CHEM-203 Survey of Physical Chemistry

1. The first law of thermodynamics

Lecture summaries

First Exam: Chapter 2, sections 2.1 to 2.5 inclusive. You should know what "extent of reaction, ξ means (basic knowledge) but I will not use it in the course and will not test it. We do ideal gas calculations after the first midterm. We will skip section 2.7

In section 2.5 skip part 3 of the sub-section Measurement of Enthalpy Changes. Part 3 is called: Variation of equilibrium constant with temperature. You are not responsible for that.

Material covered is: the above from the book; my lecture notes summarized on MyCourses, and problem in the text book for chapter 2 that are relevant.

Problems to skip: 2.13; 2.19; 2.22; any starred problems

The lecture recordings are available under MyCourses.

The following summarizes the material covered in class::

Summary of lecture 1
Lecture 2
Lecture 3
Lecture 4
Lecture 5
Lecture 6
Lecture 7
Lecture 8
Lecture 9
Lecture 10
Lecture 11
Lecture 12
Lecture 13

End of first law of thermodynamics

Fall Term
CHEMISTRY 203

Please preview the material before coming to class. I will assign problems from the solution manual in class. Do problems assigned because exams will be based on similar problems. In the tutorials a certain number of representative problems will be done.

Summary Lecture 1 (Top)

Problems:

For Chapter 2, the first law of thermodynamics, do enough problems so that you feel comfortable. Do not do the stared (*) problems and omit the section on real gases.

Summary of first lecture:

See MyCourses for instructions and outline

Nitroglycerine

$$\Delta H_{Rx}(\text{nitroglycerine}) \sim \Delta H_{Rx}(\text{sucrose})$$

But energy is released fast and there is a large volume change: an explosion or detonation
Sucrose energy of combustion is released slowly.

Thermodynamics gives equilibrium states and not how fast something happens
Chemical kinetics gives the rates of reactions.

NO ENERGY IS STORED IN BONDS

$$\Delta U_{Rx} = \sum BE_{\text{Reactants}} - \sum BE_{\text{Products}}$$

<0 then exothermic and weaker bonds go to stronger bonds
>0 then endothermic and stronger bonds go to weaker bonds

System-that part of the universe of interest (open, closed and isolated)
State: defined by the parameters that are measured and describe a system under those conditions
Temperature: at thermal equilibrium, two systems have the same temperature
Zeroth Law of Thermodynamics: If system *A* is in equilibrium with system *B*, and *B* is in equilibrium with system *C* then systems *A* and *C* are in thermal equilibrium and have the same temperature.

Summary of lecture 2: (Top)

Your grade is determined by

Midterm 1	10% or 40%	(first law only)
Modterm 2	40% or 10%	(second law only)
Final exam	50%	(qualitative questions of 1st and 2nd laws + chemical Kinetics
Grade	100%	

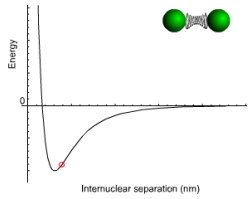
Review last time: emphasized that ATP ADP process, the electron withdrawing effects weaken bonds, so the first phosphate bond is weaker than the one formed to produce $H_2PO_4^-$.

Thermal energy: the energy around us: $\langle E \rangle_{\text{Thermal}} = RT = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \approx 2.5 \text{ J mol}^{-1}$

Since bond energies are typically 300 t0 400 kJ mol^{-1}, they are stable at thermal energies of the order of 300 K . Now the thermal energy excites modes: translation (moving); rotation and vibration. As bonds vibrate faster and faster, they eventually break.

Most bonds are stable at temperatures less than about 2,000 K:

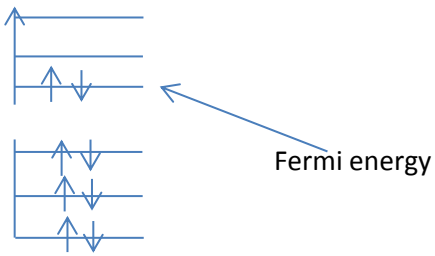
Understand the **potential energy diagram** for a diatomic molecule. (I will do this again)



On the sun, $\langle E \rangle_{\text{Thermal}} = RT = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 6,000 \text{ K} \approx 50 \text{ J mol}^{-1}$ and chemical bonds break because they vibrate too vigorously and rupture.

At the big bang, $T \approx 10^{31}\text{K}$ and only elementary particles exist (presently 16 bosons and fermions plus the Higgs Boson). So chemistry is restricted to **cold temperatures**, less than about 1,000-2,000 K. Physics is the rest.

Energy at 0 K? I asked and all but one person said no. There is lots of energy at 0 K but zero KINETIC energy. There is no motion. No translation, rotation or vibration. However, remember the Pauli Exclusion Principal? You can only put two electrons, paired up and down, in a quantum state, so higher energy levels must be filled until no electrons are left to fill the energy states:



You can see that the energy increases (vertical axis) as the energy increases because electrons must go into higher energy states. At absolute zero, the highest level occupied is called the Fermi level and the energy is called the Fermi energy. This is present at 0 K.

Because of the Pauli principle, it is impossible to push, (let's forget astrophysics, gravity and black holes), it is impossible to push the electrons from one level down to a level that is already occupied. Hence matter is rigid.

Internal energy: the energy needed to create the system from atoms. Contains kinetic energy of motion (moving, rotating and vibrating) as well as the electrostatic energy of the attraction and repulsion of electrons and nuclei.

When energy is added to a system in the form of **heat and work**, the internal energy, *U*, **increases**.
When energy is removed from a system in the form of heat and work, the internal energy, *U*, **decreases**.

Unless otherwise specified, all quantities (*U, V, T, P*, chemical species…) refer to the **system**, not the **surroundings**.

The change in internal energy, $\Delta U = U_2 - U_1$, only depends upon the initial and final states—called a **state function**.

Internal energy excludes PV work on the surroundings.

Summary of Lecture 3: (Top)

Sign convention: energy (heat and work) is positive when added to a system, and negative when removed from the system.

We always use this unless I indicate otherwise. Work is defined a force times distance. There must be a movement, otherwise work is zero. The change of *PV* work on a system is obtained as follows:

$$\Delta w = f \times \Delta d = \frac{f}{A} \times \Delta\left(Ad\right) = P \times \Delta V$$

Here the area of a piston is *A* and as this moves up (expansion) and down(compression) the piston can do work on the surroundings (expansion) or work can be done on the system (compression).

(Notice in motor vehicles, the number of liters of displacement is often stated. The greater the displacement, the more work it can do.

However this sign convention: compression $\Delta V < 0$ means $\Delta w < 0$ (above) but that is against the convention. We need work done ON the system to be positive.

Same with expansion, $\Delta V > 0$ means $\Delta w > 0$ (above) but work done BY the system (on the surroundings) must be negative.

To adopt this convention, the above definition must be changed to:

$$\boxed{\Delta w = -P\Delta V}$$

Thermo, as I said, gives relations between things measured under different conditions. In the following, think of a mole of gasoline burning. If you do this at constant volume and temperature the energy measured will be different from if the pressure and temperature are constant. However in both cases the reaction is the same. Hence there must be a relation between the two cases.

We will find that the heat at constant *T,V* is the internal energy, *U*, and the heat at constant *T, P* is the enthalpy, *H*.

Two general types of experiments (of many):

Bench top experiment: a beaker is exposed to the **constant atmospheric pressure** and is at **constant temperature**. Under these conditions, if the system expands (contracts) in a reaction then the atmosphere is pushed up (down) and PV work is done: $\Delta w = -P\Delta V$. The heat of reaction under these conditions is the enthalphy, *H*. $\Delta H = \Delta U - (PV \text{ work}) = \Delta U + P\Delta V$

At **constant temperature and pressure** then the **enthalpy** is the **heat of reaction**: $\Delta H = q_P$

The other general type of reaction is in a bomb **calorimeter** where $\Delta V = 0$ so no *PV*-work. The heat of a reaction at **constant temperature and volume** is the **internal energy** $\Delta U = q_V$.

Think of expansion. Then work is done on the surroundings and so $\Delta H > \Delta U$

(I did not say this in class): when a thermodynamic quantity depends only upon the initial and final state, then that quantity is called a state function.

Notice that *PV* is a state function. It has an equation of state: $PV = nRT$ for ideal. So, for example and constant *T* (an isothermal process) $P_1V_1 = P_2V_2$. A state function does NOT depend upon the path taken from state 1 to 2, and this is the most important property of a state function.

Define the relationship between enthalpy and internal energy:

$$H = U + PV$$

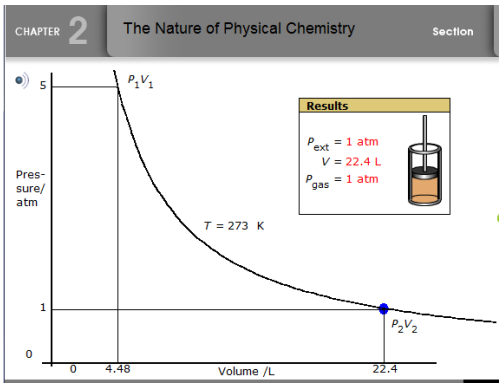
Note that $\Delta H = \Delta U + \Delta(PV) = (U_2 + P_2V_2) - (U_1 + P_1V_1)$ and the *PV* term is **not work** here, but we can still talk about ΔH and ΔU . However, these are only the heats of reaction if the enthalpy is at constant pressure and the internal energy is at constant volume.

