Lecture 2-2

Question of the Day: A system is transformed from P_1, V_1, T_1 to a higher temperature T_2 and volume V_2. If the system is an ideal gas, what is P_2? What is ΔE? what is ΔH?

Review: Heat Capacities (slide)

- Molecular Basis of Internal Energy

  → all molecular interactions in a system (H-bonds electrostatic, bond energies, vibration, kinetic...)

  → even things like $E = mc^2$ energy; thermo doesn't care (it was developed long before $E = mc^2$)

  1.) Example System #1: Trp molecule (slide)

  2.) Example System #2: Cylinder of gas (slide)

  → compression: doing work increases E by ~~storing~~ increasing interaction energy between molecules. Stored E can be reclaimed later to do work. This is 1st law.

- <u>Molecular basis of temperature</u> (ask class)
  - → temperature is related to kinetic energy of molecules. Faster molecules → higher temp
  - → Fast atoms are <u>hot</u>
- Molecular basis of heat capacity

  - → heat capacity measures a system's ability to to store energy (heat) in forms other than kinetic energy (↑Temp)

  - → example: Trp can store rotational energy (it can rotate faster), ~~bond energy~~ vibrational energy (bonds can vibrate faster), ~~electronic~~ in addition to moving faster in solution

  - → think: molecular degrees of freedom (what can I do w/ this energy other than increase my KE)

  - → (slide) water example (also handout)

How to Describe System

- (slide) does the <u>path</u> matter when describing state of a system → No. 1atm is 1atm
  - → <u>State variables</u> tell us about the <u>fundamental properties</u> of a system, not how it got there (slide)

- State equations (slide) → ways to relate state variables, often specific to system

- Think-Pair-Share (at table): are combinations of state variables also state variables, eg

$$H \equiv E + PV \quad \text{(discuss)}$$

→ yes. This is an important S.V. called ENTHALPY (memorize)

How to Calculate ΔE and ΔH

- Provided one can calculate Δq and Δw, then

$$\Delta E = \Delta q + \Delta w \qquad \Delta H = \Delta E + \Delta(PV)$$
$$= \Delta E + (P_2 V_2 - P_1 V_1)$$

- What are Δq and Δw?
  → these are path dependent; the path may involve changing temp, pressure, volume, etc.
  → many paths are irreversible; difficult to measure Δq and Δw of system by measurements of surroundings (eg. explosion)

- Step #1: Devise reversible path (slide)
  → even if actual path is complex, develop a simple transformation (reversible) - can be calculated

· Types of reversible paths (done slowly)

    isobaric - no ΔP isochoric - no ΔV ($\Delta V = 0$)

    adiabatic - $\Delta q = 0$ isothermal - $\Delta T = 0$
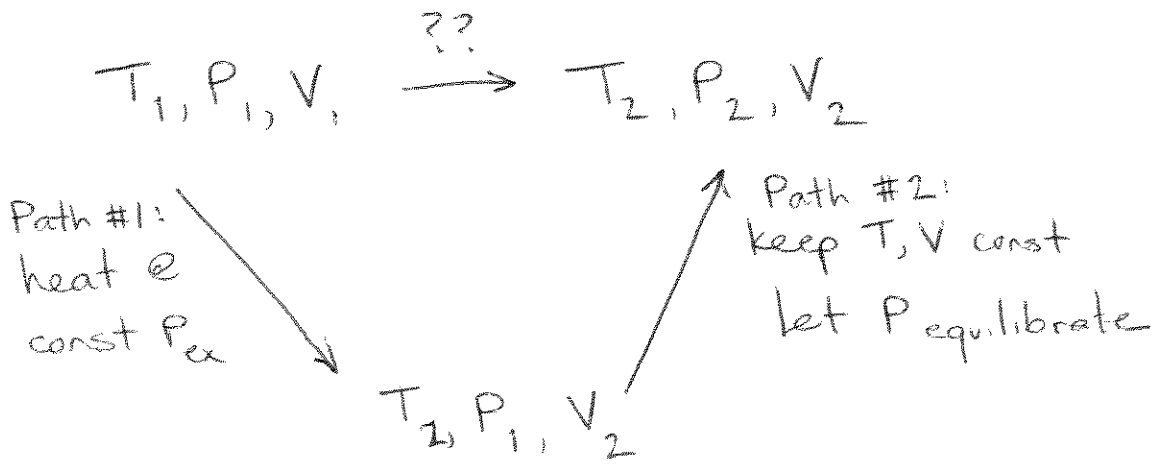
  → remember these in your problem set!

