P. Chem   Lecture Notes #3   1/25/23

Last Class: at constant volume,

$$\Delta U = q + w = q = q_v \Rightarrow C_v = \frac{q_v}{\Delta T} = \frac{\Delta U}{\Delta T} = \boxed{\left.\frac{\partial U}{\partial T}\right)_V = C_v}$$

Today: at constant Pressure

Define Enthalpy $\underbrace{H}_{\text{state function}} \equiv \underbrace{U}_{\text{state functions}} + \underbrace{PV}_{\text{state functions}}$

$$dH = dU + \overset{\text{product rule}}{P\,dV + V\,\underbrace{\cancel{dP}}_{V \cdot 0 = 0}} \rightarrow 0 \text{ bc constant pressure!}$$

get things in quantities we can actually measure experimentally

where $w = -P_{ext}\Delta V$

$$\underbrace{\Delta U = q + w}_{\text{(from previous lecture)}} = \delta q + \delta w = \delta q \underbrace{- P_{ext}\,dV}$$

$$dH = \overbrace{\delta q - P dV} = \delta q \Rightarrow \Delta H = q_P$$

$$\Rightarrow C_P = \frac{q_P}{\Delta T} = \frac{\Delta H}{\Delta T} = \boxed{\left.\frac{\partial H}{\partial T}\right)_P = C_P}$$

From HW 1, for an ideal gas

only depends on T, since ideal gas particles pass through one another. Volume doesnt matter.

$$C_P - C_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

→ substitute V for P from PV = nRT

$$C_P - C_V = \underset{U = U(T) \text{ only}}{0} \cdot \left.\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial \frac{nRT}{P}}{\partial T}\right)_P = 0 + nR \quad \left(C_P - C_V = 0 + nR \rightarrow n\bar{C}_P - n\bar{C}_V = 0 + nR\right)$$

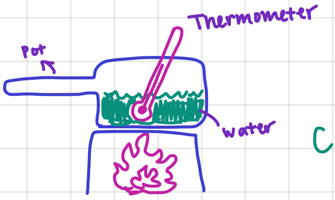
$$\boxed{\bar{C}_P - \bar{C}_V = R}$$

very important, should go on Exam note card

* $n\bar{C}_P = C_P$
$n\bar{C}_V = C_V$

(n cancels out)

* look at heat capacity links on his website under extra material. he shows you this to demonstrate real life applications. why this is important. Also, its something you can actually measure. *



$C_V = \infty$ at boiling point

H is a state function so;

calc:

$$\Delta H = H_2 - H_1 = \int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} \frac{\partial H}{\partial T}\Big)_P dT = \boxed{\int_{T_1}^{T_2} C_p dT = \Delta H \quad \text{at constant P}}$$

idk how to measure this, but I know heat capacity, point is, we manipulate measurable variables to achive our goal

Hess's Law

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta H = -110$ kJ

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H = -283$ kJ

Can combine these 2 to get an answer you don't know.

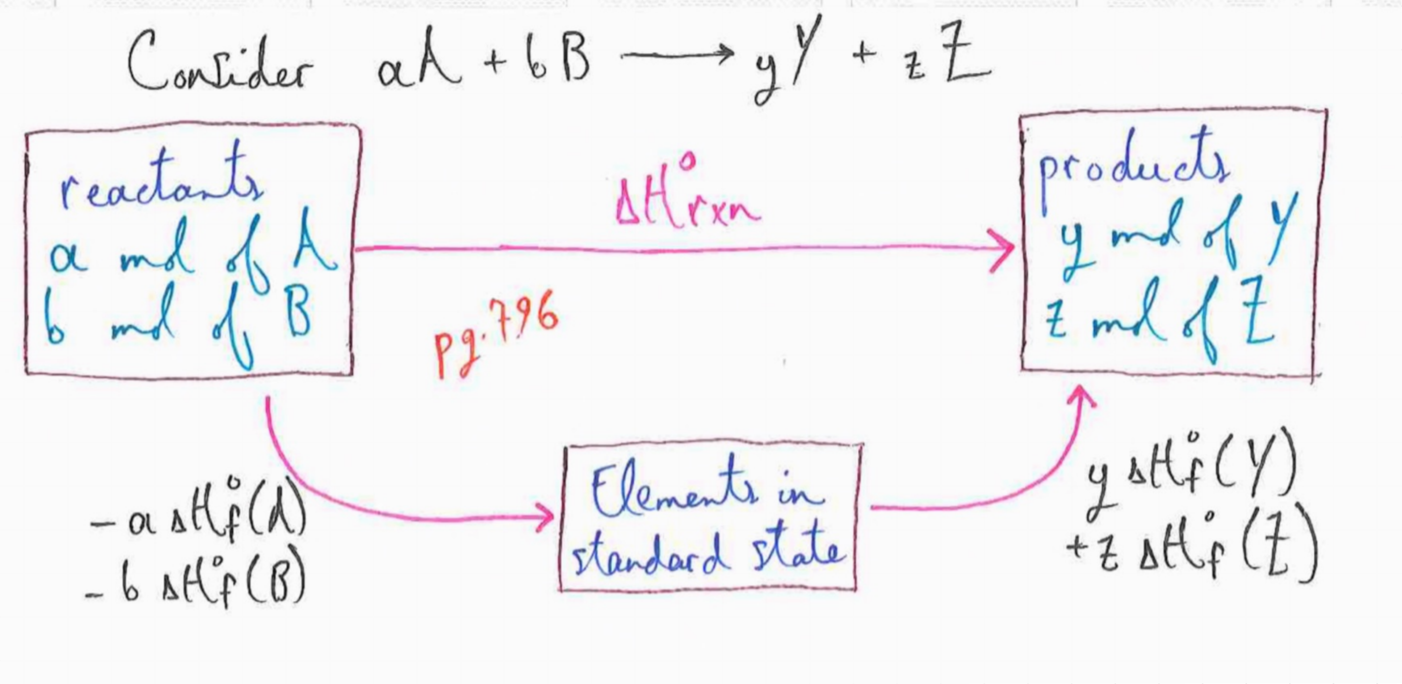
$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393$ kJ

