
Thermochemistry

Chapter 2 of Atkins: *The First Law: Concepts*

Sections 2.7-2.9 of Atkins

Standard Enthalpy Changes

Enthalpies of Physical Change
Enthalpies of Chemical Change
Hess' Law

Standard Enthalpies of Formation Changes

Reaction Enthalpy & Enthalpy of Formation
Group Contributions

Temperature Dependence of Reaction Enthalpies

Thermochemistry

Thermochemistry is the branch of thermodynamics which studies heats of reaction: heat produced by or required for a chemical reaction.

In thermochemistry, chemical reactions are divided into two categories:

exothermic reaction

$q_{\text{rxn}} < 0$; heat is produced by the reacting system (i.e., the temperature of the system is higher right after the reaction than initially; heat must be transferred from the system to the surroundings in order to return the system to its initial temperature)

endothermic reaction

$q_{\text{rxn}} > 0$; heat is absorbed by the reacting system (i.e., the temperature of the system is lower right after the reaction than initially; heat must be transferred from the surroundings to the system in order to return the system to its initial temperature)

These reactions can also be described in terms of **enthalpy**, ΔH

Standard Enthalpy Changes

Numerical values describing ΔU or ΔH of a system when some chemical or physical change occurs depend upon the nature of the reaction, as well as the physical states of reactants and products

It is useful to define a **standard enthalpy change**, ΔH° , which is the change in enthalpy for a process (chemical or physical) where initial and final substances are in **standard states**

standard states: pure form of a substance at specified temperature at pressure of 1 bar, e.g. standard state of liquid water at 298 K is pure liquid water at 298 K and 1 bar

Examples: The standard enthalpy of **vapourization**, $\Delta_{\text{vap}}H^\circ$, is change in enthalpy per mole when pure liquid vapourizes to pure gas at pressure of 1 bar. The standard enthalpy of **fusion**, $\Delta_{\text{fus}}H^\circ$, is enthalpy change accompanying change from liquid to solid



ΔH° can be reported at any temperature, convention is at 298.15 K

Enthalpy of Physical Change

standard enthalpy of transition, $\Delta_{\text{trs}}H^\circ$:

Standard enthalpy change accompanying a phase change

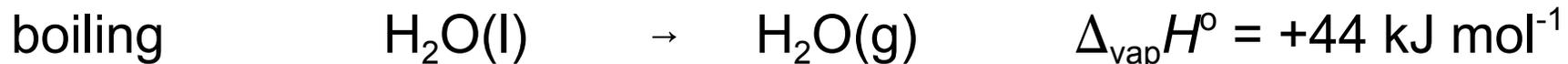
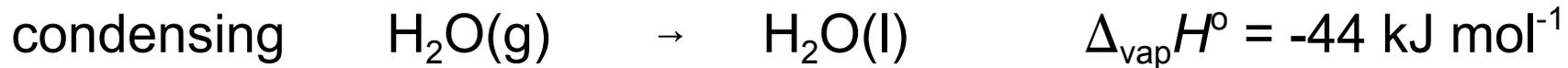
(A) Enthalpy is a *state function*, independent of path between initial and final states: same value of ΔH° occurs regardless of how change occurs!