The first law of thermodynamics: $\Delta U = q + w$

Reversible and non-reversible paths.

A change in a state function from one state to another does not depend upon the way the change is made. A state function only depends upon the initial and final values of the state.

There are many ways, or paths, of going from one state to another. However there is only one reversible path.



The reversible path is the most efficient because it maintains equilibrium between the system and surroundings throughout the change.

Look at the animation, Chapter 2 page 2-8 and see the reversible path and two irreversible paths.

The reversible path is called reversible because it is possible to move to a state, and from that state return to the original state along the same path. In this case it is isothermal, so no temperature change occurs between the initial and final states.

Important point about pressure:

You must distinguish the external pressure, P_{ext}, from the internal, or gas, pressure, P_g. The reversible path has

$$P_{ext} = P_g \rightarrow P_{ext} \pm \delta p = P_g$$

where $\pm\delta p$ is so small that $P_{\text{ext}} \cong P_g$ (almost equilibrium) but still the small difference allows the piston to expand or compress the gas. For all irreversible paths, $P_{\text{ext}} > P_g$ or $P_{\text{ext}} < P_g$, and the change is rapid. It is impossible to return to the same state along the same path.

Irreversible paths are possible but the reversible path can only be imagined (deganken or thought experiment). All processes go via irreversible paths. However since state functions do not depend on the path, we can calculate a state change using the reversible path. This is usually the easiest to calculate.

The internal energy is ONLY the heat of reaction at constant *T* and *V*

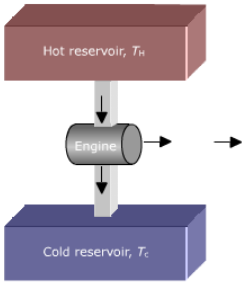
The enthalpy is ONLY the heat of reaction at constant *T* and *P*.

If otherwise, the internal energy and enthalpy still exists but they are not heat.

Summary of Lecture 4: (Top)

The first law of thermodynamics

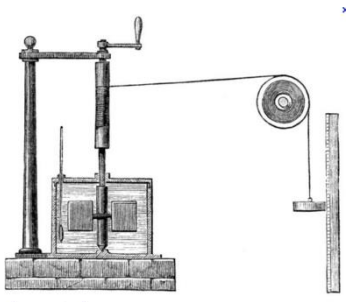
Conservation of energy: $\boxed{\Delta U = q + w}$



Von Meyer: boring cannons: the horses plod around a circle at constant speed, eating food (Δ*U*) from sacks. They drive the boring mechanism. If the bit is sharp, more work and less heat; if the bit is dull, less work and more heat, but the sum is always Δ*U*. So in this example, the internal energy is constant but the heat and work can vary, but their sum is the internal energy.

This means that heat and work are NOT state functions because there are many different conditions that give the same Δ*U.*

James Joule showed the mechanical equivalent of work in the late 18th century. He had a weight fall and turn a paddle in a vat of water. The paddle turns (work) and the water warms (heat). He showed that heat and work are interchangeable. He showed, in old units, that the heat required to raise the temperature of one gram of water by one degree is one calorie.

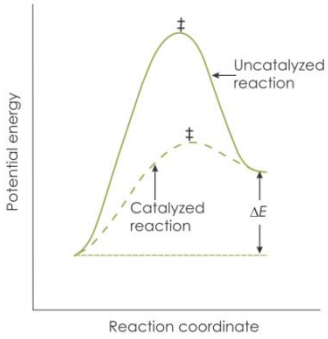


Thermodynamics: gives the relationships between states at equilibrium. (so we have seen the relationship between the enthalpy and internal energy: $H = U + PV$.) There are many more.

Thermodynamics does not give any numbers. We get numbers by relating to experiments. Thermo does not take into account the microscopic processes. Thermo is a macroscopic theory. Equilibrium thermodynamics is a closed subject with no new research (much) going on. Thermo is very general and applies to all macroscopic systems, from simple gases to the planets and universe; to plants and animals, and to chemical reactions.

One strength, and challenge, of thermo is it is so general it applies to everything and it is important to specify conditions when using thermo, like constant *T* and *P*, etc.

If we are away from equilibrium, then thermodynamics is not a complete theory with many unsolved questions. Non-equilibrium thermodynamics is a complex subject and must deal with phenomena like viscosity, turbulence, heat transfer, fluid dynamics: and entropy, when we get to it, is not easy to describe far from equilibrium. We do not do any non-equilibrium thermo, only equilibrium.



Chemical Kinetics: thermodynamics does not tell us how fast states change.

That is chemical kinetics (last third of course). On the right we see the effect of a catalyst. There is an activation barrier between reactants and products. A catalyst lowers this so the reaction can proceed with the available energy (thermal energy) surrounding it. Kinetics studies the rates of chemical reactions: the rate law, the rate constant, the mechanism, the temperature dependence and other conditions that help or hinder a reaction.

Work: see LMS and the beginning of section 2.4 on work calculations.

It is not worth me writing out the summary of work calculations because I follow very closely section 2.4 of the text book.

You should know how to use the Ideal Gas Law and calculate the work for constant pressure and for a reversible process.

The reasons that many thermodynamics courses do these Ideal Gas calculations are:

- Ideal gases are simple and allow the ideas of thermo to be clearer. The same concepts work for more complicated systems.
- There are a number of ways to introduce entropy, when we get to it, and knowing the Ideal Gas calculations for first law is needed for the second law.

Summary of Lecture 5 (Top)

Make sure you can calculate *PV*-work in the following cases: expand (compress) into vacuum; against a constant pressure; for a reversible isothermal process. (will do adiabatic later). The pressure is PV work is ALWAYS the external pressure. For a reversible process the external pressure is maintained equal to the internal gas pressure which is usually given by an equation of state, like the idea gas law, *P = nRT/V.*

(Problem 2.3 is clear but tricky:

"How much work is done by the system during the evaporation process?

You do the calculation and find the work is -X J mol^{-1}. (Hey that is right because to evaporate work is done in changing from a liquid to vapour.) But the question asks "by the system" so the correct answer is +X J mol^{-1}. The issue is –X is on the system and +X is by the system.

This is not chemistry but semantics and if this were an exam question, I would take both answers. However I prefer not to be tricky since no one benefits.)

Heat capacity units

The heat capacity is a measure of how much heat a system can hold. So write an expression which states that the heat added to a system (*q*) is proportional to its temperature change:

$$q \propto \Delta T \rightarrow q = C^{\text{Extensive}} \Delta T$$

The heat capacity is a parameter that depends upon the substance (*e.g.* Styrofoam, steel etc). However $C^{\text{Extensive}}$ with units of J K^{-1}, is extensive (as is heat). A bigger chuck of steel needs more heat to change its temperature by one degree than a smaller chunk. So we can define an intensive heat capacity by taking dividing by the quantity (moles, grams etc). So let us multiply and divide by the number of moles,

$$C = \frac{C^{Extensive}}{n} \left[\text{J K}^{-1} \text{ mol}^{-1} \right]$$

Intensive quantities are preferred over extensive quantities.

$$q = nC_m \Delta T \equiv nC\Delta T$$

I will be lazy with the subscript, *m*, because we almost always use the molar heat capacity C_m with units of J mol^{-1} K^{-1}. So I will not usually write the subscript) However we could have used some other measure of quantity, like grams, kilograms, pounds, if you want. Then the heat capacity will just have different units (and numerical value), so if mass is in grams, called, say *m*, we have

$$q = nC\Delta T = mC'\Delta T$$

So that is all there is to it. The units in the second case are J g^{-1} K^{-1}, so since $n = \frac{m}{M}$, the relation between the heat capacities is, $C = MC'$, where *M* is the molecular weight. So for water, the molar heat capacity is 18 times greater than the heat capacity per gram.

You should be able to calculate the heat from the above expressions for heat capacity.

Internal energy and Enthalpy.

Heat and work are generally not state functions. However at constant volume the heat is a state function and because of this we give it the special name *U*. So there is no work done, and

$$\Delta U = q_V$$

However we note that at constant Pressure the work is given by $w = -P\Delta V$ (PV-work) and the enthalpy at constant pressure is,

$$\Delta H = \Delta U + P\Delta V = \Delta U - \text{work}(PV)$$

That is, (think of expansion) the enthalpy has less energy than the internal energy because some has been removed to push back the constant pressure external atmospheric.

