Thermochemistry

The study of energy changes that occur during chemical ________ :

- at constant volume $\Delta U = q_V$ no ________
- at constant pressure $\Delta H = q_P$ only ______ work

For practical reasons most measurements are made at constant _____, so thermochemistry mostly deals with ΔH.

$$\Delta H_{\text{reaction}} = \sum_{\text{products}} H - \sum_{\text{reactants}} H$$

If $\Delta H > 0$ the reaction is ________ .

If $\Delta H < 0$ the reaction is ________ .

For comparison purposes we need to refer ΔH to the same ____ and ____ . To define a standard reaction enthalpy each component of the reaction must be in its ________ ________ – the most stable form at 1 bar pressure and (usually) 25°C.

1 bar = 10^5 Pa 1 atm = 1.01325 bar

Reaction Enthalpy 1

Hess's Law

The standard enthalpy change in any reaction can be expressed as the _________ of the standard enthalpy changes, at the same temperature, of a _________ of reactions into which the overall reaction can be formally divided.

Combine chemical equations as if ____________ equations, e.g.

$$
\begin{array}{lcl}
A + B \rightarrow C & & \Delta H_1 \\
C + D \rightarrow E + F & & \Delta H_2 \\
F \rightarrow B + G & & \Delta H_3 \\
\hline
A + D \rightarrow E + G & & \Delta H
\end{array}
$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Standard Reaction Enthalpy

ΔH^{o}	reaction enthalpy at _________
ΔH^{o}_{298}	… and at _________ *T*
ΔH^{o}_{500}	or some other *T*

Reaction Enthalpy 2

Standard (molar) enthalpy of ________ $\Delta H_f^o \equiv \Delta_f H^o$

Heat of formation of a substance from its elements, all substances being in their standard state.

By definition, for all ________ $\Delta H_f^o = 0$

Enthalpy of ________ $\Delta H_c^o \equiv \Delta_c H^o$

$\Delta H°$ for total oxidation of a substance

e.g. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6\ H_2O$ $\Delta_c H° = -2808$ kJ mol^{-1}

Enthalpy of ________

$\Delta H°$ when an unsaturated organic compound becomes fully saturated

e.g. $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$ $\Delta H° = -246$ kJ mol^{-1}

Enthalpy of ___________ ≡ Bond dissociation enthalpy

$\Delta H°$ for the dissociation of a molecule into its constituent gaseous atoms

e.g. C_2H_6 (g) → 2C(g) + 6H(g) $\Delta H° = 2883$ kJ mol^{-1}

Bond ________ ≡ single bond enthalpy

An average value taken from a series of compounds and often combined *for a* ________ *estimate*

e.g. $\Delta H°(C_2H_6) = \Delta H°(C\text{-}C) + 6\ \Delta H°(C\text{-}H)$

Temperature Dependence of $\Delta H°$

The temperature dependence of reaction enthalpies can be expressed in terms of the *T* dependence of the enthalpies of the reaction __________ :

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} \_\_\_ \, dT$$

$$\therefore \quad \Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \_\_\_ \, C_p \, dT$$

where $\Delta C_p = \sum_{\text{products}} C_p - \sum_{\text{reactants}} C_p$

This general phenomenon is known as Kirchoff's Law.

e.g.

$$\begin{array}{ccccccccc} \text{A} & + & \text{B} & \rightarrow & \text{C} & + & \text{D} & & \Delta H°(T_1) \\ \uparrow & & \uparrow & & \downarrow & & \downarrow & & \\ \text{A} & + & \text{B} & \rightarrow & \text{C} & + & \text{D} & & \Delta H°(T_2) \end{array}$$

$$\begin{aligned} \Delta H°(T_2) &= \left(C_p(\text{A}) + C_p(\text{B})\right)(T_1 - T_2) \\ &\quad + \Delta H°(\_\_\_) \\ &\quad + \left(C_p(\text{C}) + C_p(\text{D})\right)(\_\_\_ - \_\_\_) \\ &= \Delta H°(T_1) + \left(\sum_{\text{products}} C_p - \sum_{\text{reactants}} C_p\right) \_\_\_ \end{aligned}$$

assuming that the C_p values are ______ independent.