More systematic: use ΔH_f = heats of formation

ΔH_f of $H_2O(l)$ $\Delta H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

$\frac{1}{2}$ bc youre in single mole

Taken from his chapter 19 lecture notes on his website.



Consider $aA + bB \longrightarrow yY + zZ$

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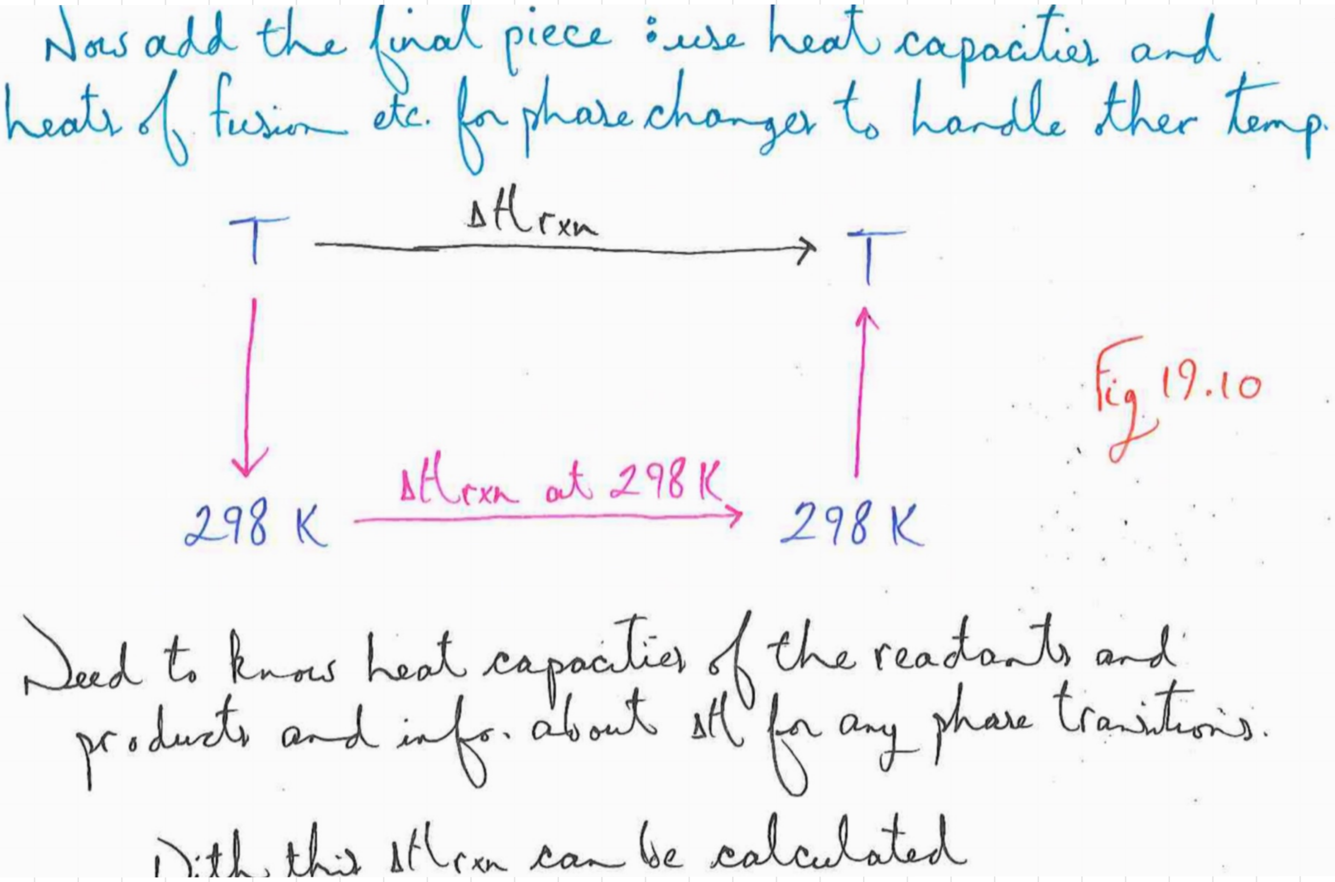

Now add the final piece: use heat capacities and heats of fusion etc. for phase changes to handle other temp.

Fig 19.10

Need to know heat capacities of the reactants and products and info. about ΔH for any phase transitions.

With this ΔH_{rxn} can be calculated