I said that you should read mathematical developments like a story (do not memorize it). So here are a couple of stories:

The *PV* term in the enthalpy:

In general the enthalpy is $H = U + PV$

So a change in enthalpy between two states is:

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

(the second term is NOT work). I prefer to use differentials, so

$$dH = dU + d(PV)$$

Now use the chain rule:

$$dH = dU + PdV + dPV$$

Let us impose constant pressure (now the *PV* term IS work)

$$dH = dU + PdV + \cancel{dPV}$$
$$= dU + PdV = dU - (-PdV)$$
$$= dU - dw$$

and use the first law

$$dH = dU - dw = dq_P + dw - dw = dq_P$$

$$\boxed{dH = dq_P}$$

Please go through this and say, "Yes I agree at each step". Before the constant pressure condition is imposed above, the enthalpy is not the heat because it has the extra term, dPV. (good to ask what that term does: dPV is the change in energy due to the pressure increase at constant volume. That term is important in bomb calorimetry—think of a constant volume that is heated).

To show that the enthalpy is the heat at constant pressure, see animations in chapter 2, **Heat of reaction** which is basically the following:

It is always really important to talk about conditions, like constant pressure, temperature etc. The internal energy is not the heat unless the volume is constant. The enthalpy is not the heat unless pressure is constant, etc. However both exist even when the temperature and pressure are not constant.

I finished up section 2.4 and showed the relationship for an ideal gas between the heat capacities at constant temperature and pressure,

$$C_P = C_V + R$$

If I just write down that equation, you should rightly ask where it comes from. The equation says that for ideal gases, the heat capacity at constant pressure is bigger by *R* than that at constant volume. Use the definitions:

$$H = U + PV$$
$$= U + RT$$

For one mole of an ideal gas (*PV=RT*). The definition of heat capacity is:

$$C \equiv \left(\frac{dq}{dT} \right)$$

At constant *P* and *V* the heat capacities are respectively $C_P \equiv \left(\frac{dq_P}{dT} \right) = \left(\frac{dH}{dT} \right)_P$ and

$$C_V \equiv \left(\frac{dq_V}{dT} \right) = \left(\frac{dU}{dT} \right)_V$$

(read the notation, it makes sense) The heat capacity at constant volume (pressure) is the change in internal energy (enthalpy) as the temperature varies.

Just understand where each step comes from. Go through it and feel comfortable with the steps.

$$\frac{dH}{dT} = \frac{dU}{dT} + R\frac{dT}{dT}$$

$$\left(\frac{dH}{dT}\right)_P = \left(\frac{dU}{dT}\right)_P + R$$

$$\left(\frac{dH}{dT}\right)_P = \left(\frac{\overbrace{dq_P - PdV}^{dq_V}}{dT}\right) + R$$

$$\left(\frac{dH}{dT}\right)_P = \left(\frac{dq_V}{dT}\right) + R$$

$$\left(\frac{dH}{dT}\right)_P = \left(\frac{dU}{dT}\right)_V + R$$

$$\boxed{C_P = C_V + R}$$

Math Interlude

Then I gave an introduction into slopes in more than one direction. In thermodynamics we have properties, state functions, which depend on parameters like *P, T, V, n*, etc. All I want to do is to show you that the concept of slope can be extended to several parameters, or variables. It is no more difficult than what you know from calculus, and partial derivatives, as they are called, crop up in thermo a lot. Also, as we will see, these slopes have meaning.

Of course in one dimension we write,

$f(x)$ and $\frac{df}{dx}$ as slope

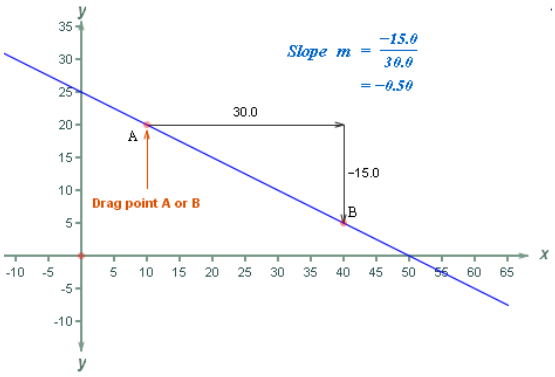
But what if the function has more than one variable,

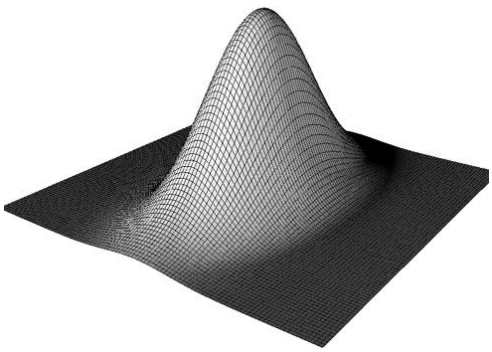
$f(x, y, z...)$

What we do is take the slopes with respect to each variable while the others are held fixed. So if we have something like,

$f(x, y, z) = x^3 y^2 z^{\frac{1}{2}}$

Then the total or exact derivative is given by





$$df(x,y,z)=\left(3x^2y^2z^{\frac{1}{2}}\right)dx+\left(2x^3yz^{\frac{1}{2}}\right)dy+\left(\frac{1}{2}x^2y^2z^{-\frac{1}{2}}\right)dz$$

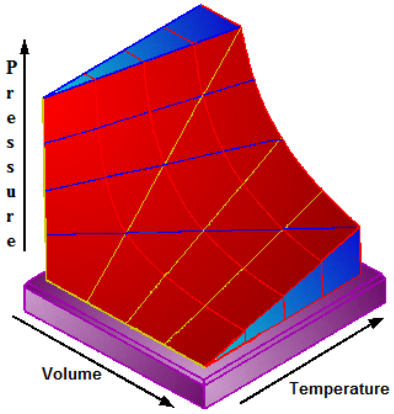
So the derivative *wrt x,* with *y* and *z* constant is,

$\left(\frac{\partial f(x,y,z)}{\partial x}\right)_{y,z}=3x^2y^2z^{\frac{1}{2}}$ and likewise $\left(\frac{\partial f(x,y,z)}{\partial y}\right)_{x,z}=2x^3yz^{\frac{1}{2}}$ and

$\left(\frac{\partial f(x,y,z)}{\partial z}\right)_{x,y}=\frac{1}{2}x^3y^2z^{-\frac{1}{2}}$

We can do this in any dimension, (any number of variables), but mostly we will consider two, like the two curves to the right.

The content of an exact differential is the same as the original function up to a constant.



Summary of Lecture 6 (Top)

BTW: you can right click the pages of the book and there is a zoom option.

Heat capacity: when a system is in equilibrium with its surroundings the molecules in the system can hold energy in their various modes. In general these modes are movement (or translation), rotation and vibration. That is the thermal energy from the surroundings (*RT*) is absorbed by the system and depending on the temperature the molecules move, rotate and vibrate faster or slower.

Heat capacity then is the ability of a system to store energy in the various degrees of freedom available.

Knowing the heat capacity allows us to calculate how much heat is required to raise its temperature,

$$dH = dq_P = nC_P dT$$
$$\Delta H = q_P = n\int_{T_1}^{T_2} C_P dT$$

I will use the heat capacity at constant pressure when the enthalpy is the heat, but the same works with different heat capacities under different conditions. Also keep in mind that heat capacities are temperature dependent, $C = C(T)$, but for convenience we will take them as a constant so we do not have to integrate,

$$\Delta H = q_P = nC_P \int_{T_1}^{T_2} dT = nC_P \Delta T$$

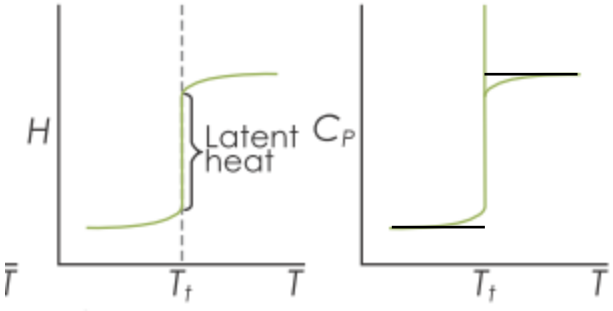
I used the example of heating ice from -20 C to 130 C at one atmosphere pressure. The total heat to do this is, (put the number of moles equal to 1)

$$\Delta H = q_P = \overset{20\text{ C}}{C_P(\text{ice})\Delta T} + \Delta H_{\text{fus}} + \overset{100\text{ C}}{C_P(\text{water})\Delta T} + \Delta H_{\text{fus}} + \overset{20\text{ C}}{C_P(\text{steam})\Delta T}$$

Ice is a crystalline solid and when it melts it does so at one fixed temperature, called the transition temperature—same for boiling. You keep adding heat to melt the ice but the temperature does not increase. All that happens is that ice melts to water.

If you have ice and water in equilibrium at 1 atm and 0 C then if you add a bit of heat, some ice melts. If you remove a bit of heat, some water freezes. A phase transition under these conditions is close to a reversible process. Such phase transitions are called first order. Not all materials have latent heats of fusion and vapourization. Glasses (amorphous materials), liquid crystals and some complex systems change phase over a range of temperature. We only consider first order phase transitions.

This is part of Figure 5.6 in the book



Notice that the heat capacity does indeed vary with temperature. If there is no temperature dependence, like we are assuming for simplicity, the black lines show the constant heat capacities.