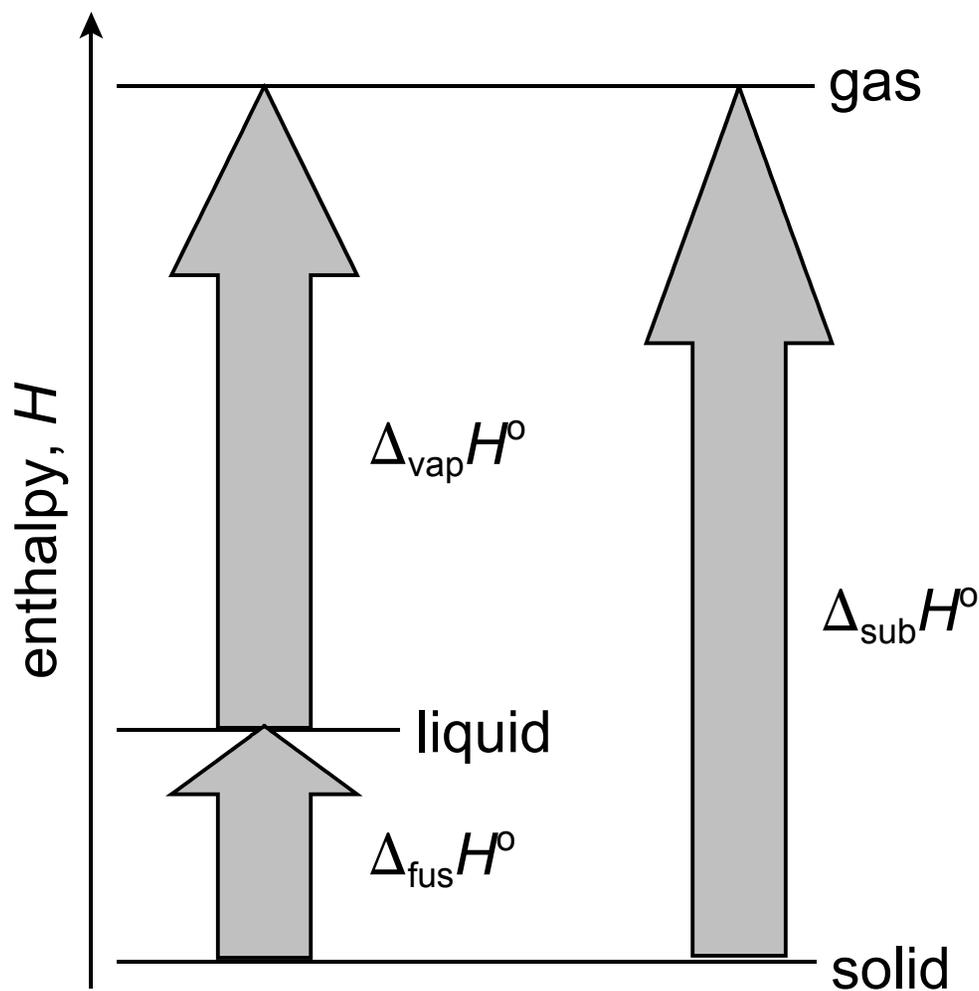
(B) Enthalpy is a *state function*, so ΔH° differs only in sign for forward and reverse processes

$$\Delta H^\circ(\text{A} \rightarrow \text{B}) = -\Delta H^\circ(\text{B} \rightarrow \text{A})$$

