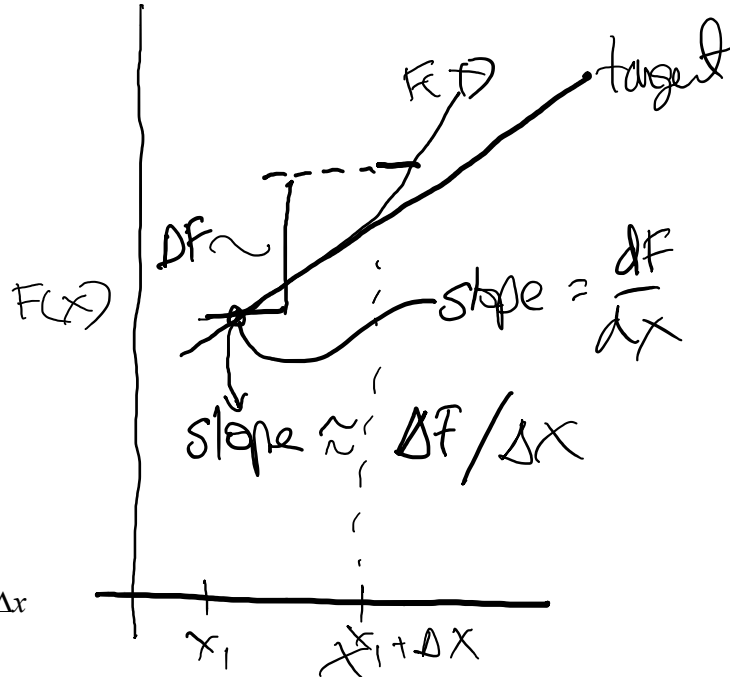
slope = $\Delta F / \Delta x$.

From calculus we also know that the slope at x_1 is equal to the derivative df/dx evaluated at x_1 ,

$$\text{slope} = \left. \frac{dF}{dx} \right|_{x_1} \approx \frac{\Delta F}{\Delta x}$$

If we want to estimate the value of ΔF , we can rearrange this result to give

$$\Delta F \approx \left. \frac{dF}{dx} \right|_{x_1} \Delta x$$



If the change in x is infinitesimal, then we write this change as dx and the estimated change in the value of the function ΔF is replaced by the actual change in F , dF , called the differential of F , given by

$$dF = \left. \frac{dF}{dx} \right|_{x_1} dx$$

When you integrate a function you're actually summing up the differentials over a series of infinitesimal intervals.

The concept of the differential can be extended to functions of two or more variables. Say we have a function $f(x, y)$ and we want to know the change df in the value of f when you go from (x_1, y_1) to $(x_1 + \delta x, y_1 + \delta y)$. In analogy to our previous result for one variable we can estimate the change in f by

$$df = \left(\frac{\partial f}{\partial x} \right)_y \Big|_{x_1} dx + \left(\frac{\partial f}{\partial y} \right)_x \Big|_{y_1} dy$$

Now so what? At this point all we've done is show that the differential can be used to approximate

a change in f over a small displacement.

The real importance of the differential is in the following point. By integrating some differentials, you can determine a previously unknown function, i.e., you can find a function $f(x)$ knowing only its differential df ,

$$f(x) = \int \left(\frac{df}{dx} \right) dx = \int df .$$

This is useful in general because there are times when it is easier to define the changes in a function than it is to define the function itself. This is particularly useful in thermodynamics because ALL of the questions we ask involve consequences of some change, like change in temperature, or change in energy, or doing work. So all of our changes can be expressed as differentials or derivatives. Some examples of integrating differentials to obtain functions are the integral $x^2 + c = \int 2x dx$, in which the quantity $2x dx$ is the differential of f , given by the product of df/dx with dx and the integral $\sin x + c = \int \cos x dx$, in which $\cos x dx$ is the differential of f . Note in both cases the function we obtain by integration is known only to within a constant.

Now we come to the question about differentials of the greatest importance to thermodynamics: precisely what is an exact differential? **An exact or perfect differential dF is one which allows you to recover the function F to within a constant.** This definition implies that all **differentials of functions of one variable are exact.**

Example: Given $df = 3x^2 dx$ we know that $f = x^3 + C$.

We can do the same type of thing for all functions of one variable (at least numerically). But say that we have a function of two variables, for example

$$f(x, y) = x^2y + y^2 + x^2.$$

Its partials are

$$\left(\frac{\partial f}{\partial x}\right)_y = 2xy + 2x \quad \text{and} \quad \left(\frac{\partial f}{\partial y}\right)_x = x^2 + 2y$$

If we want to recover a one variable function by integration we need to know only the one derivative. For a function of two variables, we need to find out whether one or both of the partial derivatives are necessary for recovery of the original function. Let's see by multiplying the partial with respect to x by dx and integrating.

$$\int \left(\frac{\partial f}{\partial x}\right) dx = x^2 y + x^2 + C(y)$$

Note that the constant of integration in this case is a function of y, because when we took our partial with respect to x, we lost all information about functions of y only since they were held constant and had a partial derivative of 0. So for this two-dimensional case, knowledge of just one partial derivative is not sufficient to completely recover the original function.

However if we know both $\left(\frac{\partial f}{\partial x}\right)_y$ and $\left(\frac{\partial f}{\partial y}\right)_x$ we can piece the function together. In this case, direct integration of the partial with respect to x yields the function above, while integration of the partial of f with respect to y gives

$$\int \left(\frac{\partial f}{\partial y}\right) dy = x^2 y + y^2 + C(x)$$

Comparing the two results shows us that $C(y) = y^2 + C$, and that

$$f(x, y) = x^2 y + y^2 + x^2 + c.$$

So knowing all of the partial derivatives of a function allows us to recover the function without any prior knowledge of the function. **A differential made up of all the partial derivatives of a function is called an exact differential or total differential.** For the case we have already

studied, a function of two variables, the exact differential is

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

and in general, for a function $f(x_1, x_2, \dots, x_n)$, the exact differential df is given by

$$df(x_1, x_2, \dots, x_n) = \sum_{j=1}^n \left(\frac{\partial f}{\partial x_j}\right)_{x_i} dx_j .$$

Removal of even one of the partials from which these sums are constructed would result in an inexact differential.

At this point we've identified state functions with exact differentials and defined exact and inexact differentials. We only need to work out a way to tell the exact and inexact differentials apart. Here's the solution! Suppose we have a differential, $df = g dx + h dy$. **df is an exact differential if and only if $(\partial g/\partial y)_x = (\partial h/\partial x)_y$.** To see where this rule comes from remember that the exact differential of $f(x,y)$ is given by

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy .$$

Therefore in the equation above, for df to be exact g must equal $(\partial f/\partial x)_y$ and h must equal $(\partial f/\partial y)_x$, where f is the same function in both cases. This means that

$$\left(\frac{\partial g}{\partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right) \text{ and } \left(\frac{\partial h}{\partial x}\right) = \left(\frac{\partial^2 f}{\partial x \partial y}\right),$$

which are always equal. Let's do a couple of quick examples.