Adding heat to a system at the transition temperature, as seen from the graph, involves a latent heat. Using the definition of heat capacity we have at the phase transition;

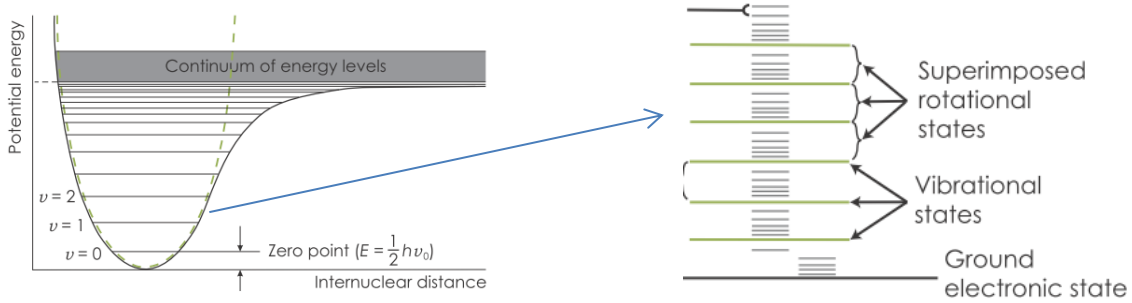
$$C_p = \frac{\Delta H_{\text{Latent}}}{\Delta T} = \frac{\Delta H_{\text{Latent}}}{0} = \infty$$

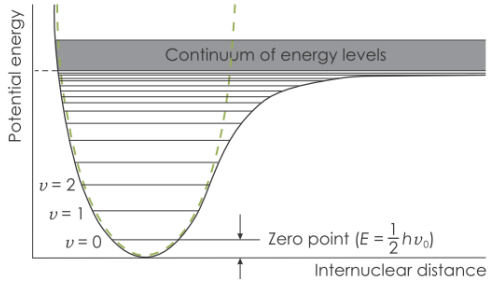
As seen from the figure, indeed the heat capacity does go to infinity. The reason for this is that at the transition temperature any heat added goes into changing the state. The heat breaks crystal bonds and changes the state. The latent heat does not go into heating the system, and the system has an infinite capacity to absorb heat until all the solid has been melted. Then any heat added will again start to raise the temperature of the system.

Summary of Lecture 7 (Top)

You should be aware of the experimental technique called Differential Scanning Calorimetry (DSC). We will talk about calorimetry in class but the technique of DSC is used to measure heat capacities and to find phase transitions. See Wikipedia: http://en.wikipedia.org/wiki/Differential_scanning_calorimetry

So many states of matter





These are parts of figures 13:14 and 13:19 in the text if you have the full text. The states of a molecule are quantized and can be put in the potential energy diagram that we have seen before. The translational states are not shown because the splitting is small relative to the rotational and vibrational energy splittings. It is true that $E_{\text{translational}} << E_{\text{rotational}} < E_{\text{vibrational}}$ so at room temperature usually all the rotational and translational levels can be excited (have molecules in those states) but often it is not possible to excite all the vibrational levels unless the temperature of the surroundings is raised.

Notice that if a molecule is in a higher excited state, it has a weaker bond energy. However as we will find out, at the temperatures we are usually interested in the bond strengths are usually much greater than the thermal energy that causes the internal kinetic motion.

Note also that the lowest vibrational state is above the minimum in the potential energy curve. This is a quantum effect due to the Heisenberg Uncertainty Principle: the equilibrium bond length and the vibrational momentum cannot be simultaneously known. Hence the first vibrational state starts above the minimum so there is always a small vibration going on even at absolute zero.

Internal energy is determined by those of translation, nuclear spin states (MRI, NMR), rotation, vibration, electronic and nuclear. At room temperture the vibrational states may not be fully excited; electronic states (Molecular Orbits, VSEPR models for bonding) are usually in their ground state and nuclear states (nuclear reactors) are always in the ground state.

Consider the energy of a diatomic molecule, N_2,

$$2N \rightarrow N_2$$
$$\Delta U = BE_{N_2} + \Delta U_{\text{thermal}}$$

Nitrogen atoms are monotomic and can only move (translate). Nitrogen gas is a diatomic and it can also rotate and vibrate.

So if we work out the energies we find at room temperature

$$\Delta U = BE_{N_2} + \Delta U_{\text{thermal}} = \left(BE_{N_2} + \Delta U_{\text{translational}} + \Delta U_{\text{rotational}} + \Delta U_{\text{vibrational}} \right)$$
$$= \left(-945,000 + \sim 0 + 2.5 \sim small \right) \text{J mol}^{-1}$$

In other words, the bond energy usually dominates the thermal energy so we usually neglect it.

However we cannot neglect the thermal energy in calculating the heat capacity because the heat capacity does not depend upon the bond energy, only upon the thermal energy.

Leading up to thermochemistry consider the process of using the Haber-Bosch process to make ammonia (131 million metric tonnes in 2010),

$$\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightleftarrows \text{NH}_3 \quad \Delta H_f$$

This is balanced with respect to mass, energy and charge. (E.g. $H_2O \rightarrow H^+ + OH^-$). Note that the enthalpy refers to this equation saying that the energy to form one mole of ammonia from its elements nitrogen and hydrogen is ΔH, and

$$\text{N}_2 + 3\text{H}_2 \rightleftarrows 2\text{NH}_3 \quad 2\Delta H_f$$

If you put one mole of nitrogen together with 3 moles of hydrogen, you would come to equilibrium given by

$$K_P = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

Not very much ammonia formed. However if you maintained a high pressure of nitrogen and hydrogen and bled off the ammonia (Haber-Bosch), then you keep producing ammonia. This is done by using the quotient product which is the same form as the equilibrium constant but with any pressures, $\hat{P}_i$

$$Q_P = \frac{\hat{P}_{\text{NH}_3}^2}{\hat{P}_{\text{N}_2} \hat{P}_{\text{H}_2}^3}$$

Note that to make ammonia continuously $Q_P << K_P$. We are feeding a chemical process to keep it producing. This is the most common in Nature—equilibrium is death.

In many cases the internal energy is obtained by counting the bonds broken and made. Since bond energies are always positive, they are the energy needed to break a bond to form atoms.

$$\Delta E_{B.E.} = \sum_i BE_i\left(\text{reactants}\right) - \sum_i BE_i\left(\text{products}\right)$$

(make stronger bonds—exothermic—make weaker bonds—endothermic)

Now in contract the internal energy is the energy released to the surroundings as bonds form, so

$$\Delta U = \Delta E_{B.E.}$$

Anon

Summary of Lecture 8 (Top)

Themochemistry

1. Relates the enthalpy and internal energy when chemical reactions occur. Again constant pressure and constant volume conditions are important. In $H = U + PV$ know how to work out $\Delta(PV)$ and meanings at constant *P*, constant *V*, and when neither are constant.
2. Again understant the heats: $q_{P,} q_V$ for reactions
3. Quantum states: recall that a chemical bond is purely quantum. When a system is studied by quantum mechanics the Schrödinger equation is solved, usually approximately, and the states are characterized by quantum numbers. We have no control over these, they define the possible states much like we define a macroscopic state by *P, T*, type of molecule, etc..
    a. Electronic states: for elements have s, p, d, f electronic states (states of the electrons) and similar parameters for molecular states.
    b. Rotational states (angular momentum) are same as other angular momentum, like orbital angular momentum of an electron (Lm_l). Rotational states are usually denoted by quantum numbers (Jm_j) where J goes from 0 to ∞, and $-J < m_j < +J$. Recall that spin is also angular momentum, but has no classical analogue: spin ½ has only two states, ±½
    c. Vibrational states: go in interger values *v* = 0 to ∞.
    d. Translational states: these are usually not of interest. We can eliminate movement and position by sitting on the center of mass (c.o.m.) of the molecule so we see the states a) to c) around us, within our frame. The c.o.m. frame subtracts off motion—when you ride a bus you are in the c.o.m. frame of the bus and the motion of the bus is the same as yours. At room temperature the energy of a mole of say argon atoms moving is 3/2RT

Quantum states are microscopic. Thermodynamic states are macroscopic and averaged over these using a distribution of energy. At equilibrium this is given by the Boltzmann distribution,

$$\text{probability} \propto \exp\left(-\frac{E}{RT}\right)$$

So when the energy is small the probability is close to one, but as the energy increases, at constant T, the probability decreases to zero. (The Maxwell-Boltzmann distribution treats the energy as only the kinetic energy,

$$\text{probability} \propto \exp\left(-\frac{\frac{1}{2}Mv^2}{RT}\right)$$

4. A balanced chemical equation expresses conservation.

$$\frac{1}{2}\mathrm{N}_2+\frac{3}{2}\mathrm{H}_2 \rightleftarrows \mathrm{NH}_3$$

a. Balanced: conservation of mass.
b. Add heat of reactions: conservation of energy
c. If have ions present, there can be no net charge: conservation of charge
d. Expresses the breaking and making of bonds
e. Expresses the amount: in this equation can say either: half mole of nitrogen used; 1.5 moles of hydrogen used; one mole of ammonia produced. All are equivalent when referring to a balanced chemical equation.

$$\frac{1}{2}\mathrm{N}_2+\frac{3}{2}\mathrm{H}_2 \rightleftarrows \mathrm{NH}_3 \qquad \Delta_{Rx}H$$
$$\mathrm{N}_2+3\mathrm{H}_2 \rightleftarrows 2\mathrm{NH}_3 \qquad 2\times\Delta_{Rx}H$$

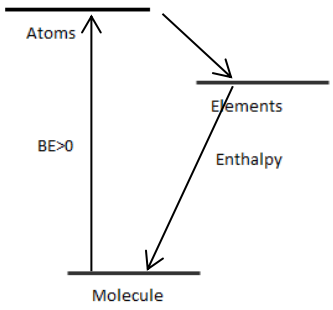
5. One can start with some non-equilibrium starting materials and let them react to equilibrium. Important to know this but not very useful. If you do not feed the reaction, it will stop, just like your heart if you do not eat. So the second general case is to feed the reaction so it continues to produce and your heart continues to beat

$$\frac{1}{2}\mathrm{N}_2+\frac{3}{2}\mathrm{H}_2 \rightleftarrows \mathrm{NH}_3 \qquad \Delta_{Rx}H$$

Feed the reaction by having high pressure of reactants and bleed off products as discussed above. For each mole of product, the heat is $\Delta_{Rx}H$ per mole of ammonia formed.