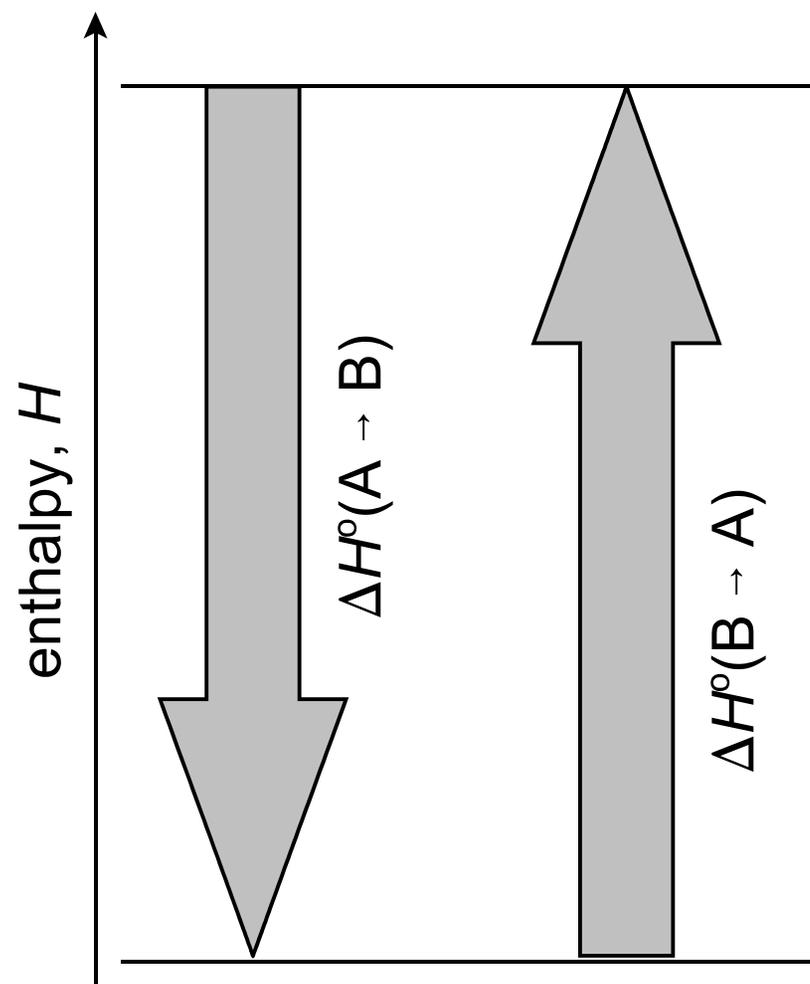
Example: At 298 K,



Graphical Depiction of Enthalpies of Transition



(A) Same ΔH° , regardless of **pathway**



(B) Forward & reverse processes, ΔH° differs only in sign

Enthalpies of Fusion and Vapourization

See Table 2.3 Atkins 6th Ed. at back of book for a listing of enthalpies of fusion and vapourization, with freezing and boiling temperatures

Table 2.3 Standard enthalpies of fusion and vaporization at the transition temperature, $\Delta_{\text{tr}}H^\circ/(\text{kJ mol}^{-1})$

	T_f/K	Fusion	T_b/K	Vaporization		T_f/K	Fusion	T_b/K	Vaporization
Elements					CO ₂	217.0	8.33	194.6	25.23 s
Ag	1234	11.30	2436	250.6	CS ₂	161.2	4.39	319.4	26.74
Ar	83.81	1.188	87.29	6.506	H ₂ O	273.15	6.008	373.15	40.656
Br ₂	265.9	10.57	332.4	29.45					44.016 at 298 K
Cl ₂	172.1	6.41	239.1	20.41	H ₂ S	187.6	2.377	212.8	18.67
F ₂	53.6	0.26	85.0	3.16	H ₂ SO ₄	283.5	2.56		
H ₂	13.96	0.117	20.38	0.916	NH ₃	195.4	5.652	239.7	23.35
He	3.5	0.021	4.22	0.084	Organic compounds				
Hg	234.3	2.292	629.7	59.30	CH ₄	90.68	0.941	111.7	8.18
I ₂	386.8	15.52	458.4	41.80	CCl ₄	250.3	2.5	350	30.0
N ₂	63.15	0.719	77.35	5.586	C ₂ H ₆	89.85	2.86	184.6	14.7
Na	371.0	2.601	1156	98.01	C ₆ H ₆	278.61	10.59	353.2	30.8
O ₂	54.36	0.444	90.18	6.820	C ₆ H ₁₄	-178	13.08	342.1	28.85
Xe	161	2.30	165	12.6	C ₁₀ H ₈	354	18.80	490.9	51.51
K	336.4	2.35	1031	80.23	CH ₃ OH	175.2	3.16	337.2	35.27
Inorganic compounds									37.99 at 298 K
CCl ₄	250.3	2.47	349.9	30.00	C ₂ H ₅ OH	158.7	4.60	352	43.5

Data: AIP; s denotes sublimation

Enthalpies of Transition †

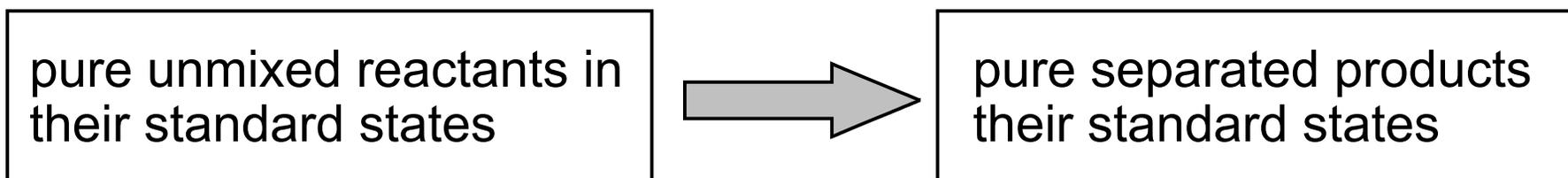
There are many different types of transitions, each of which has an associated change in enthalpy