Example 1: $df = (e^{-x} + e^{-y} - xe^{-x}) dx - xe^{-y} dy$. Is df an exact differential? We apply our test by taking the partial of the dx term with respect to y and the partial of the dy term with respect to x .

$$\frac{\partial}{\partial y}(e^{-x} + e^{-y} - xe^{-x}) = -e^{-y}$$

$$\frac{\partial}{\partial x}(-xe^{-y}) = -e^{-y}$$

Since the rule is satisfied, df is an exact differential.

Example 2: $df = (3x^2 + 7y^2) dx + (14y + 7x) dy$. Is df an exact differential? Let's check our partials.

$$\frac{\partial}{\partial y}(3x^2 + 7y^2) = 14y \text{ and } \frac{\partial}{\partial x}(14y + 7x) = 7$$

Since the partials are not equal, f is not an exact differential. **Since 1) we can now tell whether a differential is an exact differential and 2) state functions are exact differentials, we now have a rigorous mathematical test for whether a property is a state function.**

Lecture 9

We will now continue to look at how some of our thermodynamic functions change when we change our experimental conditions. In our last lecture we used the first law of thermodynamics to define a new thermodynamic state function,

$$dU = dq + dw_{\text{exp.}}$$

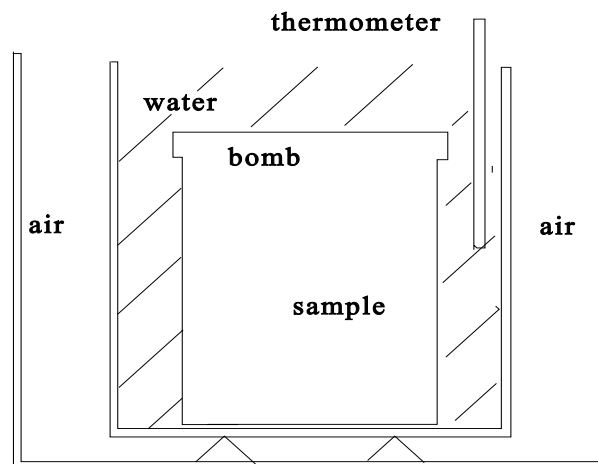
If we consider a system **at constant volume**, $dw_{\text{exp}} = 0$, so

$$dU = dq_v,$$

where q_v is the heat at constant volume.

One experiment in which this result is useful is **calorimetry**, which you will be doing in lab next semester. In bomb calorimetry, we measure the heat of a reaction at constant volume and use this to calculate the energy change. The device with which the heat of reaction is measured is called a **bomb calorimeter**. Crudely, the device is a constant volume vessel inserted in a known volume of water. The water vessel itself is contained in a vessel of air or some other insulator, so that adiabatic conditions can be approximated for the calorimeter. WHY IS AIR CONSIDERED TO BE A GOOD INSULATOR? A reaction is set off in

the vessel which releases heat into the water, causing an increase in the temperature of the water from T_i to T_f , or $\Delta T = T_f - T_i$. The observed temperature change, ΔT , is proportional to the heat, q . To convert this measured value of ΔT to q we need to measure a quantity called the heat capacity of the



Schematic of an adiabatic calorimeter

system, C , which is the amount of energy necessary to increase the temperature of a system by 1K. For a macroscopic change in temperature, the heat capacity is given by the ratio of $q/\Delta T$, although a more accurate definition is $C = dq/dT$.

The name **heat capacity** is quite illuminating. To say that a system has a large heat capacity is the same as saying that it must absorb a large amount of heat before a significant temperature rise occurs. In contrast, saying that a system has a small heat capacity means that a small amount of heat absorbed will result in a significant temperature change.

The value of **the heat capacity** that we measure for a system **is dependent on the experimental conditions**. To see this, suppose that we have a constant volume system. The heat necessary to raise the temperature of the system by dT is given by

$$dq_v = C_v dT,$$

where C_v is the heat capacity at constant volume. Since $dq_v = dU$ we can now write

$$dU = C_v dT.$$

Rearranging this yields the defining equation for the heat capacity under conditions of constant volume,

$$C_v \equiv \left(\frac{\partial U}{\partial T} \right)_v,$$

where the term on the right is read as the partial derivative of U with respect to T at constant V .

This definition also yields a new way to calculate the energy change, since

$$\Delta U = \int_{T_1}^{T_2} C_v dT$$

[Under what conditions is this equation valid?] Note that the **heat capacity** defined in this way is an **extensive quantity**, but usually the quantity tabulated is the **molar heat capacity**,

$$\bar{C}_v \equiv \frac{1}{n} \left(\frac{\partial U}{\partial T} \right)_v$$

an intensive quantity. The heat capacity and molar heat capacity are related by $C = n\bar{C}$.

Now suppose that we have this same system under conditions of **constant pressure**. IF WE WANT THE FINAL T TO BE THE SAME, WILL IT TAKE MORE HEAT OR LESS? [More] WHY? [Because pV work can now be done.] Since the heat is different for these conditions it suggests that the heat capacity at constant pressure will be different as well. We initially define our heat capacity under conditions of constant pressure as $C_p = dq_p/dT$, where q_p is the heat absorbed by the system when the pressure is constant.

Since we just concluded that $q_p > q_v$, it follows from our definitions that $C_p > C_v$. How much difference is there? Since the difference between a constant pressure process and a constant volume process is the system's ability to do work, it depends on how much work a system does when it's heated, which in turn depends on the amount the system expands as it is heated. For example, a solid or liquid doesn't expand much when heated, so C_p is not much greater than C_v . The difference is larger for a gas, which expands substantially when heated.

Having defined heat capacity, let's now return to the bomb calorimetry experiment. Remember that we've burned our sample and obtained a temperature change, ΔT . We need to determine the heat capacity of our system. However, unlike a sample consisting of a pure system like 2.7 mol of Ar, or 150 g of methane, we cannot use tabulated molar heat capacities to determine the heat capacity of our calorimeter. This is because our calorimeter is not a pure system but a complicated system composed of the steel bomb, the water, the thermometer, the stirrer, the wires, the substance being burned, and all other parts of the device. Because the calorimeter is such a complex system thermodynamically, the heat capacity of the device is often given a different name,

most commonly **the calorimeter constant**, and this constant must be determined experimentally.