Bond Energy (BE) is the energy needed to break a bond. Usually a mole of bonds are broken so it is the energy per mole. Since energy must be put into the system to break a bond, then the BE is positive (always). In contrast the heats of reaction, or say, formation of molecules, is usually a negative quantity. A molecule is usually more stable than the elements from which it is formed. Therefore when calculating the heat of reaction from bond energyies use:

$$\Delta BE=\sum_i BE_i\left(\text{reactants}\right)-\sum_i BE_i\left(products\right)$$



While for enthalpy use the reverse:

$$\Delta H=\sum_i H_i\left(\text{products}\right)-\sum_i H_i\left(\text{reactants}\right)$$

and $\Delta BE=\Delta H$ --strictly true when the atoms are the elements, like in

$$\frac{1}{2}\mathrm{N}_2+\frac{3}{2}\mathrm{H}_2 \rightleftarrows \mathrm{NH}_3 \qquad \Delta_{Rx}H$$

In fact in this case both nitrogen and hydrogen are the elements, so this is formation of ammonia from its elements. To do this, we atomize the reactants, breaking half a mole of nitrogen bonds, and 1.5 moles of hydrogen bonds. Then, to form ammonia, three moles of N-H bonds are made for every mole of ammonia.

Of course at the microscopic level, bonds make molecules, but at the macroscopical level, all those states get averaged. So bond energy is considered here as the energy to break a mole of bonds. Strictly speaking the bond energy is more exactly related to the internal energy, ΔU, but since enthalpy is more commonly used (in fact the founders of thermodynamics, Gibbs, Maxwell, Clausius… used enthalpy at the start and not internal energy). So bond energies are also called bond enthalpies.

Note however that sometimes there are additional forms of stabilization of enthalpy, for example the resonance energy of benzene gives an additional 80 kJ mol-e stabilization over the incorrect *BE* value. So $\Delta BE = \Delta H$ is frequently not correct, expecially for aromatic organic molecules and large biomolecules.

For ammonia, in detail

$$\frac{1}{2}\mathrm{N_2} + \frac{3}{2}\mathrm{H_2} \rightleftarrows \mathrm{NH_3}$$

We have half a mole of nitrogen bonds; 1.5 moles of hydrogen bonds and three N-H bonds for one mole of ammonia:

$$\Delta BE\left(\mathrm{NH_3}\right) = \frac{1}{2}BE\left(\mathrm{N_2}\right) + \frac{3}{2}BE\left(\mathrm{H_2}\right) - 3BE\left(\mathrm{H\text{-}N}\right)$$
$$= \frac{1}{2}945 + \frac{3}{2}436 - 3\times 391 = -46.5 \text{ kJ mol}^{-1}$$

and $\Delta BE\left(\mathrm{NH_3}\right) = \Delta H\left(\mathrm{NH_3}\right)$. Note in this reaction all are gases, so the number of moles that change is

$\Delta n = \left(1 - 1/2 \ -3/2\right) = -1$, so $\Delta\left(PV\right) = \left(\Delta n\right)RT = -RT$ so it is easy to find the enthalpy energy,
$\Delta H = \Delta U + \Delta\left(PV\right) = \Delta U + \left(\Delta n\right)RT = \Delta U - RT$

Extent of reaction: a common way to express how far a reaction has proceeded at time t from initial conditions. Given the symbol ξ (tse). That is for a given balanced chemical equation ξ is the same for all species:

$$\xi = \frac{n_i\left(t\right) - n_i^0}{\upsilon_i}$$

where the difference between the initial concentration and the concentration at time t is divided by the stoichiometric coefficient, υ_i (note the LHS of a chemical equation has negative stoichiometric

coefficients. We will not use it, and I will not test you on it, but it is used frequently in engineering so you should be aware of it. Best seen by example. I did several in class like problem 2.3 in the text:

EXAMPLE 2.3 When 10 mol of nitrogen and 20 mol of hydrogen are passed through a catalytic converter, after a certain time 5 mol of ammonia are produced. Calculate the amounts of nitrogen and hydrogen that remain unreacted. Calculate also the extent of reaction:
a. on the basis of the stoichiometric equation

$$N_2 + 3H_2 \rightarrow 2NH_3$$

b. on the basis of the stoichiometric equation

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$$

Solution The amounts are

	N_2	H_2	NH_3	
Initially	10	20	0	mol
Finally	7.5	12.5	5	mol

a. The extent of reaction is the amount of ammonia formed, 5 mol, divided by the stoichiometric coefficient for NH_3:

$$\xi = \frac{5}{2} = 2.5 \text{ mol}$$

The same answer is obtained if we divide the amounts of N_2 and H_2 consumed, 2.5 mol and 7.5 mol, by the respective stoichiometric coefficients:

$$\xi = \frac{2.5}{1} = \frac{7.5}{3} = 2.5 \text{ mol}$$

Summary of Lecture 9 (Top)

Hess's Law—state functions are path independent

Any path will do! Combustion: $\Delta_c H$ where subscript c means complete combustion. So we can take some sugar and:

a. Eat it
b. Burn it in a bomb calorimeter
c. Burn it is a dish
d. Add sulphuric acid
e. ….
f.

$\Delta_c H$ is the same for all. See animation on LMS Page 2.28

Bond rearrangement:

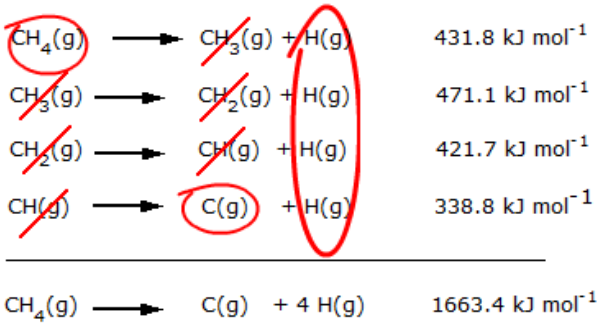
$$CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(g)$$

Think of a mechanism (like I did in class) of how products form. So you can visualize how bonds break and are formed. However, because energy is a state function we can choose other paths, like atomize the molecules or start from the elements. Note that when methane is atomized, after removing each hydrogen atom the bonds rearrange to minimize the energy so removing them one by one requires different energies: the type of bonds change as each H is removed,

$$\left(CH_4:\quad sp^3\right);\ \left(CH_3:\quad sp^2\right);\ \left(CH_2:\quad sp\right);\ \left(C:\quad p\right);$$

However the average of the four gives the total energy of atomization (and the bond strength for C-H:

$$CH_4(g)\rightarrow C(g)+4H(g)$$



Finally the C-H bond energy is the average of the total energy required to break all 4 bonds:

$$1663.4/4 = 415.6 \text{ kJ mol}^{-1}$$

(Table value, that comes from the average of many such experiments is 413 kJ mol^{-1})

Bond strengths also depend on the chemical environment and vary from molecule to molecule and within a molecule, as we saw for ATP hydrolysis. The different chemical environment leads to chemical shifts and these are picked up in spectroscopy, such as NMR, whence the positions of the resonance lines are sensitive to chemical environment.

Standard State. There are billions of reactions and an infinite number of experimental conditions. However we can reduce all these to a relatively small number of reactions because of the rules of thermodynamics and the use of Hess's law—path independent. Hence any reaction can be written in terms of the heats of formation from the elements from which a molecule is formed. Also we know how to change condtions from thermodynamics:

- We can change from one heat to another: $H=U+PV$
- If we know the heat capacities we can change the temperature of a reaction
- There is a similar relationship for changing the pressure and concentration (which we will come to later)
- Using the latent heats we can change phase from liquid to gas etc.

Therefore if we choose a "standard state" for all heats of formation then we can simply change these to different conditions by using the above sort of relations.

The standard state is chosen to be the heat of formation of a molecule from its elements when the temperature is 298.15 K, pressure is 1 bar and concentrations are 1 M. With these we can then find the enthalpies of reactions under different conditions.

