Chem 340 - Lecture Notes 5 – Fall 2013 – Thermochemistry

State Functions fit Chemical reaction issues
Since ∆H and ∆U are state functions we can get values for any change by just looking at initial and final states For chemical reactions that is particularly useful, since we can just look at properties of reagents and products to determine energetics of a reaction.

The way we monitor it is by heat, which at constant V is: $q_V = \Delta U$ and at constant P is: $q_p = \Delta H$. If reaction gives off heat, it is exothermic, and if takes in heat, endothermic. At const P it is easiest to study most chemical reactions, so more precisely term it exoenthalpic and endoenthalpic, respectively

Consider simple reaction to form ammonia
$$\tfrac{1}{2}\ N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g)$$
For ∆H we only care about these two states (reagents and products) and not about how the atoms rearranged themselves to get from one to the other molecule, consider:
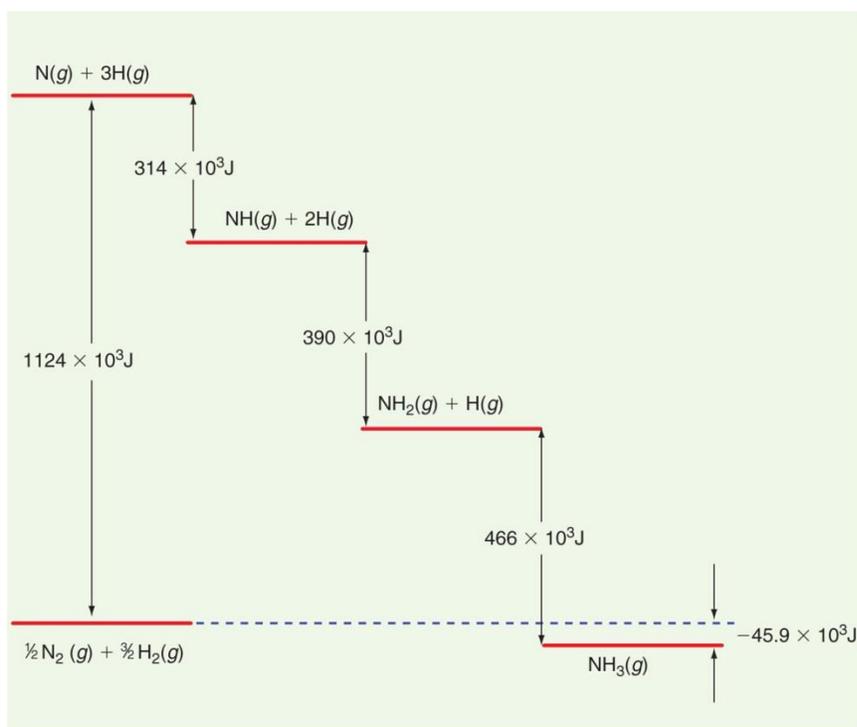

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All these hypothetical steps have energies involved, but the ∆H = - 45.9 kJ value is independent of how the process went. If choose another mechanism, get same ∆H i.e. same ∆H results for a reaction using a metal surface as a catalyst, the Haber process, or biochemically "fixing" of N_2 using an enzyme, nitrogenase, in a legume.

When we evaluate ΔU or ΔH for a reaction, we need to take into account changes in pressure and temperature as they can also affect ΔU or ΔH separate from the reaction itself. For chemistry usually like to refer to a **standard state**, or set of conditions, typically: **T=298.15 K (i.e. 25°C) and P= 1 bar**. Must also specify phase,
> Standard state specification needed *since U and H vary with phase and (T,P)*

To solve for the changes due to the reaction alone, break up into steps that can solve, and note it makes no difference if reaction actually follows these steps, since we are computing a state function, depends only on initial and final state:

Example: Consider the following reaction, with [T=298.15K, P=1 bar]
> $C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$
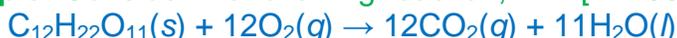
Step *a*: Let the reaction proceed in a vessel whose walls are adiabatically insulated but held at const P, this causes a temperature change from 298.15 K to *T'*, then
> $C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g)[T'$ and 1 bar$] + 11H_2O(l)$

For this step a: $q_{p,a} = 0$ and $\Delta H_a = 0$ (adiabatic, const P, i.e. $\Delta H_a = q_{p,a}$)
> *But of course T changed, and since const.P, V will also change*