The calorimeter constant is determined by burning a known amount of a substance whose heat of combustion is very accurately and precisely known, most commonly benzoic acid, and measuring ΔT . Since for this experiment, we know both q and ΔT , the calorimeter constant can be calculated

using $C = \frac{q}{\Delta T}$.

Once the calorimeter constant is determined, the experiment is carried out with a substance with an unknown molar heat of reaction. ΔT is determined, and the heat per unit mass is determined using $\frac{q}{g} = \frac{C\Delta T}{m}$, where m is the mass of the sample that has been combusted. But we have a problem here. C is always positive, and for combustion ΔT is also always positive. But a positive q means that we have an endothermic process, and we know that combustion is exothermic.

We can see how to resolve this problem by looking at our experimental setup, and see exactly where it is that we're measuring ΔT . It turns out that our thermometer is in the water, but the heat is generated by the reaction inside the bomb. The heat that increases the temperature of the water is the heat released by the reaction in the bomb. Since the whole apparatus is inside an adiabatic jacket,

$$q_T = 0 = q_{rxn} + q_{water},$$

where q_T is the total heat for the system and therefore,

$$q_{rxn} = -q_{water}.$$

This means that for our experiment

$$\frac{q_{rxn}}{g} = \frac{-C\Delta T}{m} .$$

This is also $\frac{\Delta U}{g}$, because of our result that $\Delta U = q_V$. The last step in the calculation is to convert

$\frac{\Delta U}{g}$ to the molar value, $\Delta\bar{U}$, by multiplying by the molar mass. This overall process is both

extremely precise and extremely accurate.

Lecture 10

I've shown that at constant volume $\Delta U = q_v$. If the volume is not constant the change in internal energy is no longer equal to the energy supplied as heat. This is because the system can use some of the heat energy to do expansion work. However, because the heat used in starting a chemical reaction or process is a useful piece of information, and because we most frequently carry out experiments under constant pressure conditions, it would be useful if there were a state function that was equal to the heat for a constant pressure process. Fortunately, we can define a new state function, the **enthalpy**, as

$$\mathbf{H \equiv U + pV},$$

where **p is the internal pressure of the system** and not the external pressure. We can show that as a result,

$$\mathbf{dH = dq_p},$$

where q_p is the heat at constant pressure.

To show this let's look at an infinitesimal change in H. From our definition of H we have

$$dH = dU + d(pV).$$

We use the product rule to get

$$d(pV) = p dV + V dp$$

so

$$dH = dU + p dV + V dp.$$

But we know that

$$\begin{aligned} dU &= dq + dw \\ &= dq - p_{\text{ex}} dV. \end{aligned}$$

Which yields

$$dH = dq + p dV - p_{\text{ex}} dV + Vdp.$$

If the system is in mechanical equilibrium with its surroundings, i.e., for a reversible process, for which $p_{\text{ex}} = p$ this becomes

$$dH = dq + Vdp.$$

If we now add the additional constraint of constant pressure, the $V dp$ term drops out and this becomes

$$dH = dq_p.$$

Since we now know that $dH = dq_p$, we can write another definition of C_p , namely $C_p = (\partial H/\partial T)_p$.

This in turn implies that we can find ΔH under conditions of constant pressure by using the equation

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

Our definition of H , $H = U + pV$, implies that one should be able to calculate ΔH from ΔU or vice versa. Let's do a quick example of this.

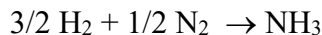
Example ΔH for formation of 1.00 mol of NH_3 from its elements at 298K is -46.1 kJ. What is ΔU ?

Solution Since $H = U + pV$, $\Delta H = \Delta U + \Delta(pV)$. Note that the term in parentheses is not $p\Delta V$ but is $\Delta(pV)$, i.e. $p_2V_2 - p_1V_1$. Unfortunately for this problem, neither p nor V has been specified. However, if we treat the gases as ideal, we can write $pV = nRT$ and the equation becomes

$$\Delta H = \Delta U + \Delta(nRT)$$

Since T is constant for this reaction, we need only find Δn to solve the problem. The reaction can

be written



We specified in our question that we end up with one mole of NH_3 , i.e. $n_f = 1.00$. To get one mole of NH_3 we needed to start out with 1.5 moles of H_2 and 0.5 moles of N_2 , so $n_i = 2.00$ mol, and $\Delta n = n_f - n_i = -1.00$ mol. Therefore,

$$\begin{aligned} \Delta U &= -46.1 \text{ kJ} - (-1 \text{ mol})(8.314 \text{ J K mol}^{-1})(298\text{K})(1\text{kJ}/1000\text{J}) \\ &= -43.6 \text{ kJ.} \end{aligned}$$

Note that we have to be careful about units since the original ΔH is in kJ/mol and the $RT\Delta n$ term is in J/mol.

Since in the last problem, we calculated the difference between U and H for an ideal gas, it seems natural at this point to calculate the difference between C_p and C_v for an ideal gas. C_v for an ideal monatomic gas can be determined to be $\frac{3}{2}nR$ by a principle of statistical mechanics called the equipartition principle. The molar heat capacity of an ideal monatomic gas at constant volume is equal to $\frac{3}{2}R$. In order to calculate the difference between C_p and C_v for an ideal gas we need to use partial derivatives.

We begin with our definitions to get

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

Our first step is to show that for an ideal gas, $(\partial U/\partial T)_v = (\partial U/\partial T)_p$. To do this we will need to write the differential of U , and we'll need to decide which variables to use as the independent variables. Since we've shown that U changes when V changes, due to pV work, and when T changes, we'll write $U = U(V, T)$. The differential of U can now be written as

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

If we divide both sides by dT and hold p constant we get

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

We already know that $(\partial U/\partial T)_v = C_v$, but to evaluate the second term, we'll have to draw on a new result, the Joule experiment.

In this experiment, Joule expanded a gas into a vacuum and measured the temperature change. When the temperature change turned out to be zero, Joule concluded that the internal energy does not depend on volume. Unfortunately for Joule, his experiment was not sensitive enough to detect the small temperature change resulting when a real gas expands into a vacuum. However, his experiment does hold true for ideal gases, so for ideal gases we can write, $(\partial U/\partial V)_T = 0$ and therefore for an ideal gas $(\partial U/\partial T)_v = (\partial U/\partial T)_p$. As an aside, this result leads to a rather nice result for an ideal gas. If we choose as our independent variables T and V , the differential of U can be written,

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

Since for an ideal gas the second term is zero, and since $\left(\frac{\partial U}{\partial T}\right)_v = C_v$, we conclude that for an ideal gas,

$$dU = C_v dT,$$

whether the conditions of the experiment are constant volume or not. Similarly we can show that for ideal gases,

$$dH = C_p dT$$

whether the conditions are constant pressure or not. In contrast, the equation $dU = C_v dT$ holds for a real gas only when the experiment is conducted under constant volume conditions., and the equation $dH = C_p dT$ holds for a real gas only under constant pressure conditions.