Reactions at Constant Volume

$$\Delta H_r = \Delta U_r + (PV)_{\text{products}} - (PV)_{\text{reactants}}$$

For ________ and liquids $\Delta(PV) \approx 0$, so $\Delta H \approx \Delta U$

For ideal gases $\Delta(PV) = \Delta n_{\text{gas}} RT$,

so $\Delta H \approx \Delta U + \Delta n_{\text{gas}} RT$

e.g. $C_3H_6(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$

$$\Delta H_r = \Delta U_r + (\text{-}\_\_\_)RT$$

The relationship between ______ and ΔU is particularly important when relating thermochemical enthalpies (ΔH) to molecular properties ($U_{\text{molecular}}$),

e.g. for a single bond energy $\Delta U = \Delta H - RT$

as seen in the case of $O_2(g) \rightarrow 2O(g)$.

In practice, ________ is usually so much smaller than ΔH that it is often ignored.

Enthalpies of Ions in Solution

Enthalpy of ________ $\Delta H°$ for solution of a substance in a *stated* amount of solvent

Enthalpy of ________ $\Delta H°$ for dilution of a solution to a lower concentration

Enthalpy of solution to ______ dilution ΔH^{o}_{soln} for an *infinite* amount of solvent

The enthalpy of formation for a species in ________ can be found by combining ΔH^{o}_{soln} with the ΔH^{o}_{f} of the ________ species:

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow HCl(g) \qquad \Delta H^{o}_{f} = -92.31 \text{ kJ mol}^{-1}$$

$$HCl(g) \rightarrow HCl(aq) \qquad \Delta H^{o}_{soln} = -75.14 \text{ kJ mol}^{-1}$$

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow HCl(aq) \quad \Delta H^{o}_{f}(\text{ion}) = \Delta H^{o}_{f} + \Delta H^{o}_{soln}$$

$$= -167.45 \text{ kJ mol}^{-1}$$

ΔH^{o}_{f} for individual ions in solution can only be found if one is arbitrarily fixed. By convention this is ________ .

$$\tfrac{1}{2}H_2(g) \rightarrow H^{+}(aq) + e^{-} \qquad \Delta H^{o}_{f}\left(H^{+}_{aq}\right) = 0$$

$$\Delta H^{o}_{f}\left(Cl^{-}_{aq}\right) = \Delta H^{o}_{f}\left(HCl_{aq}\right) - \Delta H^{o}_{f}\left(H^{+}_{aq}\right) = \Delta H^{o}_{f}\left(HCl_{aq}\right)$$

The ________ state for a substance in solution (not just ions) is a concentration of 1 mole solute in 1 kg solution (1 molal).

Enthalpy of Formation of an Ionic Solid

Consider individual steps in the formation of NaCl.

1. $\Delta H^{o}_{subl}(\text{Na})$
2. $\Delta H^{o} = \_\_(\text{Na}) + \_\_\_\_\_\_\_\_$
3. $\frac{1}{2}\Delta H^{o}(\text{Cl-Cl})$
4. $\Delta H^{o} = -\_\_(\text{Cl}) - RT$
5. $\Delta H^{o}_{sol}(\text{Na}^{+}) + \Delta H^{o}_{sol}(\text{Cl}^{-})$

≡ NaCl(aq)

Na(s) + ½Cl_2(g) → NaCl(aq) $\quad \Delta H^{o}_{f}(\text{NaCl}_{aq})$

$$\Delta H^{o}_{f}(\text{NaCl}_{aq}) = \Delta H^{o}_{subl}(\text{Na}) + I(\text{Na}) + \tfrac{1}{2}\Delta H^{o}(\text{Cl-Cl}) - E_{A}(\text{Cl}) + \Delta H^{o}_{sol}(\text{Na}^{+}) + \Delta H^{o}_{sol}(\text{Cl}^{-})$$

