

$$\text{Energy} = \text{heat} + \text{work}$$

work  $\rightarrow$  pressure volume work only

$$W = -P_{\text{ext}} \Delta V \quad \begin{array}{l} \swarrow \text{Volume final} - \text{Volume initial} \\ \downarrow \text{external} \\ \text{pressure - constant} \end{array}$$

when gas expands  $\Delta V > 0$   $P_{\text{ext}}$  always  $> 0$   $W < 0$   
work done by system, on surroundings

when gas is compressed  $\Delta V < 0$   $P_{\text{ext}}$  always  $> 0$   $W > 0$   
work done on the system by the surroundings

$$q + W = \text{total change in energy} = \Delta U \quad \leftarrow \text{"internal energy"}$$

$q, W$  are path functions  
 $\Delta U$  is state function

Most chemical reactions are carried out at constant pressure

$$\Delta U = q + W \quad \leftarrow \text{always true}$$

$$\Delta U = q_p + W_p \quad \leftarrow \text{at const pressure}$$

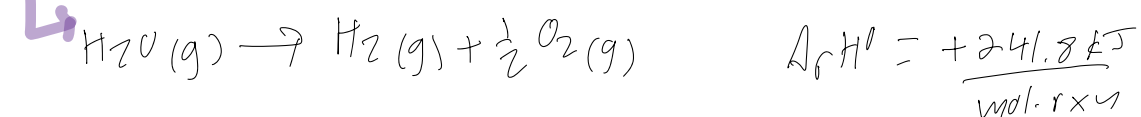
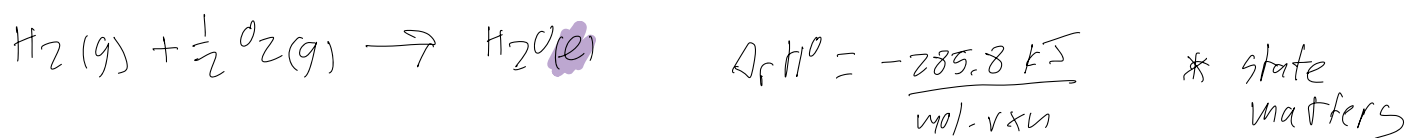
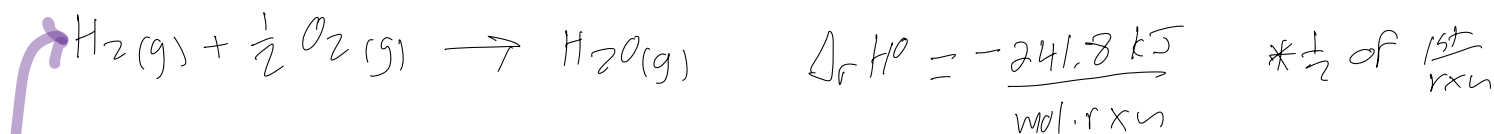
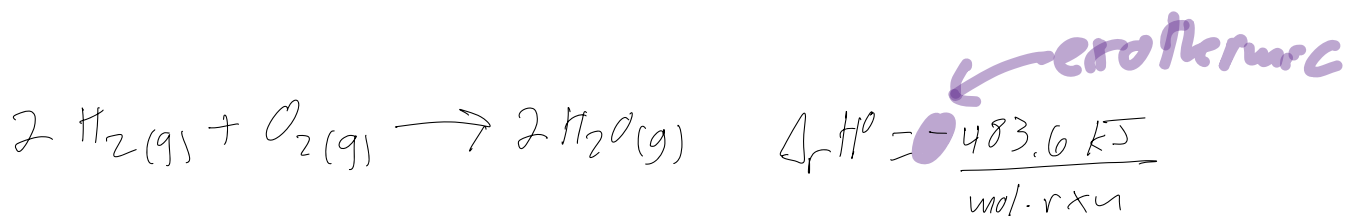
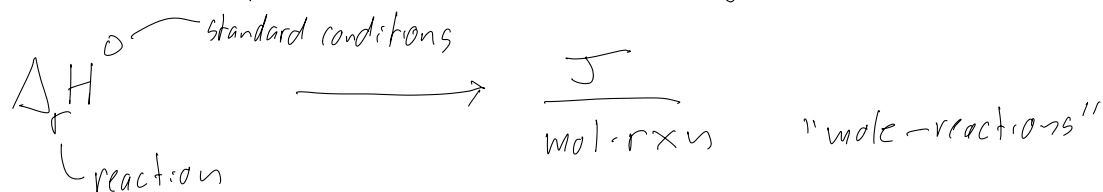
$$\downarrow \\ -P_{\text{ext}} \Delta V$$

$$q_p = \Delta U + P_{\text{ext}} \Delta V \quad \leftarrow \text{all quantities are state fns}$$