Now we return to our calculation of the difference between the C_p and C_v , and apply this result to get

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

We know that by definition $H = U + pV$ and for an ideal gas, we can also write $H = U + nRT$.

Substituting this for H we get

$$C_p - C_v = \left(\frac{\partial(U + nRT)}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + nR - \left(\frac{\partial U}{\partial T}\right)_p$$

Therefore $C_p - C_v = nR$ for an ideal gas.

When we use the equations $\Delta H = \int n\bar{C}_p dT$ and $\Delta U = \int n\bar{C}_v dT$, we will often make the simplifying assumption that our heat capacities are constant as a function of temperature. How valid is this assumption? The answer is that if the substance is a liquid or gas, not at a temperature near a phase transition, and if the temperature range is not too large, then the assumption is an acceptable one. To understand why, we need to understand something about the microscopic nature of the heat capacity.

The basic idea here is that every substance can move in a number of different ways. Each type of motion has a characteristic range of energies that it can absorb, i.e., a characteristic range of heat that it can absorb. A given type of motion will not be able to contribute to the heat capacity unless the thermal energy at a given temperature is comparable to the energy of the motion.

There are a couple of approximate ways to estimate whether the energy is comparable.

One of these is to calculate the Boltzmann factor for the motion. The Boltzmann factor is

$$\frac{N(E)}{N_{Tot}} = e^{\frac{-E}{kT}}$$

It tells us the fraction of molecules with energy E, at a given temperature T. In this

equation, N(E) is the number of molecules at energy E, N_{tot} is the total number of molecules, E is

the energy of the motion in joules, T the temperature in Kelvin and k is Boltzmann's constant, $\frac{R}{N_0}$

, $1.38 \times 10^{-23} \text{ J K}^{-1}$. Essentially this equation tells us that at a given temperature, the higher the

energy the lower the fraction of molecules at that energy, and conversely for a given energy

motion, the higher the temperature, the higher the fraction of molecules at that energy. Again, for

heat capacity, this factor is useful because a given motion will not contribute to the heat capacity

unless the Boltzmann factor is significant. A quick and dirty estimate can be made by comparing

the energy of the motion to kT, which gives a measure of the thermal energy. If they are within

an order of magnitude of each other, then the motion will contribute to the heat capacity.

All that remains is to consider the types of motions a substance has and their relative

energies. Consider a substance like carbon dioxide. At very low temperatures, it is a solid, and

the only motions that are available are vibrations of the whole crystal, which are called acoustic

phonons. These phonons have a wide range of energies, including very low energies. Their

populations grow exponentially with temperature, so at low temperatures the heat capacity starts

at 0 and grows very rapidly. The growth slows as the phase transition is reached but at the phase

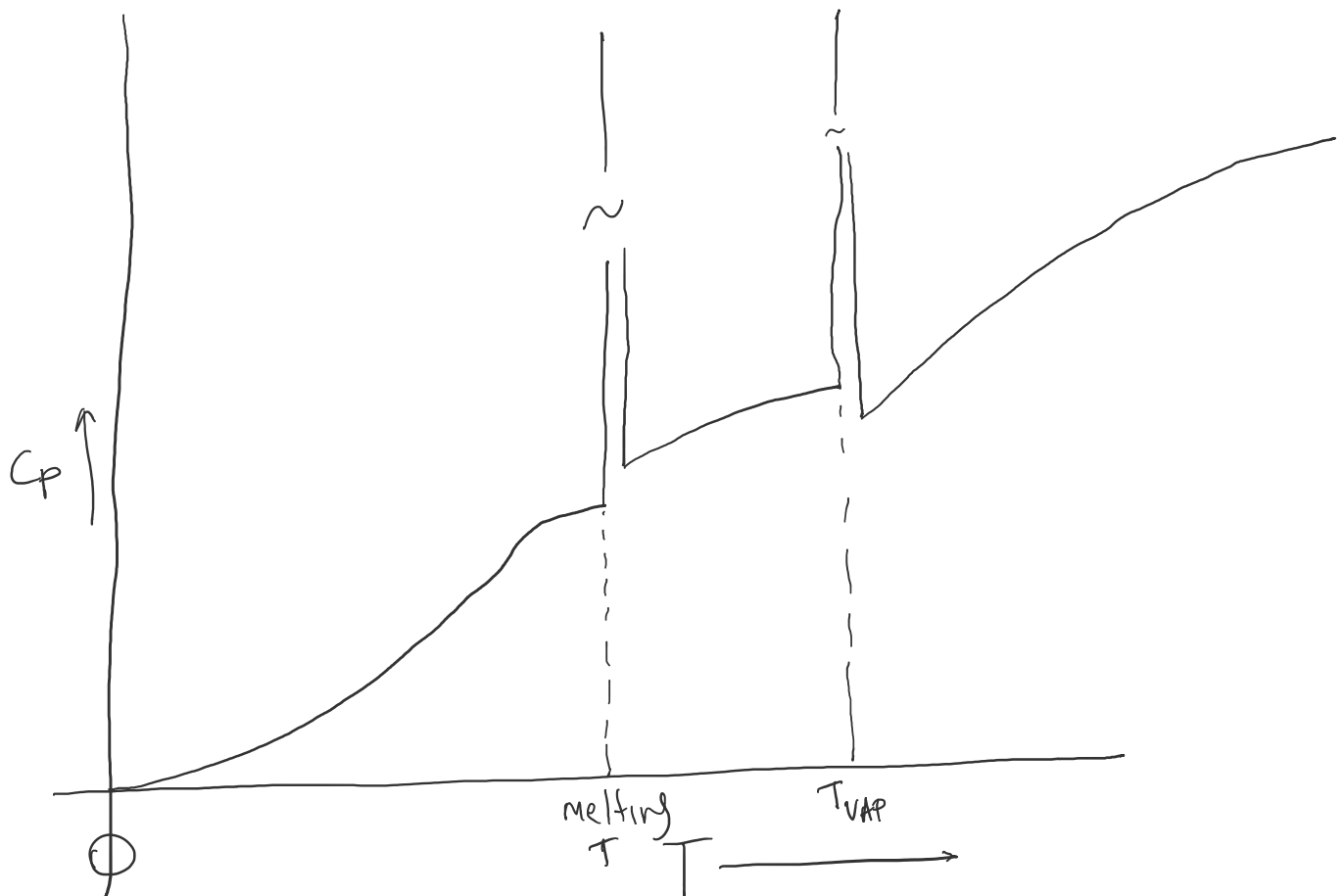
transition itself, the heat capacity becomes infinite. [WHY?] When the CO_2 is a liquid, the motions

that are available are simply translational motion against the intermolecular forces holding the

liquid together. These vary continuously in energy, but the increase in heat capacity with

temperature is slow in this range. Again, when the liquid to gas phase transition is reached, the

heat capacity again becomes infinite. At temperatures just above the phase transition the gas only has translational motion available, which means that the heat capacity of the gas at this point is lower than that of the liquid. However, as temperature increases, first rotational motions, and then vibrational motions of the molecule begin to contribute to the heat capacity. While the heat capacity of a gas increases steadily, over a moderate temperature range it can be treated as approximately constant. The result is a graph of heat capacity vs. temperature that looks like this:



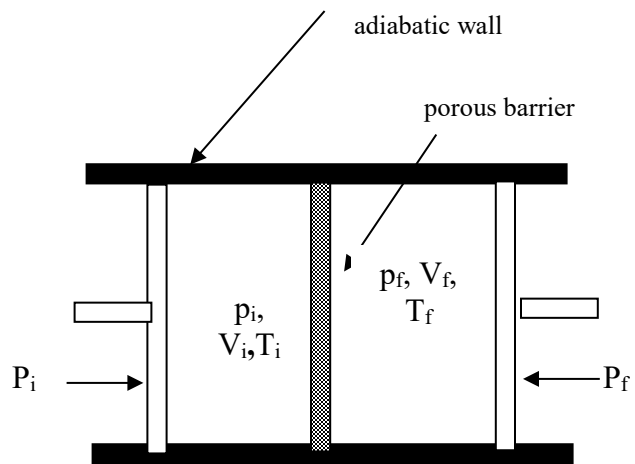
I don't want to leave you with a poor impression of Joule, so I'd like to tell you about another experiment of Joule's without which I would not have been able to do my experimental research. The experiment is called the Joule-Thomson experiment, in which Joule showed that a change in pressure under conditions of constant enthalpy leads to a change in temperature. Under the right conditions this phenomenon can lead to cooling. It is the basis of the cryogenic refrigerator I used in my research, which achieved temperatures as low as 8.6 K. The phenomenon is characterized by the Joule-Thomson

Coefficient, which is $\left(\frac{\partial T}{\partial p}\right)_H$ and which is

symbolized by μ_{JT} . (Note that the JT here refers to Joule-Thomson, and not the James Taylor album). The coefficient is measured with an

apparatus that can be represented schematically as follows. The system consists of a cylinder with a porous barrier. On one side we have a gas with a state defined by variables V_i, T_i , and with a piston that maintains the pressure at a constant

value of p_i . On the other side we have a volume V_f , a temperature T_f and a piston that maintains the pressure at a constant value of p_f . We surround the whole cylinder with an adiabatic wall so that dq will be 0 for the system. The constant is measured by moving piston 1 in so that gas passes into side 2 and measuring the temperature difference ΔT as a function of the pressure difference Δp .



Schematic of Joule-Thompson Apparatus

Let's prove that if the experiment is done under these conditions the process will be isenthalpic. To simplify our calculation we'll specify that *before* we move piston 1 in the volume on side 1 is V_i while the volume on side 2 is 0 and *after* piston 1 is moved in the volume on side 1 is 0 while the volume on side 2 is V_f . In the course of the expansion, the work done on side 1, $w_1 = -p_{\text{ex}} \Delta V = -p_i (0 - V_i) = p_i V_i$. The work done on side 2, $w_2 = -p_{\text{ex}} \Delta V = -p_f (V_f - 0) = -p_f V_f$. The total work is $w = w_1 + w_2 = p_i V_i - p_f V_f$. This is also equal to w_{ad} , since the volume changes occur under adiabatic conditions. Since $\Delta U = U_f - U_i = w_{\text{ad}}$, we have $U_f - U_i = p_i V_i - p_f V_f$, which rearranges to $U_f + p_f V_f = U_i + p_i V_i$. But what is $U + pV$? [H] So this becomes $H_f = H_i$, and we have demonstrated that under these conditions the expansion of the gas is isenthalpic.

The Joule-Thomson coefficient, $\mu_{\text{JT}} \equiv (\partial T / \partial p)_H$, is the change in temperature with pressure at constant H. This coefficient depends on both temperature and pressure. For the effect to be used in a refrigerator, the pressures and temperatures have to be carefully chosen so that the sign of the coefficient is positive, i.e., that temperature drops with pressure.

The physical basis of the Joule Thomson effect is that for real gases at most pressures there are attractive forces between atoms or molecules. Moving molecules apart requires energy to overcome the attractive forces. Now if we consume energy by expanding a gas, but add no heat to the system, the energy to move the molecules apart must come from the system itself and the system will therefore cool.

In the cryogenic refrigerator in my lab, the gas used in the Joule-Thomson expansion is helium. Q: DO YOU EXPECT HELIUM TO BE AN EFFICIENT REFRIGERANT OR AN INEFFICIENT REFRIGERANT? Q: WHY? Q: SINCE IT IS PROBABLY THE LEAST EFFICIENT REFRIGERANT, WHY IS IT USED IN MY REFRIGERATOR?

Lectures 11-12

Our next topic is adiabatic processes, processes in which $q=0$, a constraint on our system. When we studied the work due to the isothermal reversible expansion of a gas, we learned how to account for constraints in those cases where the constrained variable was included in our equation of state. When we study adiabatic processes in gaseous systems, our constraint is that $q=0$ for the process, but q is not in our equations of state! [Why can't q be in an equation of state?] In addressing adiabatic processes more broadly, we'll also be demonstrating an answer to the question, "How do we include the effect of constraints on variables that aren't in equations of state in our thermodynamic calculations?"

We've already begun studying adiabatic processes by looking at the Joule-Thompson experiment. To begin to answer our new question, let's look at the work involved in a more typical adiabatic process. Our starting point in discussing the energy changes of adiabatic expansions is our earliest definition of the first law, $dU = dw_{ad}$. For the case where we limit our considerations to perfect gases we can also say $dU = C_v dT$, which in turn implies that if C_v is a constant, $w_{ad} = C_v \Delta T$.

