office hours 9:30-10:30 for sure
I am free 10:30-noon, 1-2, 3:30-5 today,

Friday: 10:20-noon, 1:15-3, 4:15-5
Consider the process of a falling object of mass $= m$, with $T = 298$ K before and after, with surroundings at $T = 298$ K. No insulation. Mass falls, SLAMS!! into floor. Describe what happens and the new state.

**State 1**
- $U = mgh$
- $T = 298$ K

**State 2**
- $\Delta U = -mgh$
- $w = -mgh$
- $q = 0$
- $T = 298$ K

**Path 1,**
- $\Delta U = -mgh$
- $w = 0$
- $q = -mgh$

**Path 2,**
- $\Delta U = -mgh$
- $w = -mgh$
- $q = 0$

Pulley gives reversible path: forces balanced, useful work done = weight is lifted
**Enzymes** are the “pulleys” of biochemistry.”
(~ 75,000 enzymes in the human body)

Life: enzymes make a spontaneous reactions happen fast while making a useful, non-spontaneous process to HAPPEN!

The biochemical reactions in living systems are carried out in nearly reversible manner. Almost all the Gibbs energy becomes useful work.
Now Contrast irreversible and reversible for Pressure-Volume work

**IRREVERSIBLE**

\[ p = \text{changes from 3 atm to 1 atm} \]

but \( p_{\text{ext}} = 1 \text{ atm and constant} \)

**REVERSIBLE**

\[ p_{\text{ext}} = p \text{ during entire expansion} \]

by removing grains of sand from piston.

Adding one grain of sand reverses direction

\[ p_{\text{ext}} = p \text{ always} \]
“Ideal Gas”: What is it?
1. No volume
2. No interactions, i.e., NO POTENTIAL ENERGY
3. Obeys pV=nRT

How does the energy of an ideal gas change with volume at constant temperature?

U is independent of V!
U = 3/2 RT per mole for atoms;
U = U(T) in general (for ideal gas)

For ideal gas isothermal process $\Delta U = 0$

Evaporation of water can be isothermal;
Is $\Delta U = 0$??
NO. Evaporation requires energy to break H-bonds, etc.
To maintain constant T requires q=+ (endothermic
**Isothermal vs. Adiabatic**

How is an isothermal process done?

**Isothermal:** The moving piston makes the molecules move faster, i.e., gain kinetic energy, i.e., the gas becomes hotter, but the walls conduct the heat out to the cooler water bath, thus keeping the gas at the same temperature.

In an **adiabatic** compression, the cylinder is INSULATED. Therefore the gas gets hotter as the piston move down. The work done by the external pressure appears as kinetic energy of the system.
Quiz

What are signs of: $\Delta T$, $q$, $w$, $\Delta U$?

Adiabatic: $-$ 0 $-$ $-$$+ 0 + +$

Isothermal: 0 $+$ $-$ 0 0 $-$ $+$ 0
Reversible **Isothermal PV work (ideal gas)**

\[ p_{\text{ext}} = p = \frac{nRT}{V} \]  
(balanced forces)

An integral is just a sum

\[
\int_{V_1}^{V_2} p_{\text{ext}} \, dV = \int_{V_1}^{V_2} pdV = -\int_{V_1}^{V_2} \frac{nRT}{V} \, dV
\]

\[
w = -nRT \ln \frac{V_2}{V_1}
\]

**ONLY if** \[ p = p_{\text{ext}} = \text{and ideal gas} \]  
(but is common case)

What are \( \Delta U \) and \( q \)?  
\( \Delta U = 0 \) (isothermal), therefore \( q = -w \)

\[ \]
Equation of State

example, ideal gas: \( pV = nRT \)

\( n = \text{mols}, \ p = \text{pressure}, \ V = \text{volume}, \ T = \text{absolute temp.} \)

\( R = \text{“gas constant”} = 8.3145 \ \text{J mol}^{-1} \text{ K}^{-1} \)

\( = 0.083145 \ \text{L bar mol}^{-1} \text{ K}^{-1} \)

\( = 0.0821 \ \text{L atm mol}^{-1} \text{ K}^{-1} \)

Note that \( V = \frac{nRT}{P} = V(n, T, P) \)

or \( P = \frac{nRT}{V} = P(n, T, V) \)

or \( n = \frac{PV}{RT} = n(T, P, V) \)

or \( T = \frac{PV}{nR} = T(n, P, V) \)
Spontaneous reactions can be harnessed to produce “useful work” (also called “non-pV work”).

If not harnessed, the only work is typically what I call **OBLIGATORY pV work** against the atmosphere, \( w_{pv} = -p_{atm} \Delta V = -(1 \text{ bar}) \Delta V = \text{small and not “useful”} \) (this is what distinguishes \( \Delta H \) from \( \Delta U \)).

Consider burning gasoline: \( \Delta U \) is large and negative

**Unharnessed**: \( \Delta U = q + w \) so energy given off mostly as heat (very exothermic), a waste unless heat is what you want. This is totally irreversible (H\(_2\)O + CO\(_2\) don’t spontaneously make gasoline).

**Harnessed**: by enclosing the explosion in a cylinder and connecting the piston to a crankshaft to turn the wheels so that the very high p pushes against an opposing pressure that is just a little smaller (nearly reversible).

Now \( \Delta U \) (almost) = \( q_{rev} + w_{atm} + (w_{nonpV})_{rev} \), where \( (w_{nonpV})_{rev} \) is large negative and \( q_{rev} \) is therefore a much smaller negative. **Most of the large negative \( \Delta U \) is useful work instead of heat.**

*The biochemical reactions in living systems are carried out in nearly reversible manner. Almost all the Gibbs energy becomes useful work.*
Some useful state functions are **DEFINED** from other state functions. We are immediately concerned with

**Enthalpy** \( H = U + pV \) (by definition)

Why invent yet another state function?

Because \( \Delta U = q + w \). \( q \) is easy to measure, but most chemical reactions have a small work term \( -p_{\text{ext}} \Delta V = -p_{\text{atm}} \Delta V \) (due to expansion or contraction against the atmosphere).

We want to **tabulate state functions**, NOT \( q \) and \( w \). **Under the very common conditions**: \( p = p_{\text{ext}} = p_{\text{atm}} = \text{constant} \), and \( w = \text{only the obligatory } pV \text{ work on atmosphere} \), the above definition yields: \( \Delta H = q \) (nice!)
Enthalpy:
\[ H = U + pV \] by definition (always true)
\[ dH = ? \]
\[ = dU + d(pV) = dU + pdV + Vdp \]
\[ \Delta H = \Delta U + \Delta(pV) = \Delta U + p_2V_2 - p_1V_1 \]
\[ \text{(not } \Delta U + p\Delta V + V\Delta p) \]

\[ \Delta H = q \] (IF \( p_{\text{ext}} = p = \text{constant, and only } pV \text{ work done} \)

because \( \Delta U = q + w = q - p_{\text{ext}}\Delta V \text{ and } \Delta pV = p\Delta V \)

The annoying \(-p_{\text{ext}}\Delta V\) term cancels!

\[ \Delta H \text{ for an } \text{ideal gas?} \]
\[ \Delta H = \Delta U + \Delta(pV) \text{ by definition} \]
\[ pV = nRT \text{ (ideal gas)} \]
\[ \Delta(pV) = \Delta(nRT) = nR \Delta T \]

We know \( \Delta U = 0 \text{ if } \Delta T = 0, \)
so \( \Delta H \text{ also } = 0 \text{ for } \text{ideal gas} \)
if \text{isothermal} process