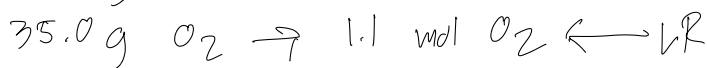
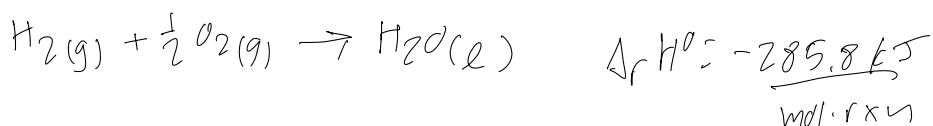
$\uparrow$   
heat for const pressure process

$\downarrow$   
so  $q_p$  is also a state fn  
called enthalpy ( $\Delta H$ )

We use enthalpy to describe energetics of chemical reactions



Ex: We have 22.3 g  $\text{H}_2(\text{g})$  and it reacts with 35.0 g  $\text{O}_2(\text{g})$   
how much heat given off - when the reaction makes liquid  $\text{H}_2\text{O}$



$$1.1 \text{ moles O}_2 \times \frac{-285.8 \text{ kJ}}{0.5 \text{ moles O}_2} = -629 \text{ kJ}$$

$\Delta_r H^\circ$  comes from either experiment or from looking up info

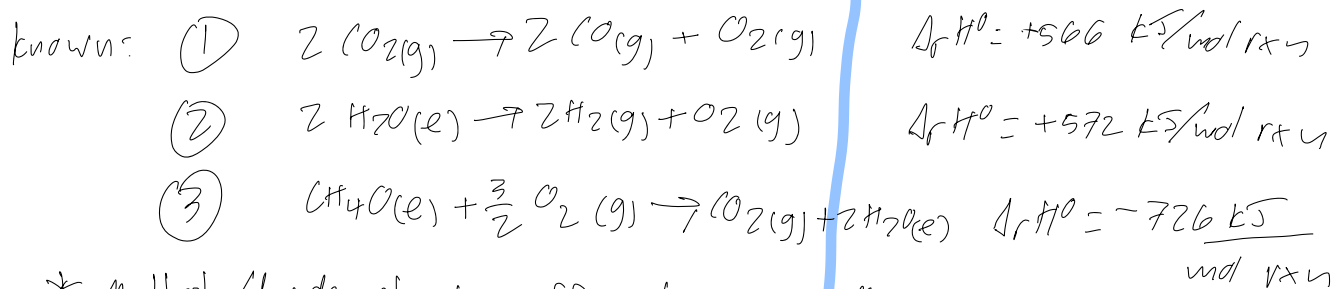
expt is "calorimetry"

↓  
ie someone else's experiment

do expt in a bucket of water and measure temp before and after → calc  $q_{\text{water}}$

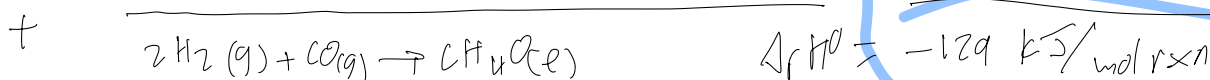
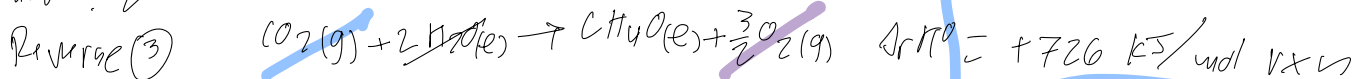
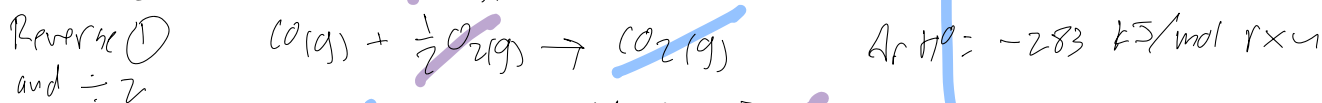
$$q_{\text{water}} = -q_{\text{reaction}} \quad \text{since we do this @ constant P} \quad q = \Delta H$$