Step *b*: In the second step the system is brought to thermal equilibrium with the surroundings. The walls of the vessel switched to diathermal and heat flows from reaction vessel to a very large water bath in the surroundings. The temperature changes from *T'* back to 298.15K
> $12CO_2(g) [T'] + 11H_2O(l) \rightarrow 12CO_2 (g) [T=298.15K] + 11H_2O(l)$

For step b: heat flow from surroundings is: $q_{p,b} = \Delta H_b$ *(again, since const P: $\Delta H_b = q_{p,b}$)*
For the overall reaction, sum the steps:
> for standard state, T=298.15 K, P=1 bar: use superscript ^{o}
> $\Delta H^o_{reaction} = \Delta H^o_a + \Delta H^o_b = 0 + q_{p,b} = q_p$

Heats of formation
Problem with this method above is that to solve for ΔH_{rxn} need to do actual reaction, measure calorimeter properties, and when want to consider a new reaction, need to do the experiment again. Can we find a way to predict reaction enthalpies for any set of reactants and products? Since a cycle, and we only care about initial and final states, it would be most efficient to know just the enthalpy of each of the reagents and products, in the same standard conditions, and just sum them up on each side and take the difference. To do this we establish standard enthalpies (heats) of formation for all the reagents/products of interest and then take combinations of them.

Consider again, $C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$

$\Delta H^o_{rxn} = \Delta H^o_{prod} - \Delta H^o_{reag}$
> $= 12H^o_m [CO_2 (g)] + 11H^o_m [H_2O (l)] - H^o_m [C_{12}H_{22}O_{11} (s)] - 12 H^o_m [O_2 (g)]$
> *where m subscript denotes molar quantities.*

This equation can be standardized by introducing the **standard enthalpy of formation,** ΔH_f^o : is the enthalpy associated with the reaction in which the only reaction product is 1 mol of the species of interest , and only pure elements in their most stable state of aggregation under the standard state appear as reactants. So, $\Delta H_f^o = 0$, for an element in its standard state because the reactants and products are identical.

So $\Delta H^o_{rxn} = \Delta H^o_{f\ prod} - \Delta H^o_{f\ react}$

Just need a table of the ΔH_f^o values and can compute ΔH^o_{rxn} for any reaction

$$\nu_A A + \nu_B B \xrightarrow{\Delta H_R^\circ} \nu_C C + \nu_D D$$

$$-\nu_A \Delta H_{f,A}^\circ - \nu_B \Delta H_{f,B}^\circ$$

$$\nu_C \Delta H_{f,C}^\circ + \nu_D \Delta H_{f,D}^\circ$$

Elements in standard reference state
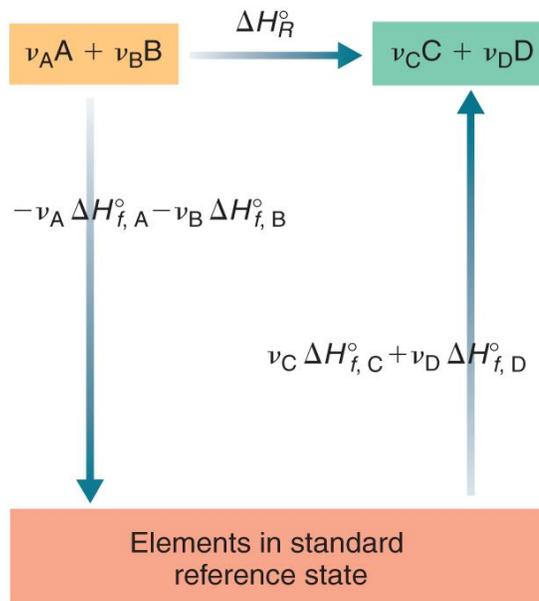
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These ΔH_f^o values are worked out in general, and are stable, so no need to remeasure

Formal process is:

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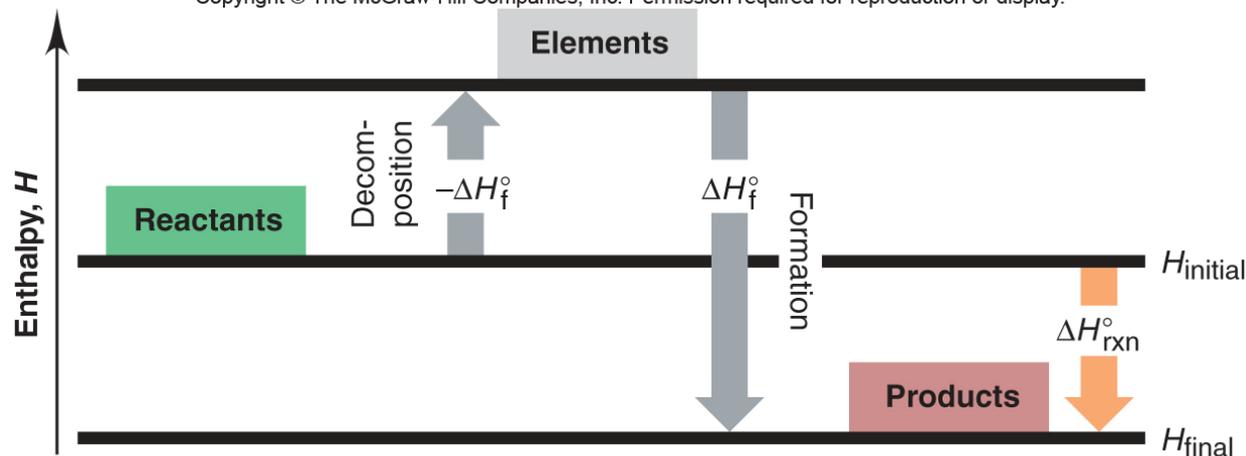
$$\Delta H_{rxn}^\circ = \Sigma m \Delta H_{f(products)}^\circ - \Sigma n \Delta H_{f(reactants)}^\circ$$

But actually can be determined by various reactions using cycles to isolate the steps of interest. One way is to measure heat of combustion of molecule of interest and reference (correct) that with heats of combustion of elements involved.

Consider again: $C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$
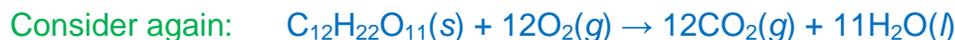
Above equation worked out reaction enthalpy from ΔH_f^o of each component, reactant or product. Could view reaction as sum of other reactions (in this case just for products):
1. $C_{12}H_{22}O_{11}$ (s) + $12O_2$ (g) $\rightarrow$ $12CO_2$ (g) + $11H_2O$ (l)
2. 12 x [C(s) + O_2 (g) $\rightarrow$ CO_2 (g)]
3. 11 x [H_2(g) + 1/2 O_2(g) $\rightarrow$ H_2O (l)]

Each of these (1-3) is a combustion reaction, but if we sum (2+3), they provide the products. The sums of the enthalpies of combustion of C and of H_2 (i.e. ΔH_{rxn} for the reactions written) provide an enthalpy of formation for the products, CO_2 and H_2O.

From above: the enthalpy of sucrose, $C_{12}H_{22}O_{11}(s)$, oxidation reaction:
$\Delta H_{rxn}^o(suc) = [\ 11\ \Delta H_f^o(H_2O) - 12\ \Delta H_f^o\ (CO_2)] - \Delta H_f^o(sucrose) = -5873\ kJ\ mol^{-1}$
   Use: $\Delta H_f^o(H_2O) = -285\ kJ\ mol^{-1}$ $\Delta H_f^o(sucrose) = -2226\ kJ\ mol^{-1}$
         $\Delta H_f^o\ (CO_2)]\ = -412\ kJ\ mol^{-1}$

Rearrange to obtain the enthalpy of formation for $C_{12}H_{22}O_{11}(s)$*:*
$\Delta H_f^o(sucrose) = -[\Delta H_{rxn}^o(suc) - 11\Delta H_f^o(H_2O) - 12\Delta H_f^o\ (CO_2)]$ *sign (−) sucrose reagent*
      so if $\Delta H_f^o(sucrose)$ unknown, determine from $\Delta H_{rxn}^o(suc)$ and $\Delta H_f^o(H_2O,\ CO_2\ )$

From combustion point of view, all these steps are actually combustion reactions, so
      $\Delta H_f^o(sucrose)\ = -\ [\Delta H_c^o(1) - 12\ \Delta H_c^o(2) - 11\ \Delta H_c^o(3)]$
         where $\Delta H_c^o(n)$ is enthalpy of combustion, (-) again $\rightarrow$ sucrose is reagent
Thus the difference in the enthalpy of combustion for step 1 and that for steps 2 and 3 gives the negative formation enthalpy of the reagent, and a means of determining it