Step 5 could be creation of solid NaCl instead of solution

5'. $\Delta H^{o}_{lattice}(\text{NaCl})$

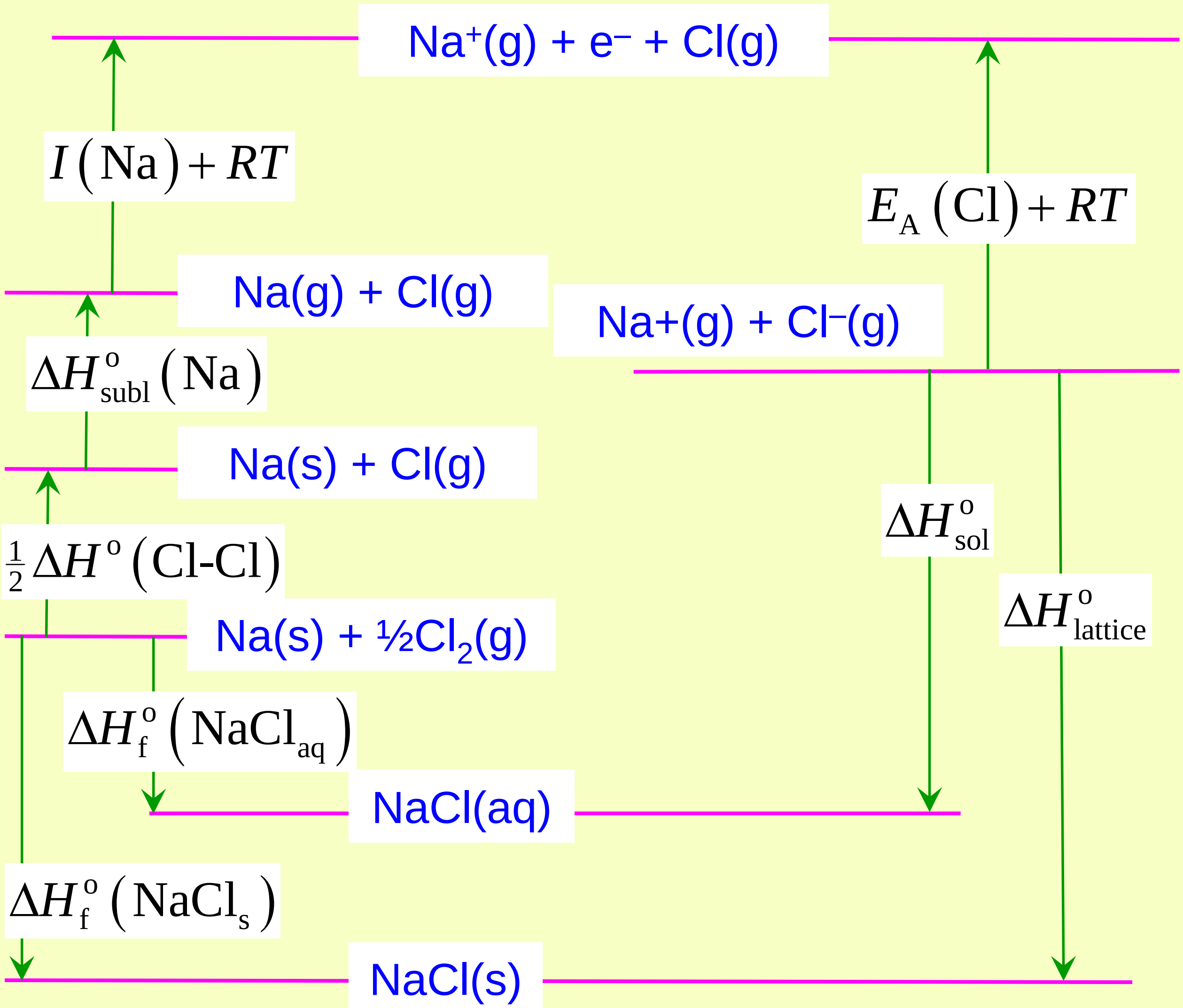
leading us to the enthalpy of formation of solid NaCl:

Na(s) + ½Cl_2(g) → NaCl(s)

$$\Delta H^{o}_{f}(\text{NaCl}_{s}) = \Delta H^{o}_{subl}(\text{Na}) + I(\text{Na}) + \tfrac{1}{2}\Delta H^{o}(\text{Cl-Cl}) - E_{A}(\text{Cl}) + \Delta H^{o}_{lattice}(\text{NaCl})$$

A ______________ Cycle for NaCl

Enthalpy changes can also be expressed in a diagram, e.g.



Since *H* is a state variable, the sum of enthalpy changes around the cycle must be ________ . Consequently, if all but one of the enthalpy changes is known, it can be readily calculated.

This is equivalent to using _______ Law to sum reaction steps.