Internal Energy and the 0th/1st Law of Thermodyamics

* The total energy of a system, including all kinetic and potential energies of all subatomic particles is called the internal energy, U. *The absolute value of U can never be known*. However, changes in U are easily calculated, based on the first law of thermodynamics:

ΔU = q + w Eq. 2.1a (2.11) *Change in internal energy*

* + This quite simply means that energy must enter or exit a system as heat or work. *ΔU is a state function, even though q and w are not*!! (Demonstrate state function concept)
* The 0th law of thermodynamics essentially introduces the concept of state functions. The 0th law of thermodynamics states that: If any systems at different temperatures, isolated from the surroundings, are in physical contact, energy will transfer from the hotter system to the cooler system until the two systems reach thermal equilibrium.
  + Temperature is a measure of the kinetic energy of a system, but is itself not a form of energy, as described by the kinetic theory of gases

*Kinetic Theory of Gases*

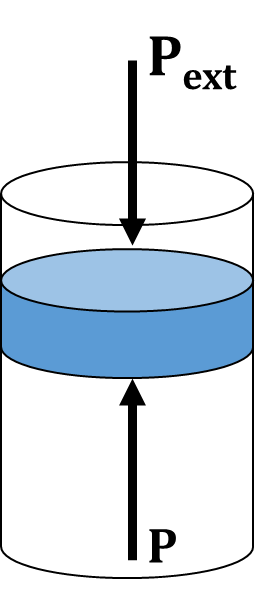
* Kinetic energy of a system cannot change without a corresponding change in temperature. Therefore:

Eq. 2.1b *Isothermal conditions*

Work

* Work is performed when mass is moved over some distance d by an applied force F acting over some surface area. (w=FΔd). Work has units of joule, because it is an expenditure of energy. In chemistry, it is easier to describe work in terms of the expansion or compression of a system, so we can manipulate the equation to a more usable form:

eq. 2.2 (2.4)  *PV work*

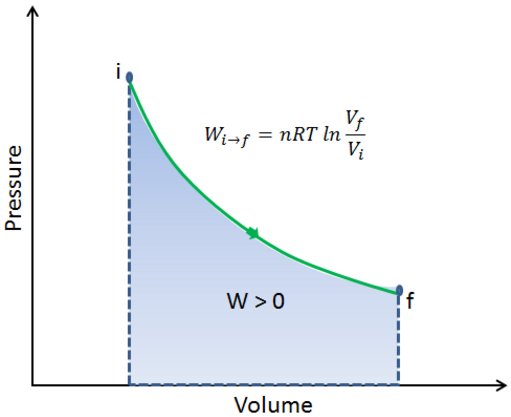
* + P represents the external pressure acting on a system. The negative sign is added to indicate that an external pressure acting on a system is opposing the internal pressure. Thus, the work of an expanding system is negative (expends energy, *does work on surroundings*) and a system being compressed has positive work (absorbs energy, *work done on system by surroundings*)
  + Free expansion in vacuum is spontaneous, and Pext = 0, so w = 0
  + From eq 2.2, we see that maximum work can be accomplished if the external pressure is at some optimal value. From the figure to the right, it is obvious that max work can be done by the system if Pext = P. *This is known as mechanical equilibrium*. Under this condition, any infinitesimal change in Pext would cause the piston to shift one way or another and require virtually no energy. Thus, the process would be thermodynamically reversible (requiring no work from the surroundings), and the value of w is obtained by integrating eq 2.2 w.r.t. pressure:

Eq. 2.3a (2.8) *max, reversible work*

Applying Boyle’s law: Eq. 2.3b (2.7)

More on Reversibility and Infinitesimally small changes

* While mainly theoretical, the concept of infinitesimally small changes in variables is central to the concept of reversible change. As previously stated, a reversible process is one in which the system, after undergoing the process, can be returned to its original state without work from the surroundings.
* Referring back to the cylinder and piston shown above. Imagine that Pext is only *slightly lower* than P by some very tiny quantity dP: Pext = P – dP. The gas will expand by some tiny volume element dV. The work done is dw = -PextdV. The value of work is essentially negligible. During this step, the process remains isothermal, and dU = 0. Thus, a small amount of heat dq must enter the system to compensate for the work energy expended, so dq= -dw.
  + At each step, mechanical equilibrium is established before the next step proceeds. Thus, we can imagine a path where the system expands from V1 to V2, which involves a massive number of small, reversible expansion steps of dV.
    - **REVERSIBLE WORK IS DONE ISOTHERMALLY!! (constant T)**



* + - Thus, the total work is, theoretically, the sum of the work performed in each reversible step, which is defined as the integral over ΔV of -PextdV.

Molecular Interpretation of work vs heat

* Work is a mode of energy transfer that involves ordered, uniform motion of mass, such as lifting a weight or electric current. *Heat*, however, is energy transfer that generates random, chaotic motion. Thus, heat energy goes toward increasing universal entropy, whereas work does not.