Solutions often use concentration in **molality** units, rather than **molarity**, because molality is temperature independent, (moles per kg of solvent) where as molarity changes with temperature, (moles per liter of solvent). We prefer the concentration to be temperature independent.

Given the heats of formation of molecules you should be able to find the enthalpy for their reactions.

Recall that STP is standard temperature and pressure of 273K and 1 atm pressure which is different from the conditions for standard states.

Calorimetry was started.

I continued on from lecture 10 with more about the tables of heats of formation and thermochemistry. Defined what an element is at standard conditions: elements as they occur in Nature at 298.15 K and 1 bar pressure.

Since we can use thermodynamics to change temperature, pressure, concentration and other parameters, then we only list the heats of formation for molecules and use Hess's law.

I mentioned that sometime it is not possible to have one molar concentrations, like with small ionizations of molecules like water to (H^+ and OH^-) or from insoluble AgCl(s) to (Ag^+ and Cl^-) but since we know how to change concentrations, they are listed as 1 molar or 1 molal.

You should be able to do examples, like in the book and problems, using Hess's law and calculating the enthalpies of a reaction using the heats of formation from the tables.

Calorimetry: need to understand how to calibrate a bomb calorimeter and obtain the heat of reaction at constant volume, ΔU.

Contrast the bond energies and heats of formation:

Bond energy: to break a molecule up into its constituent atoms.

Heat of formation of the molecule: the heat of forming one mole of a chemical from its elements.

That is atoms are different from elements.

Bond enthalpies (or energies) need to be considered as less reliable that heats of formation because other stabalization can occur that bond energies miss: e.g. if a solid, we must first make a gas and then atomize the gaseous molecule to get the bond energy. Also note that some molecules, like benzene, have extra stabalization that bond energies miss. I will do an example next time using benzene.

Except where indicated as exceptions, this covers all the material in the book. On Monday I will do a couple of examples and also talk about benzene.

We have basically covered: the first law of thermodynamics, 2 to 4. I spent time calculating PV work in different cases and talking about a reversible path. I also spent time talking about heat and heat capacity. You are responsible for the equipartition that is in my notes.

The first law has wide applicability to many phonomena. Because this is chemistry, we applied the first law chemical reactions.

Summary of Lecture 10 (Top)

Ideal gas calculations

We have studied the First Law of Thermodynamics which is conservation of energy, so we have

$$\Delta U = q + w$$

We related internal energy to enthalpy. Then we considered application of the first law to chemical reactions. That means that in the conservation of energy we need to know the difference of energy between the reactants and products. The above equation is still correct but now the internal energy changes because of chemical reactions.

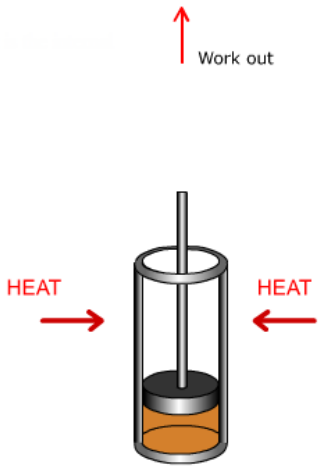
In section 2.6 we look at a few processes and calculate the changes in internal energy, enthalpy, heat and work for Ideal Gases. No chemical reactions. We look at reversible and irreversible processes and apply conditions of constant pressure or volume or temperature or adiabatic processes.

I will follow the text book in section 2.6 and not reproduce the material here.

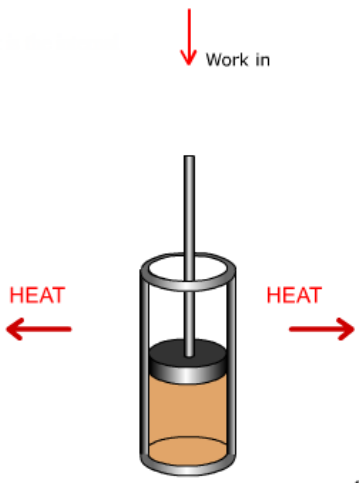
We do ideal gases for the following main reasons:

- Gases are simple to understand processes are intuitive.
- The thermo concepts that we obtain for an ideal gas are quite general and apply to more complicated systems.
- These gas calculations are needed to understand the Second Law. We obtain the second law by studying a steam engine (Carnot cycle) in order to find the maximum efficiency.

Please note that behind the formalism of thermodynamics are real physical phenomena and through the study of thermo we build insight and intuition into physical processes. Recall that thermo does not give number but just the relationships between things we can measure. Hence we can related enthalpy to internal energy and heat capacity at constant pressure to that at constant volume.

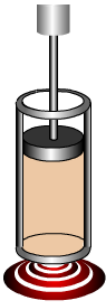


Since we deal with gases, and we will be doing calculations under different conditions, a physical intution of how gases change state is important. We deal with ideal gases which obey the ideal gas law, $PV=nRT$. This is simple and perhaps a little too simple but nonetheless they are useful For example, when a real gas expands, it cools. This is because there are forces that hold a real gas together (absent for ideal gases) and when those diluted because of expansion, energy must be lost (like putting energy into a bond to break it). Hence the expanding system cools. Likewise compressing a gas hot because weak bonds are forming in the gas and energy is released.



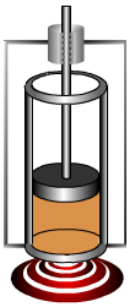
Now for a reversible process it is done so slowly that there is time to draw heat into the piston as the work leaves it, then equilibrium is maintained, the temperature does not change (isothermal process) and heat in equals work out, and vice versa (ideal gas)

$$q = -w \rightarrow \Delta U = 0$$



Consider a constant pressure process and heat the gas (LHS). Then the gas will expand and do work against the constant external pressure. Since we are heating and doing work, we have (as you should now well know)

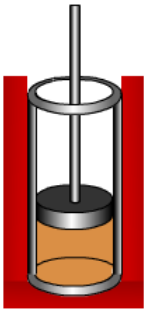
$$\Delta U = q_P - P\Delta V$$
$$\Delta H = q_P - P\Delta V + P\Delta V = q_P$$



If the gas is heated but the volume cannot change (RHS) then we have

$$\Delta U = q_V$$
$$\Delta H = q_V + \Delta(PV) = q_V + R\Delta T$$

for one mole. We have used the ideal gas law for the last step and we are assuming that no chemical reactions are taking place.



The final important process is adiabatic which by definition means that no heat can enter or leave the system. In this case as work is done the gas must cool. In contrast to the isothermal case no heat can be drawn in to replace that lost in doing work. Hence less work is done in an adiabatic expansion. A adiabatic compression is the same in reverse: compression heats the gas but there is no place for the heat to escape. Hence it is harder to compress it than for an isothermal case.

For gases between two states:

Isothermal:

$$P_1V_1T_1 \rightarrow P_2V_2T_1$$

Isochoric:

$$P_1V_1T_1 \rightarrow P_2V_1T_2$$

Isobaric:

$$P_1V_1T_1 \rightarrow P_1V_2T_2$$

Adiabatic:

$$P_1V_1T_1 \rightarrow P_2V_2T_2$$

For ideal gases you need to understand these processes both physically and mathematically. In the next lecture or two we will calculate these four cases which are in section 2.6 of the book.

Then we will be able to look at the Second and Third Laws of thermodynamics.

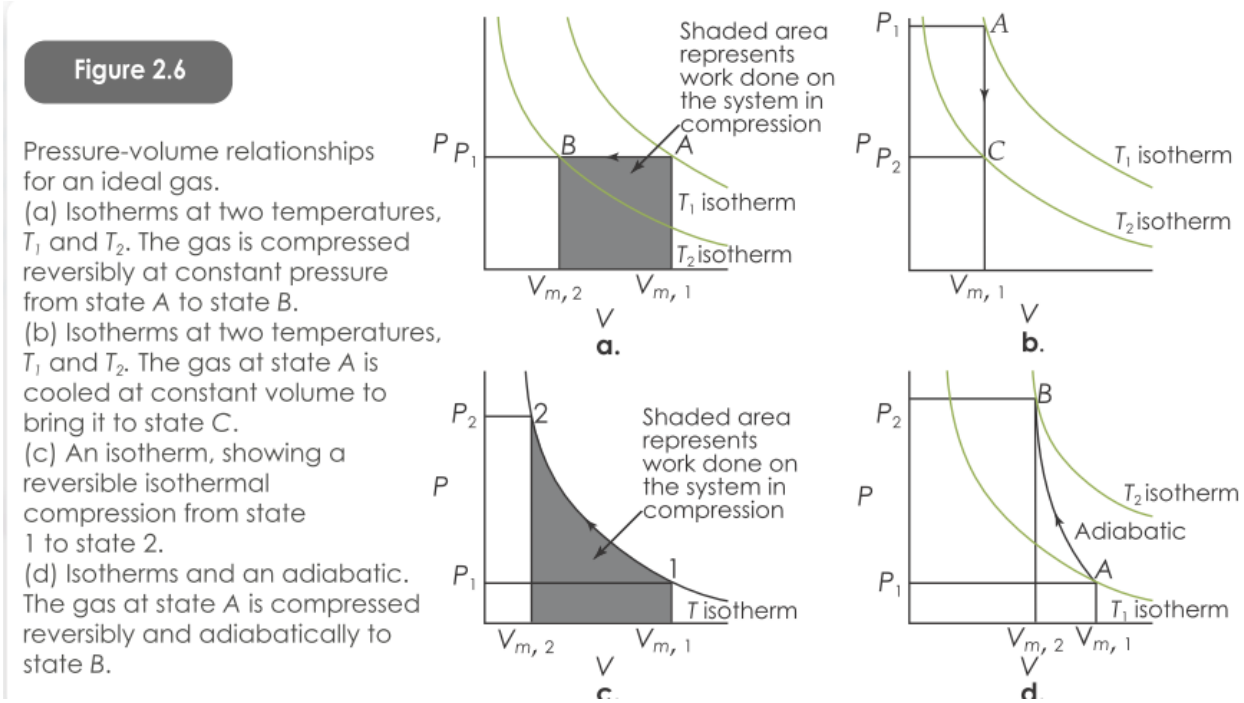
Summary of lecture 11: (Top)

We covered most of the ideal has calculations. I will only summarize these cases because they are done in the book, section 2.6. Please look at the cases in Figure 2.6 and understand these with respect to the text explanations.

