Energy = heat + work

work → pressure volume work only

$w = -P_{ext}\,\Delta V$ ← Volume final − Volume initial

P_{ext}: external pressure - constant

when gas expands $\Delta V > 0$ P_{ext} always > 0 $w < 0$

work done by system, on surroundings

when gas is compressed $\Delta V < 0$ P_{ext} always > 0 $w > 0$

work done on the system by the surroundings

$q + w$ = total change in energy = ΔU ← "internal energy"

q, w are path functions

ΔU is state function

Most chemical reactions are carried out at constant pressure

$\Delta U = q + w$ ← always true

$\Delta U = q_p + w_p$ ← at const pressure

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

$q_p = \Delta U + P_{ext}\Delta V$ ← all quantities are state fxns

↑ heat for const pressure process

↓ so q_p is also a state fxn called enthalpy (ΔH)

We use enthalpy to describe energetics of chemical reactions

standard conditions

$\Delta_r H^\circ \longrightarrow \frac{J}{mol \cdot rxn}$ "mole-reactions"

reaction

exothermic

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$ $\Delta_r H^\circ = -\frac{483.6\ kJ}{mol \cdot rxn}$

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$ $\Delta_r H^\circ = -\frac{241.8\ kJ}{mol \cdot rxn}$ * $\frac{1}{2}$ of 1st rxn

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)}$ $\Delta_r H^\circ = -\frac{285.8\ kJ}{mol \cdot rxn}$ * state matters

$H_2O_{(g)} \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)}$ $\Delta_r H^\circ = +\frac{241.8\ kJ}{mol \cdot rxn}$

Ex: We have 22.3g $H_{2(g)}$ and it reacts with 35.0g $O_{2(g)}$
how much heat given off – when the reaction makes liquid H_2O

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)}$ $\Delta_r H^\circ = -\frac{285.8\ kJ}{mol \cdot rxn}$

22.3 g H_2 → 11.1 mol H_2

35.0 g O_2 → 1.1 mol O_2 ← LR

$1.1 \text{ moles } O_2 \times \frac{-285.8\ kJ}{0.5 \text{ moles } O_2} = -629\ kJ$

$\Delta_r H^\circ$ comes from either experiment or from looking up info
↓
ie someone else's experiment

expt is "calorimetry"

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

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

Hess's Law – combine reactions with known values of $\Delta_r H^0$ to get $\Delta_r H^0$ for reaction of interest

$2\,H_{2(g)} + CO_{(g)} \rightarrow CH_4O_{(\ell)}$ $\quad \Delta_r H^0 = ???$

known: ① $2\,CO_{2(g)} \rightarrow 2\,CO_{(g)} + O_{2(g)}$ $\quad \Delta_r H^0 = +566$ kJ/mol rxn

② $2\,H_2O(\ell) \rightarrow 2H_2(g) + O_2(g)$ $\quad \Delta_r H^0 = +572$ kJ/mol rxn

③ $CH_4O(\ell) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$ $\quad \Delta_r H^0 = -726$ kJ/mol rxn

* Multiply/divide stoich coefficients and $\Delta_r H^0$

* Reverse rxns + change sign of $\Delta_r H^0$

Reverse ② $\quad 2H_2(g) + \cancel{O_2}(g) \rightarrow \cancel{2H_2O}(\ell)$ $\quad \Delta_r H^0 = -572$ kJ/mol rxn

Reverse ① and ÷ 2 $\quad CO(g) + \cancel{\frac{1}{2}O_2}(g) \rightarrow \cancel{CO_2(g)}$ $\quad \Delta_r H^0 = -283$ kJ/mol rxn

Reverse ③ $\quad \cancel{CO_2(g)} + \cancel{2H_2O(\ell)} \rightarrow CH_4O(\ell) + \cancel{\frac{3}{2}O_2}(g)$ $\quad \Delta_r H^0 = +726$ kJ/mol rxn

\+

$2H_2(g) + CO(g) \rightarrow CH_4O(\ell)$ $\quad \Delta_r H^0 = -129$ kJ/mol rxn

Can also calculate $\Delta_r H^0$ using $\Delta_f H^0$ ← "ΔH of formation"

$\Delta_f H^0$ is the enthalpy change for making one mole of a substance from pure elements

$\Delta_f H^0$ are look-up-able

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

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$

$\Delta_r H^0 = \Delta_f H^0$ of $NH_3(g)$

$\Delta_r H^0 = [$sum of $\Delta_f H^0$ of products$] - [$sum of $\Delta_f H^0$ of reactants$]$

$2\,H_2(g) + CO(g) \rightarrow CH_4O(\ell)$

$H_2(g)$: $\Delta_f H^0 = 0$

$CO(g)$: $\Delta_f H^0 = -110$ kJ/mol

$CH_4O(\ell)$: $\Delta_f H^0 = -239$ kJ/mol

$\Delta_r H^0 = \left[-239\ \frac{kJ}{mol}\right] - \left[-110\ \frac{kJ}{mol}\right]$

$\Delta_r H^0 = -129\ \frac{kJ}{mol\ rxn}$

$$1\,C_6H_6(l) + \frac{15}{2}\,O_2(g) \rightarrow 6\,CO_2(g) + 3\,H_2O(l)$$

state matters for $\Delta_f H^0$

$C_6H_6(l)$: $\downarrow$ $\Delta_f H^0 = +48.9$ kJ/mol

$O_2(g)$: $\downarrow$ 0

$CO_2(g)$: $\downarrow$ $\Delta_f H^0 = -393.5$ kJ/mol

$H_2O(l)$: $\downarrow$ $\Delta_f H^0 = -285.8 \frac{kJ}{mol}$

$\Delta_f H^0$ $H_2O(g) = -241.8$ kJ/mol

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

$$\Delta_r H^0 = -3267 \frac{kJ}{mol\ rxn}$$