ΔH_{rxn} , can be considered as the sum of the enthalpy changes for the decomposition of reactants to their elements and the formation of products from their elements. The factors *n* and *m* are the proportionality of the products and reactants and are set equal the stoichiometric coefficients in the balanced equation. Note elements in standard states do not appear, since $\Delta H_f^o(element) = 0$ by definition

Hess's law – standard enthalpy of a reaction is sum of standard enthalpy of individual reactions into which it can be divided, independent of if individual rxn are realizable (v_i – reag, v_i + prod)

$$\Delta H_R^\circ = \sum_i v_i \Delta H_{f,i}^\circ$$

**Table 2.6*** Standard enthalpies of formation and combustion of organic compounds at 298 K

	$\Delta_f H^\ominus$/(kJ mol^{-1})	$\Delta_c H^\ominus$/(kJ mol^{-1})
Benzene, C_6H_6(l)	+49.0	−3268
Ethane, C_2H_6(g)	−84.7	−1560
Glucose, $C_6H_{12}O_6$(s)	−1274	−2808
Methane, CH_4(g)	−74.8	−890
Methanol, CH_3OH(l)	−238.7	−726

* More values are given in the *Data section*.

fits figures above, cycle reagents to elements and back to products

example data from Atkins textbook, much more available in Table 2.8, inorganic, and Table 2.6, organic, in back pages of the textbook

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Example

$$2 \ C_3H_5(NO_3)_3 \ (l) \rightarrow 3N_2(g) + \tfrac{1}{2} \ O_2 \ (g) + 6 \ CO_2 \ (g) + 5 \ H_2O \ (g)$$

$$\Delta H^o_{rxn} = 6 \ \Delta H^o_f[CO_2 \ (g)] + 5 \ \Delta H^o_f[H_2O \ (g)] + \cancel{\tfrac{1}{2} \Delta H^o_f[O_2 \ (g)]} + \cancel{3 \ \Delta H^o_f[N_2(g)]} -$$
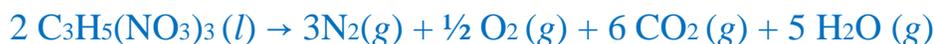
$$2 \ \Delta H_{of}[\ C_3H_5(NO_3)_3 \ (l)] \qquad \qquad elements \rightarrow \Delta H^o_f = 0$$

$$= 6(-393.5) + 5(-241.8) - 2(-364) = -2842 \ kJ \rightarrow react \ 2 \ mol \ C_3H_5(NO_3)_3 \ (l)$$

Now, we seek the ΔH^o_{rxn} for reaction of 10 g of $C_3H_5(NO_3)_3$ (l)

n for $C_3H_5(NO_3)_3$ (l) = 10 g / 227.1 g mol^{-1} = 0.0440 mol

and $\Delta H^o_{rxn} \ (10 \ g)$ = (0.0440 mol) (-2842 kJ/2 mol) = -62.6 kJ

Absolute enthalpies, all above in terms of ΔH_f^o or a difference, possible to define an absolute value of enthalpy, H^o_m by letting H^o(elements) = 0 then $\Delta H_f^o = H^o_m$

In all of this important to remember, H is extensive variable, so if change amount of reagents, change H, similarly, if use set of stoichiometric coefficients that are double, then ΔH_{rxn} doubles, so must specify the stoichiometric coefficients