There are four cases and you should understand these physically and then be able to translate these into the relevant equations using the first law:

$$\Delta U = q + w$$

There are an infinite number of irreversible paths. We will look at some if time permits but the main paths are reversible. You should have a feel for reversible paths. What we have not said, but which should make sense to you because I know that you know of entropy. For a reversible path only the entropy change of the system is exactly the opposite for the surroundings. We will get to that.



The four reversible paths (all for n = 1 mole):

Isobaric:

$$P_1, V_1, T_1 \rightarrow P_1, V_2, T_2$$
$$\Delta U = q_p + w = q_p - P_1\Delta V = q_p - R\Delta T = C_p\Delta T - R\Delta T = C_V\Delta T$$
$$\Delta H = q_p - P_1\Delta V + P_1\Delta V = q_p = C_p\Delta T$$

Isochoric:

$$P_1, V_1, T_1 \rightarrow P_2, V_1, T_2$$
$$\Delta U = q_V + w = q_V + 0 = q_V = C_V \Delta T$$
$$\Delta H = q_V + \Delta(PV) = q_V + R\Delta(T) = C_V \Delta T + R\Delta T = C_P \Delta T$$

Isothermal:

$$P_1, V_1, T_1 \rightarrow P_2, V_2, T_1$$
$$w = RT \ln \frac{V_1}{V_2}$$
$$\Delta U = 0 = q + w \rightarrow q = -w = RT \ln \frac{V_2}{V_1}$$
$$\Delta H = \Delta U + \Delta(PV) = 0 + R\Delta(T) = 0$$

Adiabatic:

$$P_1, V_1, T_1 \rightarrow P_2, V_2, T_2$$
$$q = 0$$
$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$
$$\gamma = \frac{C_P}{C_V}$$
$$\Delta U = q + w = w = C_V \Delta T$$
$$\Delta H = C_P \Delta T$$

For an ideal gas in all cases:

$$\Delta U = C_V \Delta T$$
$$\Delta H = C_P \Delta T$$

I finished up the reversible ideal gas calculations from Chapter 2.6 for and adiabatic process. You should know:

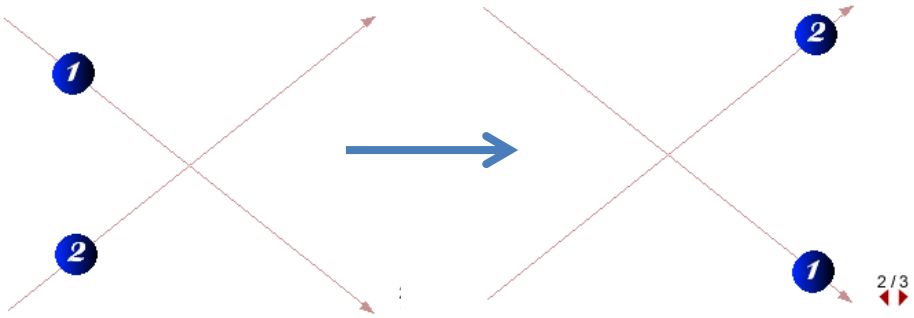
$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$ adiabatic reversible process with $T_1 \neq T_2$

$P_1 V_1 = P_2 V_2$ isothermal reversible process with $T_1 = T_2$

For all these processes the enthalpy and internal energy are always given by

$$\Delta U = C_V \Delta T$$
$$\Delta H = C_P \Delta T$$

But this is special for an ideal gas. Recall the kinetic molecular model assumes elastic collisions and I pointed out that elastic collisions, which conserve energy and momentum, can be ignored. Elastic collisions, like billard balls, are like the collision never took place:



But real gases have forces and inelastic collisions. Real molecules attract and repel each other, so if the volume decreases then the molecules are closer together and the forces can play a role that is absent in idea gases. We can express this generally using Thermodynamics by writing a total derivative,

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

We know the first term already and we used it for the ideal gas. The second term reads: $\left(\frac{\partial U}{\partial V}\right)_T$ at constant temperature, the internal energy of a system changes as the volume changes, as it does for real gases, liquids, solids and anything with intermolecular forces, which is pretty much anything.

Summary of lecture 11: (Top)

EQUIPARTITION OF ENERGY

Consider the different forms of molecular energy. One form is translational energy, which is the energy arising from the movement of the center of mass of a molecule from one position to another. We have already discussed this form of energy in Section 1.9, where we saw that the average kinetic energy per molecule resulting from translational motion is equal to 3/2*RT* (Eq. 1.50). This average energy can be split into three equal contributions for the energies corresponding to motion along the three Cartesian axes *X,Y,Z*. The energy splits in this manner

$$\frac{1}{2}E_X + \frac{1}{2}E_Y + \frac{1}{2}E_Z = \frac{3}{2}RT$$

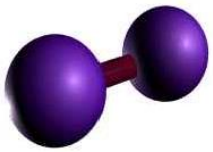
and is referred to as the equipartition of energy. It is obvious that there must be an equal division as far as translational energy is concerned, since there is no reason why any one direction should be favored over the others. So as you found when you derived the ideal gas law from the kinetic molecular theory, you found the energy of a gas is equal to 3/2RT, and this is consistent with equipartition.

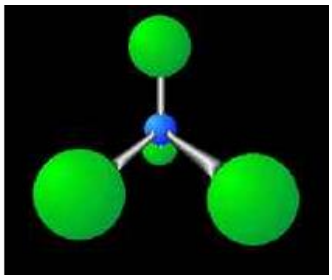
Equipartition of energy assumes that the available thermal energy of the surroundings can excite the molecules of a gaseous system with ½ RT energy for each translation and rotation degree of freedom and RT energy per vibration degree of freedom.

However, as we will see there must be enough thermal energy to excite all the states.

We refer to the components along the three Cartesian axes as three degrees for the translational freedom. Energy can also be stored in the rotational motion of molecules. For a non-linear molecule there are three degrees of rotational freedom, corresponding to rotation about the three Cartesian axes. For a linear molecule there are two degrees of rotational freedom, corresponding to rotation about two axes at right angles to the axis of the molecule. The reason that we do not count the rotation about the principal axis of the linear molecule is that the mass is almost completely concentrated in the atomic nuclei, so that the moment of inertia corresponding to this rotation is negligible.

rotate about *x*-axis
rotate about *y*-axis
rotate about *z*-axis





In addition, the vibrational motion can be resolved into a certain number of normal modes of vibration, which are known as the degrees of freedom for vibration.

To describe the position of an atom in space we need to specify three position coordinates X, Y and Z. If, therefore, a molecule contains *N* atoms, 3 *N* position coordinates must be specified. It is much more convenient, however, to work with degrees of freedom, which give us much more insight into the atomic motions. If a molecule contains *N* atoms, it must have 3*N* degrees of freedom, and it is easy to see how these are distributed among the different kinds of motion. Let us consider some simple examples of molecules in the gas phase.

1. A monatomic molecule, such He. There are 3 degrees of freedom, all corresponding to translation motion in the x-, y-, and z-directions.
2. A diatomic molecule, such as H_2. There are now 3 x 2 = 6 degrees of freedom, three of which are from translation. Since the molecule is linear, there are 2 degrees of rotational freedom. There is therefore 1 degree of vibrational freedom. (2 atoms x 3 trans) = 6 degrees of freedom; 6 – 3 vib – 2 rot = 1 vib.
3. A linear triatomic molecule, such as CO_2. There are 3 x 3 = 9 degrees of freedom, of which 3 are for translation and 2 for rotation. That leaves 4 degrees of vibration freedom.
4. A nonlinear triatomic molecule, such as H_2O. Again there are 9 degrees of freedom, of which 3 are for translation, 3 are for rotation, and 3 are for vibration. Here, 3 are for rotation, and therefore 9 – 6 = 3 are for vibration.

We can generalize our conclusions and give the following numbers of degree of freedom for a gaseous polyatomic molecule containing *N* atoms:

	Translational		Rotational		Vibrational		Total
Linear	3	+	2	+	$3N-5$	=	$3N$
Nonlinear	3	+	3	+	$3N-6$	=	$3N$

Note that the number of vibrational modes can be large, for benzene, for example, with *N* = 12, there are 3 x 12 – 6 = 30 vibrational degrees of freedom.