Transition	Process	Symbol
Transition	Phase $\alpha \rightarrow$ Phase β	$\Delta_{\text{trs}}H$
Fusion	s \rightarrow l	$\Delta_{\text{fus}}H$
Vapourization	l \rightarrow g	$\Delta_{\text{vap}}H$
Sublimation	s \rightarrow g	$\Delta_{\text{sub}}H$
Mixing fluids	Pure \rightarrow mixture	$\Delta_{\text{mix}}H$
Solution	Solute \rightarrow solution	$\Delta_{\text{sol}}H$
Hydration	$X^{\pm}(\text{g}) \rightarrow X^{\pm}(\text{aq})$	$\Delta_{\text{hyd}}H$
Atomization	Species(s,l,g) \rightarrow atoms(g)	$\Delta_{\text{at}}H, \Delta_{\text{diss}}H$
Ionization	$X(\text{g}) \rightarrow X^{+}(\text{g}) + e^{-}(\text{g})$	$\Delta_{\text{ion}}H$
Electron gain	$X(\text{g}) + e^{-}(\text{g}) \rightarrow X^{-}(\text{g})$	$\Delta_{\text{eg}}H$
Reaction	Reactants \rightarrow products	$\Delta_{\text{r}}H$
Combustion	Cmpd(s,l,g) + O ₂ (g) \rightarrow CO ₂ (g) + H ₂ O(l,g)	$\Delta_{\text{c}}H$
Formation	Elements \rightarrow compound	$\Delta_{\text{f}}H$
Activation	Reactants \rightarrow activated complex	$\Delta^{\ddagger}H$

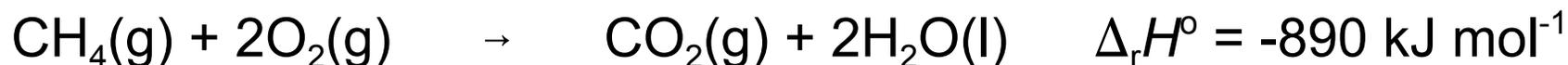
Enthalpies of Chemical Change

standard reaction enthalpy, $\Delta_r H^\circ$:

Change in enthalpy when reactants in standard states change to products in standard states



Example:

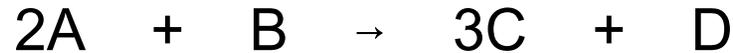


The change in enthalpy for the above **thermochemical equation** is for 1 mole of pure $\text{CH}_4(\text{g})$ reacting with 2 moles of pure $\text{O}_2(\text{g})$ at 1 bar to produce 1 mole of pure $\text{CO}_2(\text{g})$ and 2 moles of pure $\text{H}_2\text{O}(\text{l})$ at 1 bar

Changes in enthalpies of mixing and separation are insignificant compared to the standard reaction enthalpy, and may be neglected in this case

Standard Molar Enthalpies

Consider the reaction:



Standard enthalpy is calculated from:

$$\Delta_r H^\circ = \sum_{\text{products}} \nu H_m^\circ - \sum_{\text{reactants}} \nu H_m^\circ$$

where ν are stoichiometric coefficients. Thus,

$$\Delta_r H^\circ = [3H_m^\circ(C) + H_m^\circ(D)] - [2H_m^\circ(A) + H_m^\circ(B)]$$

where $H_m^\circ(J)$ is standard molar enthalpy of species J.

Symbolically, we write $0 = 3C + D - 2A - B$, or

$$0 = \sum_J \nu_J J$$

Here J denotes substances and ν_J the stoichiometric numbers,

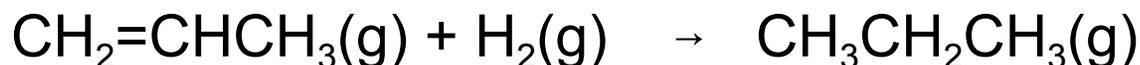
$$\nu_A = -2 \quad \nu_B = -1 \quad \nu_C = +3 \quad \nu_D = +1$$

Thus, standard reaction enthalpy is: $\Delta_r H^\circ = \sum_J \nu_J H_m^\circ(J)$

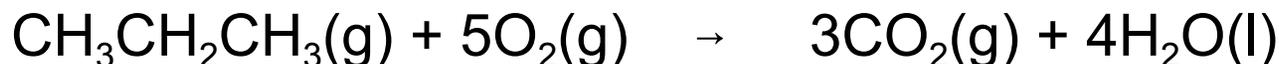
Hess' Law †

The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which the overall reaction may be divided - Individual steps may not be “real” reactions, but must balance

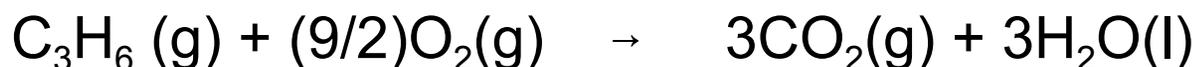
Standard reaction enthalpy for hydrogenation of propene: -124 kJ mol^{-1}