Units of H are kJ/mol, so units of ΔH_{rxn} are kJ/mol

If ask per mol of what? → *per mole of reaction as written*

Approximation: Bond enthalpies:
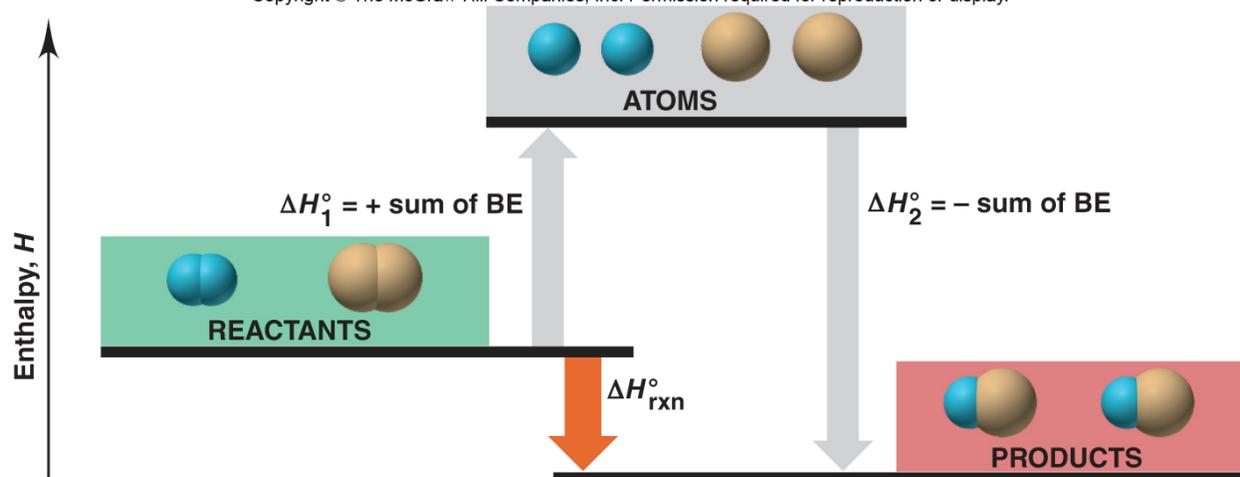
ΔH^o_{rxn} is estimated by average bond enthalpies (BE)

a) Break all bonds in reactants to generate free atoms in gas phase –Atomization

b) Make the product molecules from the free atoms

$$\Delta H^o = \Sigma \Delta H(bonds \ broken) + \Sigma \Delta H(bonds \ formed)$$

Example: consider average bond enthalpy of O-H bond in water to be half the enthalpy of dissociation : $H_2O \rightarrow 2H + O$ [all in gas phase, this not $-\Delta H_f(H_2O)$ since not elements in standard states but atoms]. Use $\Delta H^{\circ}_f(H,g) = 218$ kJ/mol, $\Delta H_f(O,g) = 249$ kJ/mole and $\Delta H_f(H_2O,g) = -242$ kJ/mol

Determine average bond enthalpy O-H, and average bond energy:

a. H_2O (g) $\rightarrow$ H_2(g) + ½ O_2(g) $\Delta H^{\circ} = 242$ kJ/mol
b. H_2(g) $\rightarrow$ 2 H(g) $\Delta H^{\circ} = 2$ x 218 kJ/mol
c. ½ O_2(g) $\rightarrow$ O(g) $\Delta H^{\circ} = 249$ kJ/mol
d. H_2O (g) $\rightarrow$ 2H (g) + O (g) $\Delta H^{\circ} = 927$ kJ/mol (from sum of the above)

➔ Bond enthalpy: $\Delta H^{\circ}_{avg}(O\text{-}H) = $ ½ $\Delta H^{\circ}(d) = $ ½ 927 kJ/mol = 464 kJ/mol

$\Delta U^{\circ}_{avg}(rxn) = \Delta H^{\circ}_{avg} - \Delta(PV)_{avg} = \Delta H^{\circ}_{avg} - \Delta nRT$

= 927 kJ/mol – 2x8.314 J/molK x 298 K = 922 kJ/mol *very similar value*

$\Delta U^{\circ}_{avg}(O\text{-}H) = $ ½ $\Delta U^{\circ}_{avg}(rxn) = 461$ kJ/mol

Important to realize that *these are really not very accurate*. Each bond being broken will have an energy that depends on the molecule from which it is being broken away, so in H_2O, each O-H bond will be different, since first one leaves H· +O-H· and second one leaves O· +2H., but historically they were used to estimate structure stabilities

Born-Haber Cycles : applying Hess's Law

There are two routes from **elements** to **ionic compound**

enthalpy H

Na⁺ (g) + e⁻ + Cl (g)

ΔH first ionisation energy ΔH first electron affinity

Na (g) + Cl (g)

ΔH atomisation   Na⁺ (g) + Cl⁻ (g)

Na (g) + ½ Cl_2 (g)

ΔH atomisation ΔH lattice association

Na (s) + ½ Cl_2 (g)

Apply Hess's Law: ΔH formation

NaCl (s)