Let's look at a quick example: A sample of 1 mol of krypton expands adiabatically and irreversibly from 1.0 L to 3.0 L against a constant pressure of 1 atm. \bar{C}_p for Kr = 20.786 J K⁻¹ mol⁻¹. What is ΔU and what is ΔT ? Assume that krypton is an ideal gas. Solution: Since this is an adiabatic system, $\Delta U = w$. $dw = -p_{ex} dV$. Since in this problem p_{ex} is constant, $\Delta U = w = -p_{ex} \Delta V = -(1.01 \times 10^5 \text{ Pa})(2 \times 10^{-3} \text{ m}^3) = -202\text{J}$. To find ΔT we note that $\Delta T = \Delta U/C_v$, as long as the temperature range is small.. There are two things we have to do to get the heat capacity. First, we need to convert from the molar heat capacity to heat capacity by $C_p = n\bar{C}_p$. Since $n = 1$, this does

not affect the answer but does give us correct units. Now to get C_v we use the result we obtained a short while ago for an ideal gas, $C_v = C_p - nR = 20.786 \text{ J K}^{-1} - 8.314 \text{ J K}^{-1} = 12.47 \text{ J K}^{-1}$. Now $\Delta T = -202 \text{ J} / 12.47 \text{ J K}^{-1} = -16.20 \text{ K}$.

Now let's examine the work of a **reversible adiabatic expansion** of an ideal gas. This will yield the **maximum adiabatic work**. Q: What is our definition for work? [$dw = -p_{\text{ex}} dV$]. For an adiabatic expansion this equals dU which is also equal to $C_v dT$, so we can write, $-p_{\text{ex}} dV = C_v dT$. This is reversible so what will our next step be? [$-p dV = C_v dT$] Since this is an ideal gas what do you think our next step will be? [$-nRT/V dV = C_v dT$] Rearranging we get

$$\frac{C_v}{nR} \frac{dT}{T} = -\frac{dV}{V}$$

which we integrate to obtain

$$\frac{C_v}{nR} \ln \frac{T_2}{T_1} = -\ln \frac{V_2}{V_1}$$

Using the relation $a \ln x = \ln x^a$ we get

$$\ln \left(\frac{T_2}{T_1} \right)^{\frac{C_v}{nR}} = \ln \left(\frac{V_1}{V_2} \right)$$

which in turn gives us

$$\left(\frac{T_2}{T_1} \right)^{\frac{C_v}{nR}} = \left(\frac{V_1}{V_2} \right) \text{ or } \left(\frac{T_2}{T_1} \right) = \left(\frac{V_1}{V_2} \right)^{\frac{nR}{C_v}}$$

For an ideal gas we can show, $\frac{nR}{C_v} = \frac{C_p}{C_v} - 1$ as follows. Since for an ideal gas $C_p - C_v = nR$, our

equation becomes $\frac{nR}{C_v} = \frac{C_p - C_v}{C_v}$, which simplifies to $\frac{nR}{C_v} = \frac{C_p}{C_v} - 1$.

The ratio C_p/C_v is commonly called γ so this may be rewritten as

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

To calculate the change in energy we need to know $T_2 - T_1$, since $\Delta U = C_v \Delta T$, so we solve this equation for T_2 and then use this to calculate ΔT . When we plug this into our equation for ΔU , we get

$$\Delta U = C_v T_1 \left(\left(\frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right)$$

Let's look at an example. A sample of 1 mol of Xe is expanded adiabatically and reversibly from 0.5 L to 1.0 L at an initial temperature of 145 K. What are the final temperature and the work for the process? For Xe, \bar{C}_v is $12.47 \text{ J K}^{-1} \text{ mol}^{-1}$. To calculate ΔU we need to know ΔT and therefore T_2 . From our results we have

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

Plugging in the numbers gives

$$T_2 = 145(0.5/1.0)^{1.667} = 91.3 \text{ K.}$$

$$w = n C_v \Delta T = (12.47 \text{ J K}^{-1} \text{ mol}^{-1}) (1 \text{ mol}) (91.3 \text{ K} - 145 \text{ K}) = -670 \text{ J.}$$

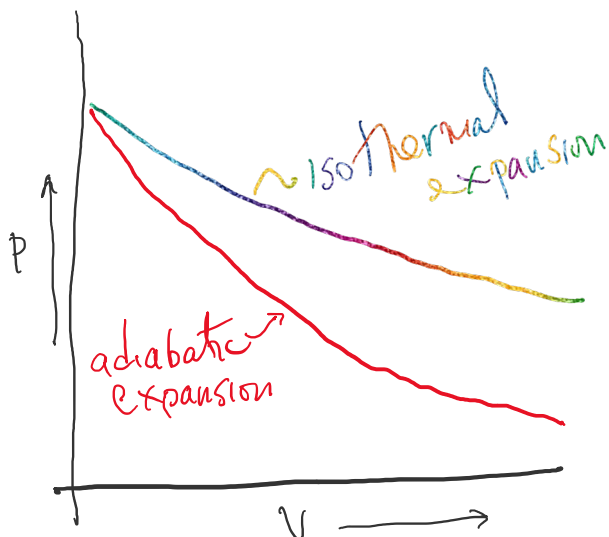
WHY IS THE WORK NEGATIVE?

[Because in expanding the system did work]

WHY COULDN'T WE JUST USE $dW = -P_{\text{EX}} dV$?

[At this point we don't know how to calculate the p-V curve for an adiabatic process.]

However, with a little work it can be shown that the p-V relationship for an adiabatic



expansion is $p_1 \bar{V}_1^\gamma = p_2 \bar{V}_2^\gamma$. If we plot p vs. V for an isothermal expansion and for an adiabatic expansion we find that the pressure falls more rapidly for the adiabat. WHY? [The heat flow into the system during an isothermal expansion helps keep the pressure up.]

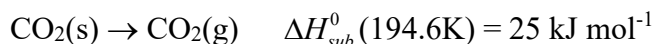
Our discussion of heat leads us naturally to the topic of thermochemistry. Thermochemistry is the study of the heat produced or required by chemical reactions. The reason that we're particularly interested in heat is that traditionally chemists have supplied the necessary energy to drive chemical reactions in the form of heat. While this is no longer always the case, with lasers and other light sources playing a greater and greater role in the initiation of chemical reactions, thermally initiated reactions still dominate synthetic chemistry. Thus the importance of the equations

$$\Delta U = q_v \quad \text{and} \quad \Delta H = q_p$$

describing the changes in the two state functions solely in terms of the heat. For most benchtop chemists, ΔH is particularly important, because much synthesis occurs in open vessels subject to constant atmospheric pressure of about 1 bar. For this reason, and because enthalpy changes are pressure dependent, enthalpy changes are usually reported at a standard pressure of 1 bar. Enthalpy changes reported at this pressure are called **standard enthalpy changes**, ΔH° , and are defined as **the change in enthalpy for a process in which the initial and final substances are in their standard states**. The **standard state** of a substance is defined as **its pure form at 1 bar pressure**.