About heat

* Heat, q, is a measure of thermal energy transferred to/from a system, which *can* be determined by a change in T. Adding thermal energy to a system usually causes its temperature to increase (not the case during a phase change). The temperature change is proportional to the mass of the system by the specific heat capacity, (an intensive value):

q = mΔT Eq. 2.4 (2.9) *heat change associated with a temperature change*

, which has units of or can be expressed as an extensive value called *heat capacity*, C, which accounts for the amount of material (C = x mass or moles) and has units of J/K is just equal to:

Eq. 2.5

* + Endothermic processes have positive values of q, while exothermic ones have negative q values.
  + As was discussed earlier, isothermal expansions/compressions of gases involve heat transfer in order to maintain ΔU=0.

From eq. 2.3b Eq. 2.6 *Heat transferred during reversible process (ideal gas)*

More on Internal Energy

* Internal energy is dependent on the independent state variables T and V: U(T,V). The total differential of U can be expressed as:

Eq. 2.7 (2.21) *Total differential of U*

Relating this back to eq 2.1a:

Setting w = -PdV

Assuming constant V

Refer back to eq 2.5

We can now define the heat capacity of a system at constant volume:

Eq. 2.8 (2.23) *Heat capacity at constant volume*

* Since w = 0 for a constant volume process, ΔU = q, and thus:

Eq. 2.9 (2.27) *Change in U at constant V and changing T*

where is the molar heat capacity (J/mol K) at constant volume. If the heat capacity changes with temperature, the change in internal energy will have to be evaluated as an integral:

Eq. 2.10 (2.25) *Change in U for temperature dependent Cv, fixed V*

Special Considerations

* Isolated Systems
  + Perfectly insulated, so no flow of energy from/to surroundings
  + q = 0, w = 0
  + ΔU = 0
* Closed systems
  + ΔV = 0, w = 0
  + ΔU = qV
* Isothermal processes
  + w = -q
  + ΔU = q + (-q) = 0

Enthalpy (open systems)

* Most processes occur in open systems. An open system experiences constant atmospheric pressure, in which case:

ΔU = qP + w

qP = ΔU + PΔV

qP = ΔH eq. 2.11 (2.20) *Enthalpy*

* + Enthalpy is a convenient state function in the sense that we can avoid the complexity of calculating work. *By simply measuring the heat in or out, we can get a good approximation of the total energy change because in many cases ΔH and ΔU are very close in value*.
* We can therefore approximate enthalpy as a function of T and P: H(T,P). Revisiting the approach we took for eq. 2.8:

eq. 2.12 (2.29) *Total differential of H*

At constant P

Now, we can define the heat capacity at constant pressure as:

Eq. 2.13 (2.30) *Heat capacity at constant P*

And similar to eq 2.10:

Eq. 2.14a (2.32) *Enthalpy change at constant P with change in T*

Eq. 2.14b (2.31) *Change in H for temperature dependent Cp, fixed P*

* CP and CV are not the same!!! You must know if the process is *isobaric* (constant P) or *isochoric* (constant V) in order to determine what value to use.
* For Ideal gases:

eq. 2.15 (2.33, 2.28) *Ideal gas approx.*

Relationships between Cp and CV for Ideal gases

\*Recap

* Molecules have translational, rotational and vibrational degrees of freedom
  + Thermal energy is distributed to these modes,
  + Since ΔT α ΔEk, and C α ΔT, then C α ΔEk.
    - The heat capacity of a molecule is dictated by the magnitude of thermal energy consumed by each degree of freedom. Since temperature is most affected by translational modes, molecules with large allocations of energy to rotational and vibrational modes will have high heat capacities, as more thermal energy is needed to increase the temperatures of these systems.
  + Remember:
    - Etrans:
    - Erot:
    - Evib:
* For ideal gases:

eq. 2.16 (2.38) *Heat capacity conversion for ideal gases*

* + From kinetic theory, we can set the total translational energy as :

and therefore:

eq. 2.17 *Contribution of translational energy to the heat capacity at constant V*

* Important note: if we are discussing monatomic ideal gases, then the terms above represent the total constant volume heat capacity, as monatomic species lack rotational and vibrational modes. We can see then that, for a monatomic gas, the total constant pressure heat capacity would be 5/2 R. If the gas is not monatomic, then there are also contributions to the total heat capacity from the remaining degrees of freedom.
  + Total heat capacities under isobaric or isochoric condition is the sum of the contributions from all modes.
* Ex. Group work. Estimate the minimum and maximum value of and for nitrogen gas acting ideally.

Minimum (low T) = (trans) + (rot) + (min vib) = (3/2 R) + (R) + (3N-5)(0) =

Maximum (high T): (trans) + (rot) + (max vib) = (3/2 R) + (R) + (3N-5)(R) =

Minimum

Maximum

* Since the temperature dependence of the vibrational contribution affects the overall value of the heat capacity, a power series is used to estimate for real gases:

eq. 2.18 *Temperature-dependent heat capacity of a real gas*

Here, the lowercase letters represent experimentally determined values, not to be confused with van der waals constants.