· Step 2: Using simple path, calculate Δq, Δw
    for each step (slide)

· Step 3: Sum up Δq, Δw, (slide)

Example #1: ΔH, ΔE in a liquid (slide)   derivation (skip if need be - refer to book)

  → note ~~samp~~ similar for solid (see book)

$$T_1, P_1, V_1 \xrightarrow{\;??\;} T_2, P_2, V_2$$

Path #1:
heat @
const P_{ex}

Path #2:
keep T, V const
let P equilibrate

$$T_1, P_1, V_2$$

→ path 1:

$$q_1 = n \bar{C}_p (T_2 - T_1) \qquad w_1 = -\int P_{ex} \, dV$$

$$\overset{const}{\qquad\qquad\qquad\qquad\qquad} = -P_{ex}(V_2 - V_1) \approx 0$$

approx: a liquid will not
expand much

→ path #2:

$$w_2 = -\int P \, dV = 0 \qquad q_2 \approx 0$$

↑
No ΔV

approx: you don't get warm
when ΔP in an airplane

→ So $\Delta E = q_1 + w_1 + q_2 + w_2$

$$= n\bar{C}_p (T_2 - T_1) \quad \text{(for a liquid)}$$

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

$$= n\bar{C}_p (T_2 - T_1) + (P_2 V_2 - P_1 V_1)$$

↓
again, $\Delta V \approx 0$, so $= 0$

$$\Delta H \approx \Delta E = n\bar{C}_p \Delta T$$

(for liquids, no significant expansion)

→ see book (example is there for solid as well)

→ summary (slide)

~~Examp~~

(end slip section)

Transformations of Ideal Gasses

• What is ideal gas? (review) — ask students

→ No volume of molecules   } important!

→ No interactions between molecules

→ State equation $PV = nRT$

• If we derive general path for isochoric, isobaric,
isothermal, we can calculate ΔE, ΔH for nearly any path
(slide)

1.) Reversible isochoric (see book for derivation)

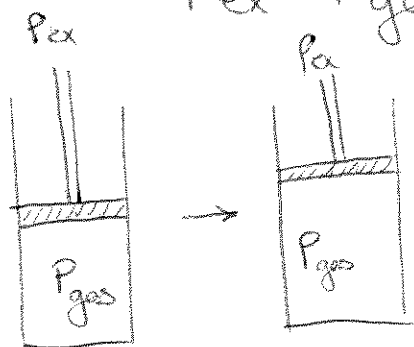$$w_v = 0 \qquad q_v = n\bar{C}_v(T_2 - T_1)$$

→ use $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2}$ if you aren't given all info.

Ideal gas law always applies for ideal gasses

2.) Reversible isobaric

→ reversible: done slowly so at each step

$$P_{ex} = P_{gas} = P$$

$$w_P = -\int_{V_1}^{V_2} P_{ex}\, dV = -\int_{V_1}^{V_2} P_{gas}\, dV = -\int_{V_1}^{V_2} P\, dV$$

$$= -P(V_2 - V_1)$$

$$q_P = n\bar{C}_P(T_2 - T_1) = \frac{\bar{C}_P P}{R}(V_2 - V_1)$$

↑
use PV=NRT

3.) Isothermal

→ does ΔE depend on V, P? No (why?)

→ ΔE only depends on T, so if $\Delta T = 0$, $\Delta E = 0$

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

$$w_T = -\int P_{ex}\, dV = -\int P\, dV \quad \leftarrow \text{cannot integrate, since}$$

P changes. Use gas law

$$= -\int_{V_1}^{V_2} \frac{\overbrace{NRT}}{V}\, dV = -NRT \int_{V_1}^{V_2} \frac{dV}{V} = -NRT \ln\left(\frac{V_2}{V_1}\right)$$

—constant

$$w_T = -NRT \ln\left(\frac{V_2}{V_1}\right), \text{ so } q_T = -w_T = NRT \ln\left(\frac{V_2}{V_1}\right)$$

$\rightarrow$ note that $\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{P_1}{P_2}\right)$ from $PV = nRT$

· Summary - ideal gasses (slides)

· QOTD: ~~you~~ for an ideal gas, you don't need to know specific path; you can calculate $\Delta E, \Delta H$ from some combination of isoT, isoP, etc.