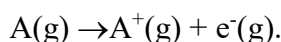
Standard enthalpy changes have been defined for a wide variety of processes. Let's look at some of them. First there's a whole group of standard enthalpies for phase transitions called **standard enthalpies of transition**, which are exemplified by the **standard enthalpy of sublimation**, ΔH_{sub}^0 , defined as **the enthalpy change per mole when a solid at 1 bar vaporizes**

to form a gas at 1 bar. For example, for the process



You can imagine almost identical definitions for the Standard Enthalpy of Fusion, ΔH_{fus}^0 , where the process is melting, i.e., for some substance A, $\text{A}(\text{s}) \rightarrow \text{A}(\text{l})$, or for the Standard Enthalpy of Vaporization, ΔH_{vap}^0 , where the process is, well, vaporization, i.e., for some substance A, $\text{A}(\text{l}) \rightarrow \text{A}(\text{g})$.

Standard enthalpies can be (and have been) defined for a multitude of different processes. What is important for you to know about this multitude of standard enthalpies? In my (seldom) humble opinion there are four main points. The first point is that these definitions really are standard. And that means all you need to be able to do to understand the meaning of a standard enthalpy is to be able to recognize the process referred to and write an equation for it. For example, if I talk about the standard enthalpy of ionization, you should recognize that the process is



If I talk about the enthalpy of fusion, you should recognize that the attendant process is melting.

A second important thing for you to recognize is that if a process is tabulated, its opposite process is usually not tabulated separately. For example, the enthalpy of fusion for the process $\text{A}(\text{s}) \rightarrow \text{A}(\text{l})$ is tabulated while enthalpy of freezing is not. This is because if we write the process for enthalpy of freezing, $\text{A}(\text{l}) \rightarrow \text{A}(\text{s})$, we find that it is just the opposite of fusion, and logically, since enthalpy is a state function, whose change is dependent only on its initial and final states, its enthalpy will just be the negative of the enthalpy of fusion. So for example, for H_2S , $\Delta H_{\text{fus}}^0(187.6\text{K}) = 2.377 \text{ kJ mol}^{-1}$, and $\Delta H_{\text{freezing}}^0(187.6\text{K}) = -2.377 \text{ kJ mol}^{-1}$.

A third important thing for you to know is that these standard enthalpies are temperature dependent. For example, $\Delta H_{\text{vap}}^0(373\text{K}) \neq \Delta H_{\text{vap}}^0(473)$.

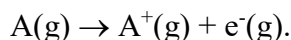
The final important thing is to know how to convert standard enthalpies to standard energies, i.e., how to convert ΔH^0 to ΔU^0 . As we said earlier our general formula is

$$\Delta H = \Delta U + \Delta(pV).$$

This formula is completely rigorous and involves no approximations. In some cases we won't have the necessary pV information to use this formula, and will have to seek alternative methods. If we can approximate our gas as ideal, we can replace pV with nRT, and our equation becomes

$$\Delta H = \Delta U + \Delta(nRT).$$

If we take ionization as an example, our process is



We begin with one mole of gas, and end with two moles, the A cations and the electrons, so $n_f = 2$, $n_i = 1$, and $\Delta n = n_f - n_i = 1$, so for ionization we have

$$\Delta H_i = \Delta U_i + RT.$$

It is very important to realize that the equation $\Delta H = \Delta U + \Delta(nRT)$ is accurate only for ideal gases.

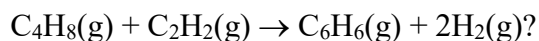
For real gases you must use $\Delta H = \Delta U + \Delta(pV) = \Delta U + p_2V_2 - p_1V_1$. Q: GIVEN THIS LIMITATION, IS OUR RESULT FOR THE ENTHALPY OF IONIZATION ACCURATE? WHY?

An especially important standard enthalpy is the **standard enthalpy of formation**, ΔH_f^0 , defined as **the enthalpy for the formation of one mole of a substance at 1 bar from its elements in their reference states**. Of course, now we need to define a reference state. The **reference state** of an element is **its most stable form at the specified temperature and a pressure of 1 bar**. The reference states at room temperature of hydrogen, mercury and carbon are $\text{H}_2(\text{g})$, $\text{Hg}(\text{l})$,

and C(graphite). This definition of reference states implies that the enthalpy of formation of elements in their reference states is 0, zip, null, nada. These definitions, of standard enthalpies of formation and of reference states, are critical to remember.

When I first mentioned enthalpy, I introduced it as a new state function. That enthalpy is a state function results in a powerful tool of thermochemistry, **Hess's Law**, which states “for any reaction, the overall reaction enthalpy can be expressed as the sum of the reaction enthalpies of any sequence of reactions into which a reaction may be divided.” This may sound complicated but essentially what Hess's law says is that 1) Enthalpy is a state function. 2) The value of a state function is independent of path. 3) Because of this when we are calculating the enthalpy for a reaction, we can find it by adding the enthalpies of any reactions which add up to the reaction we are interested in and which make the calculation easy. One consequence of Hess's law that you may already be familiar with is that standard enthalpies of reaction can be calculated from standard enthalpies of formation.

Example What is the ΔH_{298}^0 for the reaction

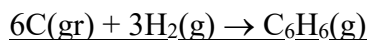
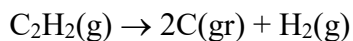
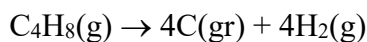


Solution To use standard enthalpies of formation to calculate standard enthalpies of reaction, we just take the enthalpies of formation of the products and subtract the enthalpies of formation of the reactants, so for this reaction,

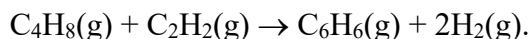
$$\begin{aligned} \Delta H_{rxn}^0 &= \Delta H_{f,298}^0(\text{C}_6\text{H}_6) + 2 \Delta H_{f,298}^0(\text{H}_2) - \Delta H_{f,298}^0(\text{C}_2\text{H}_2) - \Delta H_{f,298}^0(\text{C}_4\text{H}_8) \\ &= 82.93 \text{ kJ mol}^{-1} + 0 \text{ kJ mol}^{-1} - 226.73 \text{ kJ mol}^{-1} - (-.13 \text{ kJ mol}^{-1}) \\ &= -143.67 \text{ kJ mol}^{-1}. \end{aligned}$$

But calculating this enthalpy of reaction with enthalpies of formation is the same as specifying the

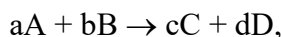
path



which of course sums up to



This calculation of enthalpies of reaction from enthalpies of formation can be put in a more general and abstract form if we do the following. First, we write down a generalized chemical reaction,



where the small letters are stoichiometric coefficients and the large letters represent reactants and products. We can rearrange this to get

$$0 = c\text{C} + d\text{D} - a\text{A} - b\text{B}.$$

Notice that the effect of rewriting our reaction this way makes the stoichiometric coefficients of the reactants negative and the stoichiometric coefficients of the products positive. This in turn suggests that we can write any general chemical reaction involving n reactants and products in the form

$$0 = \nu_1 S_1 + \nu_2 S_2 + \nu_3 S_3 + \dots + \nu_n S_n$$

$$= \sum_{j=1}^n \nu_j S_j$$

where the ν_j 's are stoichiometric coefficients and ν_j is positive if S_j is a product and negative if S_j is a reactant.