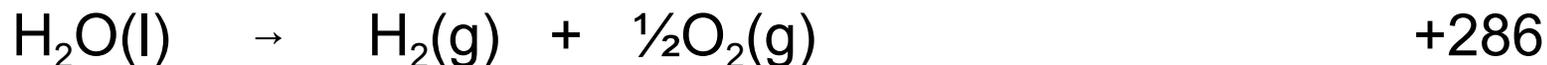
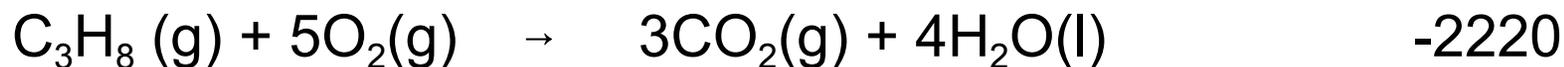
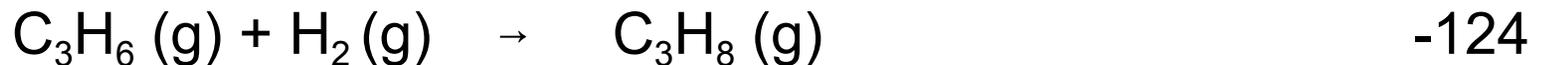
Standard reaction enthalpy for combustion of propane: $-2220 \text{ kJ mol}^{-1}$



Calculate the standard enthalpy of combustion of propene:



$\Delta_f H^\circ / \text{kJ mol}^{-1}$

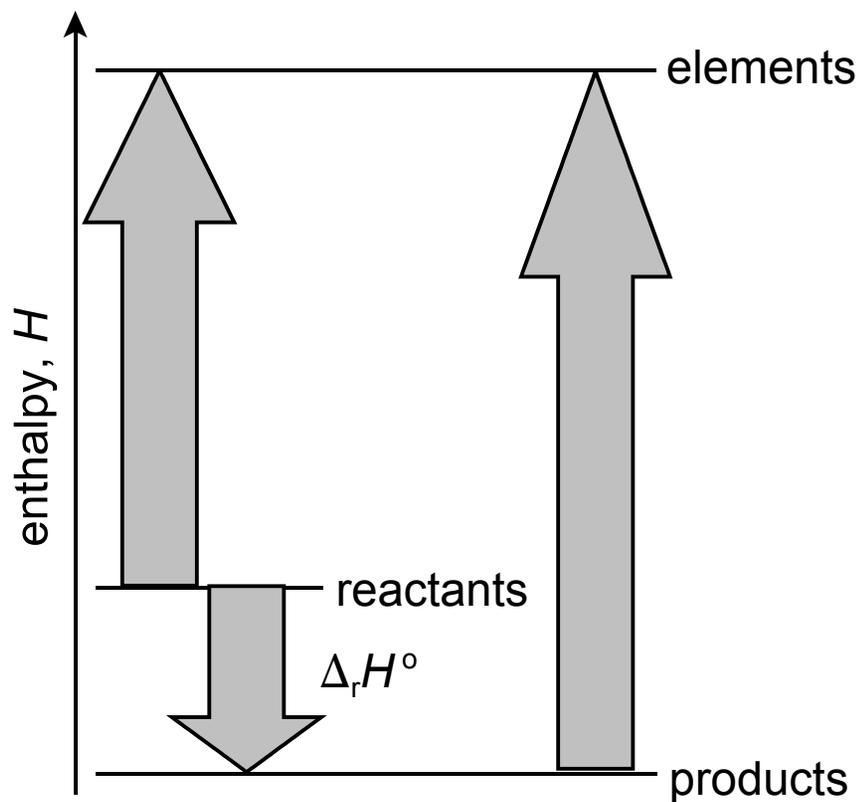


Standard Enthalpies of Formation

standard enthalpy of formation, $\Delta_f H^\circ$:

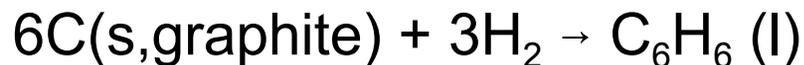
Change in enthalpy for formation of compound from its constituent elements in their *reference states*

reference state: the most stable state of an element at the specified temperature and 1 bar pressure