* Group work. Ex 2.10b. Calculate ΔU for 1 mole of O2 going from -20oC to 37oC at constant volume while acting as: a) an ideal gas with no vibrational energy, and b) as a real gas with
  + a.) = (3/2)R + R = 5/2 R ΔU= n ΔT = 1184J
  + b.) (see pg 47) We must use revisit equation 2.10b and integrate the expression over the interval dT
* We can define a new term, γ:

eq. 2.21 (2.45)

*This term is used to define relationships between V, T and P during reversible* ***adiabatic******(q=0)*** *processes.*

Adiabatic, reversible expansions and compressions

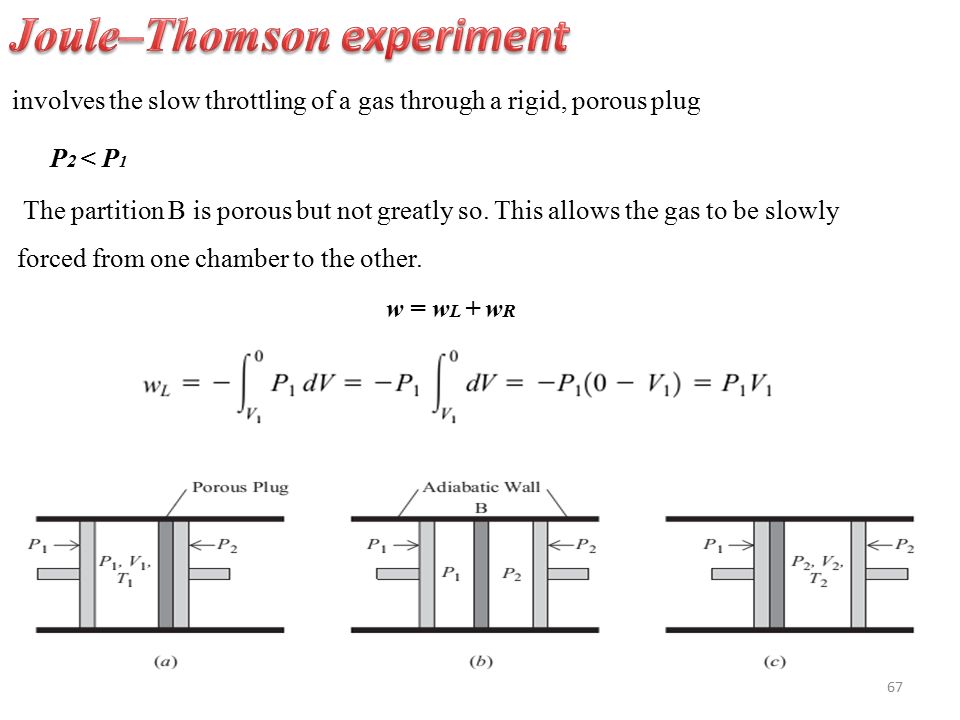
eq. 2.22a

eq. 2.22b

eq. 2.22c (2.46, 2.48, 2.49)

Joule-Thomson Effect

* Referring back to eq 2.1, the speed of a molecule is proportional to its temperature. *Thus, reducing the speed of a molecule is equivalent to cooling it*.
* For *real* gases with strong intermolecular attractions, a gas can be rapidly cooled by allowing the gas to *expand adiabatically*. During the expansion, the molecules move apart to fill the available volume. This work consumes internal energy and the molecules slow. Thus, by continuously expanding a gas, it can be cooled substantially, and eventually liquefied. *This is known as the Joule-Thomson effect, and it is the primary way that gases such as nitrogen are liquefied.*
  + Imagine a gas at pressure P1 being forced through a porous barrier. The gas can freely expand on the other side of the barrier, at which point the pressure drops to P2. The figure below describes this.



* We can write an expression for the total work of the process by adding the work done by the gas (expansion) and the work done on the gas (compression):

* Since the free expansion of a gas is adiabatic, ΔU = w

Apply eq. 2.11

*Isoenthalpic process*

* This is a strange result because we have a process that is isoenthalpic, but not isothermal. *Thus, we can express a change in T caused by the change in P at constant H. This is known as a Joule-Thompson coefficient*.

eq. 2.23 (2.34) *Joule-Thompson coefficients*

* + These values are experimentally determined for a vast array of gases. The value of the coefficient depends on the initial temperature and pressure of the gas. A table is found in your textbook on page 51. Below the *inversion temperature*, the value of µJT is negative, meaning that the gas heats on expansion. Oddly, before a gas can be cooled by the JT method of expansion, it must first be cooled below its inversion temperature by normal means.
  + Class example: Ex. 2.11 Pg 50