Hess's Law - combine reactions with known values of  $\Delta_r H^\circ$  to get  $\Delta_r H^\circ$  for reaction of interest



\* Multiply/divide stoich coefficients and  $\Delta_r H^\circ$

\* Reverse rxns + change sign of  $\Delta_r H^\circ$

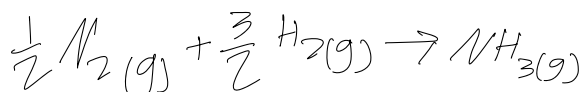


Can also calculate  $\Delta_r H^\circ$  using  $\Delta_f H^\circ$  ("ΔH of formation")

$\Delta_f H^\circ$  is the enthalpy change for making one mole of a substance from pure elements

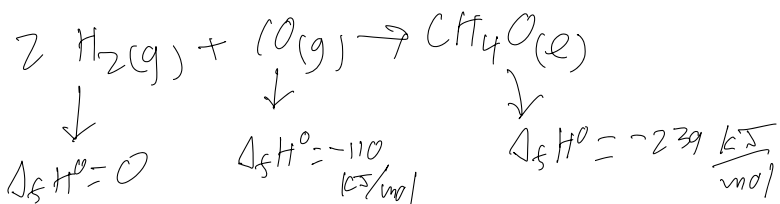
$\Delta_f H^\circ$  are look-up-able

$\Delta_f H^\circ$  of pure element is 0



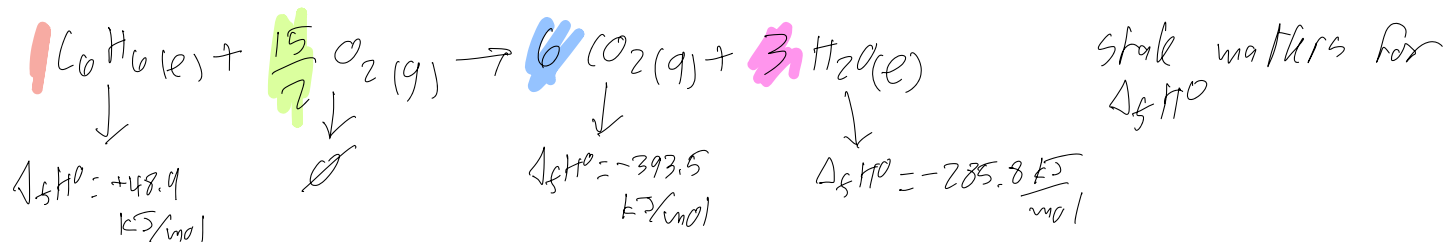
$$\Delta_r H^\circ = \Delta_f H^\circ \text{ of } \text{NH}_3(\text{g})$$

$$\Delta_r H^\circ = [\text{sum of } \Delta_f H^\circ \text{ of products}] - [\text{sum of } \Delta_f H^\circ \text{ of reactants}]$$



$$\Delta_r H^\circ = \left[ -239 \frac{\text{kJ}}{\text{mol}} \right] - \left[ -110 \frac{\text{kJ}}{\text{mol}} \right]$$

$$\Delta_r H^\circ = -129 \frac{\text{kJ}}{\text{mol rxn}}$$



$$\left[ (6 \times -393.5 \frac{\text{kJ}}{\text{mol}}) + (3 \times -285.8 \frac{\text{kJ}}{\text{mol}}) \right] - \left[ (1 \times 48.9 \frac{\text{kJ}}{\text{mol}}) + (\frac{15}{2} \times 0) \right]$$

$\Delta_f H^\circ \text{ H}_2\text{O}(\text{g}) = -241.8 \frac{\text{kJ}}{\text{mol}}$

$$\Delta_r H^\circ = -3207 \frac{\text{kJ}}{\text{mol rxn}}$$