Examples:

nitrogen	$N_2(g)$
mercury	$Hg(l)$
carbon	$C(s)$ (graphite)



$$\Delta_r H^\circ = +49.0 \text{ kJ mol}^{-1}$$



$$\Delta_r H^\circ = 0 \quad \text{null, reference state}$$

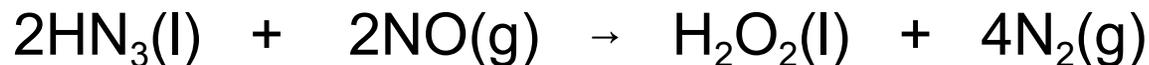
Reaction Enthalpy in Terms of Formation

Conceptual Reaction: Decompose the reactants into their elements, form these elements into products

Value of $\Delta_r H^\circ$ for reaction is sum of forming and “unforming” enthalpies

$$\Delta_r H^\circ = \sum_{\text{products}} v \Delta_f H^\circ - \sum_{\text{reactants}} v \Delta_f H^\circ$$

Example



$$\begin{aligned} \Delta_r H^\circ &= [\Delta_f H^\circ(\text{H}_2\text{O}_2, \text{l}) + 4\Delta_f H^\circ(\text{N}_2, \text{g})] \\ &- [2\Delta_f H^\circ(\text{HN}_3, \text{l}) + 2\Delta_f H^\circ(\text{NO}, \text{g})] \\ &= [-187.78 + 4(0)] - [2(264.0) + 2(90.25)] \text{ kJ mol}^{-1} \\ &= -896.3 \text{ kJ mol}^{-1} \end{aligned}$$

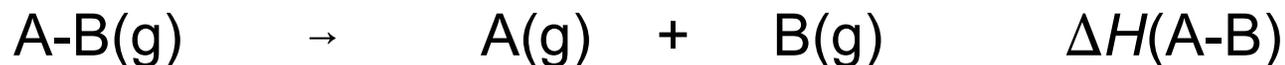
$$\Delta_r H^\circ = \sum_{\text{J}} v_{\text{J}} \Delta_f H^\circ(\text{J})$$

Group Contributions

Sometimes it is difficult to exactly thermodynamically break enthalpies of formation down into contributions from individual atoms and bonds

mean bond enthalpies, $\Delta H(\text{A-B})$

enthalpy change associated with breaking of a specific bond, A-B



This is an *unreliable method*, since $\Delta H(\text{A-B})$ are average values for series of unrelated compounds (different geometries, isomers, etc.)

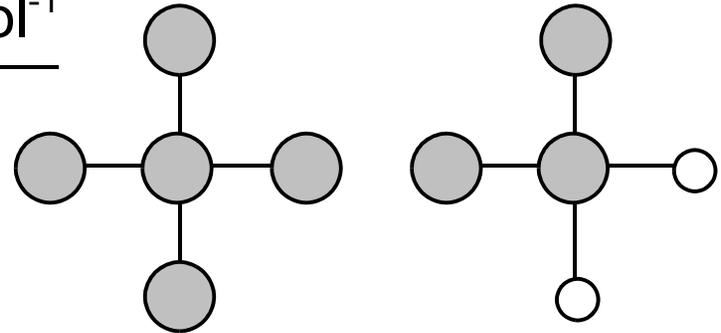
thermochemical groups

atom or physical group of atoms bound to at least two other atoms

enthalpy of formation is associated with sum of contributions associated with all of the thermochemical groups into which the molecule can be divided - sometimes called **Benson thermochemical groups**

Benson Group Contributions

Group	$\Delta_r H^\circ / \text{kJ mol}^{-1}$	$C_{p,m}^\circ / \text{J K}^{-1} \text{mol}^{-1}$
$\text{C}(\text{H})_3(\text{C})$	-42.17	25.9
$\text{C}(\text{H})_2(\text{C})_2$	-20.7	22.8
$\text{C}(\text{H})\text{C}_3$	-6.19	18.7
$\text{C}(\text{C})_4$	+8.16	18.2