The enthalpy of reaction of our letter reaction will be

$$\Delta H_{rxn}^0 = c \Delta H_f^0(\text{C}) + d \Delta H_f^0(\text{D}) - a \Delta H_f^0(\text{A}) - b \Delta H_f^0(\text{B}).$$

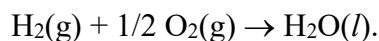
This suggests that for our most abstract representation that

$$\Delta H_{rxn}^0 = \nu_1 \Delta H_f^0(1) + \nu_2 \Delta H_f^0(2) + \dots + \nu_n \Delta H_f^0(n)$$

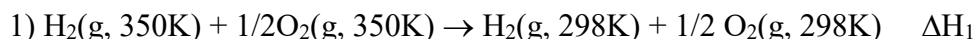
$$= \sum_{j=1}^n \nu_j \Delta H_f^0(j)$$

All three formulas for the calculation of the enthalpy of reaction are essentially the same. Later when we start dealing quantitatively with the thermodynamic treatment of equilibrium, this abstract representation will be an extremely powerful tool.

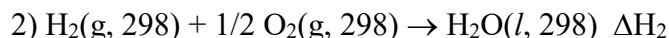
Now remember that when we defined our standard enthalpies we always used the phrase, "The standard enthalpy of X is the enthalpy of X at 1 bar pressure and the specified temperature. This implies that ΔH changes with temperature. To discuss the way ΔH changes with temperature quantitatively, we need to return to the concept of heat capacity. To see how heat capacities help us with this consider the following reaction.



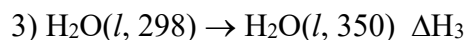
At 298K, suppose we know the characteristic enthalpy change, ΔH_{298}^0 . What is the enthalpy if the reaction is carried out at 350K, ΔH_{350}^0 ? The easiest way to approach this question is to break the high temperature reaction into three steps. First start with the 350K reactants and remove heat so that their temperature is lowered to 298K.



The second step is to allow the reaction to proceed at 298K.



Finally we add heat to the product to raise its temperature to 350K.



These three steps taken together are the same as if we had allowed the reaction to proceed at 350K.

WHY? Now remember that $\Delta H = q_p$. Our 350 K reaction has steps that include adding and removing heat, so it seems reasonable that ΔH for the higher temperature process will be different than ΔH for the lower temperature process. To find the ΔH for the reaction at 350K, we just add the enthalpy changes of our three steps. ΔH_1 is just the enthalpy of cooling our reactants. We can calculate this because we know that $C_p = dq_p/dT$, which rearranges to $dq_p = C_p dT$, and therefore $dH = C_p dT$. To get the enthalpy change for a macroscopic temperature change we integrate to get

$$\Delta H_1 = \int_{350}^{298} \bar{C}_p(\text{H}_2(\text{g}))dT + \frac{1}{2} \int_{350}^{298} \bar{C}_p(\text{O}_2(\text{g}))dT$$

$$\Delta H_2 = \Delta H_f^0(\text{H}_2\text{O}, 298)$$

$$\Delta H_3 = \int_{298}^{350} \bar{C}_p(\text{H}_2\text{O}(l))dT \quad \text{and}$$

$$\Delta H_{\text{react}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$= \Delta H_f^0(\text{H}_2\text{O}, 298) + \int_{298}^{350} \bar{C}_p(\text{H}_2\text{O}(l))dT + \int_{350}^{298} \left(\bar{C}_p(\text{H}_2(\text{g})) + \left(\frac{1}{2}\bar{C}_p(\text{O}_2(\text{g}))\right) \right) dT.$$

Remember now that

$$\int_a^b f(x)dx = -\int_b^a f(x)dx$$

So this becomes

$$= \Delta H_f^0(\text{H}_2\text{O}, 298) + \int_{298}^{350} \left[C_p(\text{H}_2\text{O}(l)) - C_p(\text{H}_2(\text{g})) - \frac{1}{2}C_p(\text{O}_2(\text{g})) \right] dT$$

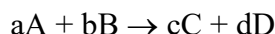
If we now make the definition

$$\Delta C_p = C_p(\text{products}) - C_p(\text{reactants})$$

then this becomes

$$\Delta H_{f,350}^0(H_2O) = \Delta H_{f,298}^0(H_2O) + \int_{298}^{350} \Delta C_p dT$$

If we consider again our generalized reaction



then

$$\Delta C_p = [c\bar{C}_p(C) + d\bar{C}_p(D)] - [a\bar{C}_p(A) + b\bar{C}_p(B)]$$

and using the more general notation we developed earlier,

$$\Delta C_p = \sum_{j=1}^n \nu_j \bar{C}_p(j).$$

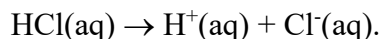
Therefore, in general

$$\Delta H^0(T_2) = \Delta H^0(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

This is known as Kirchoff's law.

Generally, heat capacities will depend on temperature. However, for many cases it is sufficient to make the approximation that C_p is independent of temperature. For other cases, where the temperature variation of C_p is of importance, the temperature dependence is usually represented by the empirical formula, $C_p(T) = a + bT + c/T^2$, where a , b , and c are tabulated in reference books and are different for each substance.

For ionic reactions in solution, we can use enthalpies of formation to calculate reaction enthalpies. However, we need to define a new set of standard states. Suppose we have a substance such as HCl that is fully ionized in solution, i.e,



Since the HCl is fully dissociated, we can think of the enthalpy of formation of HCl(aq) as the enthalpy of formation of its two component ions,

$$\Delta H_f(\text{HCl}(\text{aq})) = \Delta H_f(\text{H}^+(\text{aq})) + \Delta H_f(\text{Cl}^-(\text{aq})).$$

The problem in using this equation is finding the enthalpy of formation of any given ion in solution, since solution phase ions are always formed in pairs, for example, Na^+ and Cl^- or K^+ and CrO_4^{2-} . The solution is that we arbitrarily choose $\Delta H_f^0(\text{H}^+(\text{aq})) \equiv 0$ at all temperatures. With this as a starting point we can go ahead and calculate the enthalpies of all other ions in solution. This does mean that all of the heats of formation of ions in aqueous solution are measured relative to hydrogen ion and are not based on the same standard as heats of formation of neutral substances.