Equipartition of energy states that at temperatures high enough so that all the energy states are excited and that each translational and rotational degree of freedom contains $\frac{1}{2}RT$ energy, and each vibrational degree of freedom contains RT energy. Vibration has twice as much per degree of freedom than the other two because they have both potential energy and kinetic energy.

Hence the heat capacities are given by

	Translational	Rotational	Vibrational	Total
Linear	$\frac{3}{2}R$	R	$(3N-5)R$	$\left[\frac{5}{2}+(3N-5)\right]R$
Nonlinear	$\frac{3}{2}R$	$\frac{3}{2}R$	$(3N-6)R$	$\left[3+(3N-6)\right]R$

Summary of lecture 12: (Top)

Molar Heat Capacities of Gases: Classical Interpretations

First consider the molar heat capacities of gases at constant volume C_V since the gas performs no work of expansion and thus simplifies the calculation. Therefore, the heat capacity arises merely with the increase of temperature (Section 2.4). For a monatomic gas its internal energy resides solely in the translational motion and its average internal energy per molecule is *½RT* for each degree of freedom. At the same temperature, monatomic gases move faster than diatomic molecules. One mole the internal energy is therefore

$$U = \frac{3}{2}RT$$

We predict that C_V is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}R$$

We therefore predict the value of C_V is 1.500. This is confirmed by the experimental values in Table 15.1.

Table 15.1 Experimental and Calculated Values of C_V/R for Gases at 298.15 K

		C_V Calculated	
Molecule	Experimental	trans + rot	trans. + rot. + vib.
Monatomics			
He, Ne, Ar, Kr,Xe	1.500	1.500	1.500
Diatomics			
H_2	2.468	2.500	3.500
N_2	2.503	2.500	3.500
HF	2.505	2.500	3.500
HCl	2.504	2.500	3.500
HBr	2.506	2.500	2.500
O_2	2.533	2.500	3.500
NO	2.590	2.500	3.500
Cl_2	3.083	2.500	3.500
Linear triatomics			
CO_2	3.466	2.500	6.500
CS_2	4.447	2.500	6.500
Nonlinear triatomics			

H_2O	3.040	3.000	6.000
NO_2	3.447	3.000	6.000
SO_2	3.796	2.500	9.500
Linear polyatomics			
C_2H_2	4.304	2.500	9.500
NH_3	3.288	3.000	9.000
P_4	7.078	3.000	9.000

The experimental values in this table are calculated from the C_P values given in the JANAF Thermochemical Tables (Ed. M. W. Chase et al.), New York: American Chemical Society and the American Institute of Physics, 3rd edition, 1985.

The situation for other than monatomic molecules is, however, considerably more complicated. Some energy will reside in other degrees of freedom, but how much? Let us consider first the rotational motions. If the molecule is linear, we can express the rotational energy as

$$E_{\text{Rot}} = \frac{1}{2} I \left(r_X^2 + r_Y^2 \right)$$

For a linear molecule the two moments of inertia I_X and I_Y are the same and can be written simply as I ; ω is the angular velocity about the axis indicated. If the molecule is nonlinear, we have

$$E_{\text{Rot}} = \frac{1}{2} \left(I_X r_X^2 + I_Y r_Y^2 + I_Z r_Z^2 \right)$$

In the third column of Table 15.1 are the contributions to C_V/R that arise from the translational and rotational energies. Notice from Table 15.1 that the calculated translational and rotational energies are approximately the same but a little less than the experimental values down through the diatomics molecules. The agreement becomes decidedly worse when we include larger, non-linear molecules. The important point is that with the addition of the vibrational contribution in the fourth column, a great over shooting of the heat capacity values occurs in all but monoatomic and diatomic molecules. The conclusion is that not all of the vibrational modes are functioning. The question now becomes, why?

Molar Heat Capacities of Gases: Quantum Restrictions

If we were to look at the heat capacity at high temperatures, we would find that there was much better agreement with the values in the last column of the table, which means that there was equipartition of energy at high enough temperatures. At lower temperatures, the principle of equipartition of energy

breaks down, particularly for the vibration modes. We have seen in lecture 6 that the vibrational levels are much more widely spaced than the rotational and translational levels. Because of this wider spacing, energy cannot move as freely into and out of vibrational modes; a transition can occur only if a sufficiently large quantum of energy is involved (In spectroscopy, recall we add energy to excite the states: heat (atomic emission); shine on light (IR, Vis, UV etc); lasers. These ideas were first put forward in 1906 by Albert Einstein, who applied them quantitatively to the heat capacity of solids, a matter dealt with in 1911 to 1914, and in 1913 Einstein and Stern deduced a zero-point energy from an analysis of the specific heat of hydrogen gas at low temperatures.

Equipartition works if the temperature is high enough. Otherwise there is not enough energy to excite all the vibrational states.

Summary of lecture 13: (Top)

In this lecture I reviewed the eight paths for an Ideal Gas. Please think physically about each process in terms of heat and work, and what is going on. Why does reversible isothermal give the maximum work (All the heat in is converted to all the work out).

See Figure 2.6 and understand it.

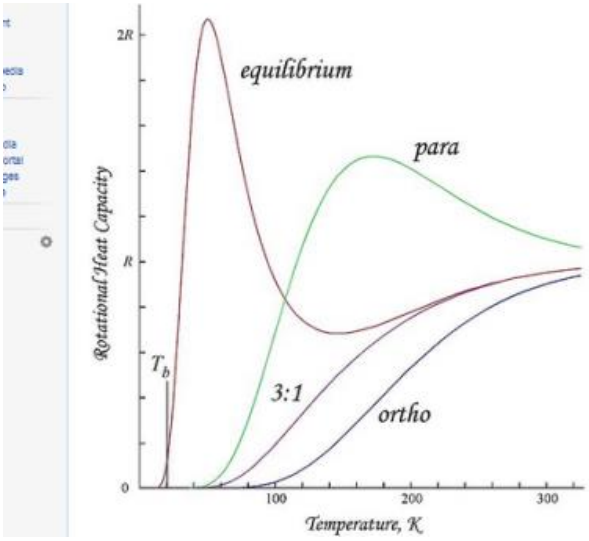
Adiabatic process. First if you compare the final volume of an isothermal process with an adiabatic process, the volume is much larger for isothermal than adiabatic. That is all the heat is converted into work.

For an adiabatic process, there is less heat available because no heat can enter. So as the gas cools, it expands until it can expand no more. The final volume is V^{γ} where $\gamma=C_P/C_V$ (you do need to understand the derivation of reversible adiabatic for an ideal gas). Clearly the smaller C_V, the larger γ and the larger is the final volume. This has the following physical interpretation: more heat is converted into work for a gas with a smaller C_V. From equipartition, we see that a monatomic gas has the smallest heat capacity and so this can do more work (larger final volume) than for a diatomic or polyatomic gas.

The first law says, $\Delta U = q + w$, and for an adiabatic reversible process, the work is increased as C_V decreases. If only movement occurs, translational motion, then the atoms move faster and transfer more momentum to the piston than if rotational and vibrational states were present.

Finally, I mentioned Ortho and Para hydrogen.

↑ ↑	↑ ↓
H – H	H - H
ortho	para
Spin 1	Spin 0
Triplet	Singlet
(3 states)	(1 state)



The heat capacities are shown for the orthohydrogen and the parahydrogen. The 3:1 ratio curve is what is expected, with three times more heat carried in the triplet than the singlet. But that 3:1 curve is not observed. Rather the experimental curve is observed. Is this a failure of equipartition? This caused a lot of problem in the 1940's and was finally resolved when it is realized that conversion between ortho and parahydrogen is a very slow process, about a year in a glass bottle. Hence the 3:1 curve cannot be maintained. That is,

$$H_2(\text{orth}) \underbrace{\overset{\text{no catalyst}}{\rightleftarrows}}_{\text{very slow}} H_2(\text{para})$$

So as the temperature increases, the ratio 3:1 ratio should be maintained, but cannot because of the slow conversion. This gives the experimental curve in the figure above. If, however, a catalyst is used, like platinum powder, the conversion between the two forms is fast; equilibrium is maintained, and the experimental curve then becomes the 3:1 curve and everything is ok.

The platinum works as a catalyst because the hydrogen molecule adsorbs to the platinum and the H-H bond breaks. When it reforms as H_2, it forms in the 3:1 ratio.

This is an interesting case of the effect of degrees of nuclear spin states that in fact affect the heat capacity of hydrogen.

Because of the slow conversion, parahydrogen is a good candidate for quantum computing because spin up, $\uparrow$, is used as a quantum bit (qubit) of +1 and spin down, $\downarrow$, is a qubit of -1, just what is needed for computers. Hence info is stored in a series of spins up and down, 0010011110, etc, and these are stable for a long time. To flip a spin, need to add energy, but once flipped, it is again stable (as long as the temperature is not too high).

We now have the ideal gas calculations clear and we can now turn to chapter 3 and understand entropy.