$\text{C}(\text{C})_4$

$\text{C}(\text{H})_2(\text{C})_2$

Example

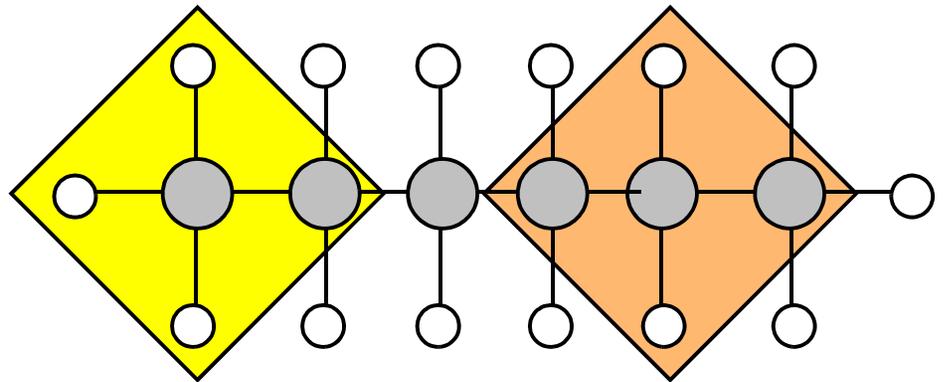
Estimate standard enthalpy of formation for hexane (g & l) at 298 K:

Decomposition: two $\text{C}(\text{H})_3(\text{C})$ groups and four $\text{C}(\text{H})_2(\text{C})_2$ groups

$$\begin{aligned} \Delta_f H^\circ(\text{C}_6\text{H}_{14}, \text{g}) &= 2(-42.17) + 4(-20.7) \\ &= -167.1 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta_{\text{vap}} H^\circ(\text{C}_6\text{H}_{14}) = 28.9 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta_f H^\circ(\text{C}_6\text{H}_{14}, \text{l}) &= -167.1 - 28.9 \\ &= -196.0 \text{ kJ mol}^{-1} \end{aligned}$$



Experimental: $-198.7 \text{ kJ mol}^{-1}$

Temperature Dependence of Reaction Enthalpies

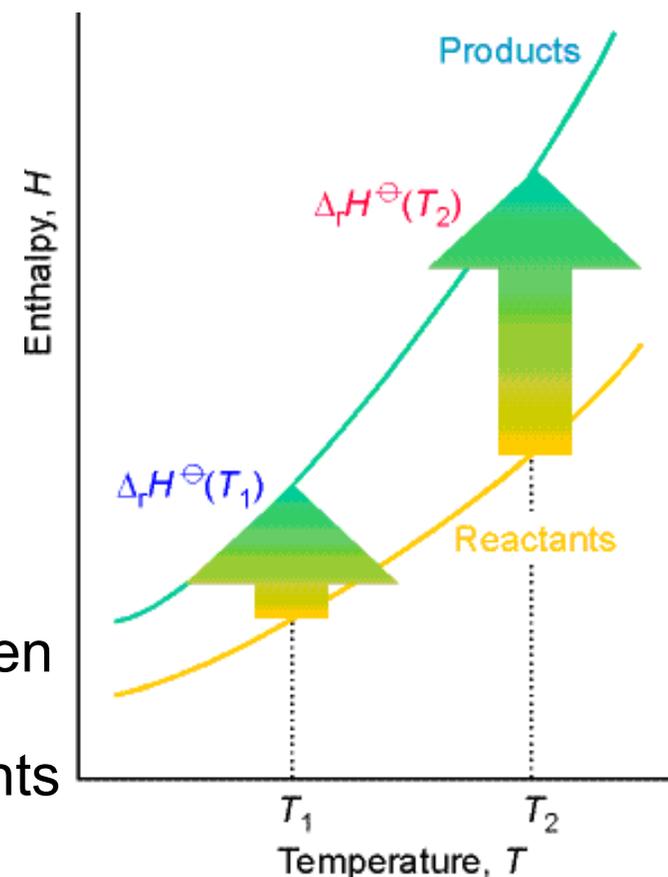
Standard enthalpies have been measured at many temperatures for many substances - however, in absence of such information, the standard enthalpies of formation may be estimated from heat capacities

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

Here, we have heated from T_1 to T_2 , no phase transitions. **Kirchoff's Law** is written as

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\circ dT$$

$\Delta_r C_p^\circ$ is the difference in heat capacities between reactants and products under standard conditions, weighed by stoichiometric coefficients



$$\Delta_r C_p^\circ = \sum_{\text{products}} \nu C_{p,m}^\circ - \sum_{\text{reactants}} \nu C_{p,m}^\circ = \sum_J \nu_J C_{p,m}^\circ(J)$$