Energy — heat and work

work is "pressure-volume work"

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

$\Delta V = V_f - V_i$

P_{ext} = constant external pressure

Expanding gas has $\Delta V > 0$ so $w < 0$ work done by system on surroundings

Compressing gas has $\Delta V < 0$ so $w > 0$ work done on system by surroundings

$q + w$ = total change in energy = $\Delta U = U_f - U_i$

U = "internal energy"

difficult to measure ΔU directly so usually measure q and w individually

q, w path fxns ↓ depends on process

ΔU state fxn ↓ doesn't depend on process - only start + finish

Usually chemistry done @ constant pressure

$\Delta U = q_p - P_{ext}\Delta V$

q_p = q @ const pressure

rearranged to $q_p = \Delta U + P_{ext}\Delta V$

q_p = heat at constant pressure = useful to know

$q_p = \Delta U + P_{ext}\Delta V = \Delta H$

H = change in "enthalpy"

ΔH and ΔU differ by $P_{ext}\Delta V$

if $\Delta V = 0$ then $\Delta H = \Delta U$

ΔH will be our main focus in chemistry

$\Delta_r H^\circ$ ← under standard conditions = pure substances / 1 bar pressure
* need to specify temp
↳ for a reaction

units of $\Delta_r H^\circ$ are $\frac{J}{mol \cdot rxn}$ ← for the reaction as written

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $\Delta_r H^\circ = -483.6 \frac{kJ}{mol \cdot rxn}$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\Delta_r H^\circ = -241.8 \frac{kJ}{mol \cdot rxn}$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$ $\Delta_r H^\circ = -285.8 \frac{kJ}{mol \cdot rxn}$

* state of matter matters

→ write it backwards

$H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ $\Delta_r H^\circ = +241.8 \frac{kJ}{mol \cdot rxn}$

Ex: 22.3 g $H_2(g)$ is reacted w/ 35.0 g of O_2 to make liquid water - what is $\Delta_r H^\circ$ for this process

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$ $\Delta_r H^\circ = -285.8 \frac{kJ}{mol\ rxn}$

$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$ $\Delta_r H^\circ = -571.6 \frac{kJ}{mol\ rxn}$

$22.3\ g\ H_2 \times \frac{1\ mol}{2\ g} = 11.1\ moles\ H_2$

$35\ g\ O_2 \times \frac{1\ mol}{32\ g} = 1.1\ moles\ O_2$ ← LR

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

$$1.1 \text{ mole } O_2 \times \frac{-571.6 \text{ kJ}}{1 \text{ mol } O_2}$$

Where does $\Delta_r H^\circ$ come from

- Experiment
- looking stuff up

Experiment is calorimetry

- do reaction in a bucket of water
- reaction will either give off heat into water or take in heat from water
- Measure ΔT of water, know mass of water
- Find q_{H_2O}

$q_{rxn} = -q_{H_2O}$

b/c constant pressure $q_p = \Delta H$

$\Delta_r H^\circ$ from looking things up

Hess's Law – combine reactions and their $\Delta_r H^\circ$ to "make" the one we want

$$2 H_2(g) + CO(g) \rightarrow CH_4O(\ell) \quad \Delta_r H^\circ = ?$$

known

(1) $2 CO_2(g) \rightarrow 2 CO(g) + O_2(g)$ $\Delta_r H^\circ = +566 \text{ kJ/mol rxn}$

(2) $2 H_2O(\ell) \rightarrow 2 H_2(g) + O_2(g)$ $\Delta_r H^\circ = +572 \text{ kJ/mol rxn}$

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

Reverse ① and divide by 2

Reverse ②

Reverse ③

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta_f H^\circ = -283\ kJ/mol\ rxn$

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

$+$

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

$CO(g) + 2H_2(g) \rightarrow CH_4O(\ell)$ $\Delta_r H^\circ = -283 + -572 + 726 = -129\ \frac{kJ}{mol\ rxn}$

other way to calc $\Delta_r H^\circ$ is to use what is call $\Delta_f H^\circ$ formation

$\Delta_f H^\circ$ is $\Delta_r H^\circ$ for forming 1 mole of a compound from the elements

$\Delta_f H^\circ = 0$ for pure element

For $NH_3(g)$

$\Delta_f H^\circ_{NH_3}$ is $\Delta_r H^\circ$ for $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$

$\Delta_f H^\circ_{NH_3} = -45.9\ \frac{kJ}{mol}$

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

$\Delta_f H^\circ = 0$ $\Delta_f H^\circ = -110.5\ \frac{kJ}{mol}$ $\Delta_f H^\circ = -239\ \frac{kJ}{mol}$

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

$\Delta_r H^\circ = -239\ \frac{kJ}{mol} - -110.5\ kJ/mol = -129\ kJ/mol$

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

$\Delta_f H^\circ = +48.9 \frac{kJ}{mol}$ $\Delta_f H^\circ = -393.5 \frac{kJ}{mol}$ $\Delta_f H^\circ = -285.8 \frac{kJ}{mol}$

$\Delta_f H^\circ = \left[6 \times -393.5 \frac{kJ}{mol} + 3 \times -285.8 \frac{kJ}{mol}\right] - \left[48.9 \frac{kJ}{mol}\right] = -3267.3 \frac{kJ}{mol}$ rxn

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$H_2SO_4 + OH^- \rightarrow HSO_4^- + H_2O$

$HSO_4^- + OH^- \rightarrow SO_4^{2-} + H_2O$

$H_2SO_4(aq) + 2OH^- \rightarrow SO_4^{2-}(aq) + 2H_2O$

not same $2H_3O^+(aq) + SO_4^{2-}(aq)$

50 mL of
0.1 M H_2SO_4
.005 moles H_2SO_4
$\times 2$ mol OH^- / 1 mol H_2SO_4

$Na^+(aq) + X^-(aq) \rightleftharpoons NaX(aq)$

$K_2Cr_2O_7(aq)$

$Cr_2O_7^{2-}$

$2K^+$

$HCN + H_2O \rightleftharpoons H_3O^+ + CN^- + OH^-$

$HCN(aq) + OH^- \rightarrow H_2O + CN^-$

HX is an acid. 0.72M HX solution has pH of 1.75. Is HX a strong acid?

Redox titration

$Cr_2O_7^{2-} + C_2H_6O + H_3O^+ \longrightarrow Cr^{3+} + CO_2 + H_2O$

37.5 mL blood sample requires 19.25 mL of 0.085M $K_2Cr_2O_7$ to titrate
what is $[C_2H_6O]$? what is v/v% of BAC

HCl/NaOH titration

25.00 mL HCl titrate w/ 17.35 mL of 0.25M NaOH to get to equiv pt. pH of original HCl? What pH in flask if we add 1.7 mL NaOH after equiv pt

C_6H_{14} combustion. If you burn 75g how many grams CO_2 produced

$$2Cr_2O_7^{2-} + C_2H_6O + (16)H_3O^+ \longrightarrow 4Cr^{3+} + 2CO_2 + 27H_2O$$

(+6 under $Cr_2O_7^{2-}$; −2 under C_2H_6O; +3 under Cr^{3+}; +4 under CO_2)

Cr $6^+ \rightarrow 3^+$

C $-2 \rightarrow +4$

Oxygens: $15 + a = 4 + b$

$11 + a = b$

Hydrogens: $6 + 3a = 2b$

$6 + 3a = 2b$

$6 + 3a = 22 + 2a$

$a = 16$