$\Delta H_{atm}Na + \Delta H_{atm}Cl + \Delta H_{1st\ IE} + \Delta H_{1st\ EA} + \Delta H_{lattice} = \Delta H_{formation}$
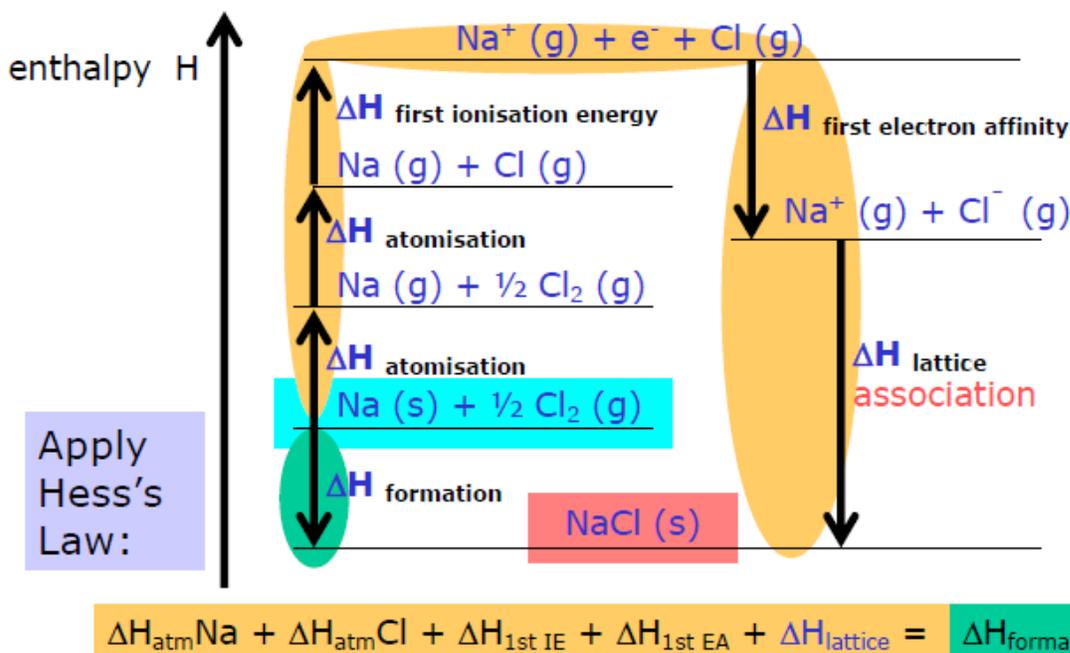
This cycle shows derivation of ΔH_f (NaCl), but if knew ΔH_f could get $\Delta H_{lattice}$

Temperature dependence of ΔH_{rxn}

At const. P, $\Delta H = q_p = \int C_p dT$, so if we have a standard state and wish to know enthalpy at higher temp, then change is just dependent on Cp and temperature difference

$$H^\circ_T = H^\circ_{298.15\,K} + \int_{298.15\,K}^{T} C_P(T')dT'$$

integrate from std T to new T, use T' as "dummy"

Can do the same for all reactants and products, have same integral, different C_p

$$\Delta H^\circ_{R,T} = \Delta H^\circ_{R,298.15\,K} + \int_{298.15\,K}^{T} \Delta C_P(T')dT' \qquad \Delta C_P(T') = \sum_i \nu_i C_{P,i}(T')$$

where

Kirchhoff's Law, → where sum over C_p values includes all reactants and products, i.e. must include elements and compounds

Example: ΔH^o_f for glucose and lactic acid are -1274 and -694 kJ/mol, and C_p are 218 and 128 J/molK at 298K, respectively. Calculate ΔH^o_{rxn} for forming lactic acid from glucose at T= 298 K and at T=310 K.

$C_6H_{12}O_6$ (s) → 2 $CH_3CHOHCOOH$ (s)

a. $\Delta H^o_{rxn} = 2\,\Delta H^o_f(lactic) - \Delta H^o_f(glucose) = 2x(-694) - (-1274) = -114\ kJ/mol$

b. at T=310 K add term for $\Delta C_p = 2x128 - 218 = 38\ J/molK$ -- constant

$\Delta H^o_{rxn}\ (310\ K) = \Delta H^o_{rxn}\ (310\ K) + \Delta Cp\Delta T = 114\ kJ - 38x(310-298)\ J = 113.5\ kJ/mol$