Physical Chemistry lecture

Part 2.3. Thermochemistry

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Thermochemistry

2.3. 2

thermochemistry deals with the measurement and quantitative analysis of heat flow during chemical reactions.

HEAT OF REACTION - HESS'S LAW

Under isochoric conditions

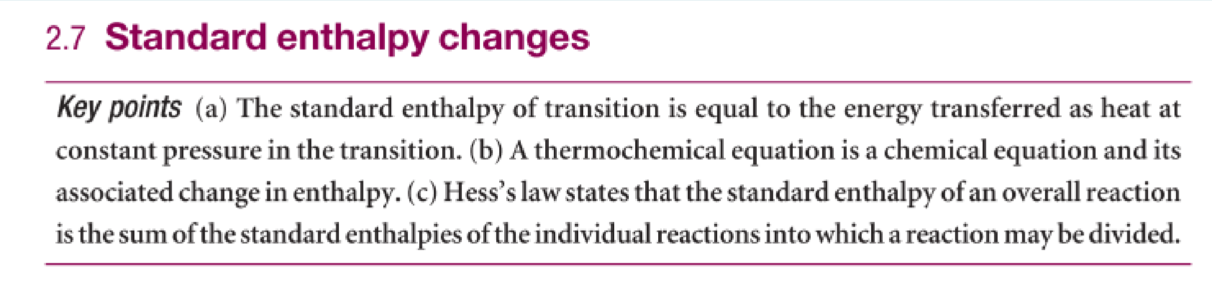
$$Q_{r,V} = \Delta U_r$$

Under isobaric conditions

$$Q_{r,p} = \Delta U + p\Delta V =$$

$$Q = \Delta\left(U + pV\right) = \Delta H_r$$

Under these conditions, heat is a state function.



2.7 **Standard enthalpy changes**

Key points (a) The standard enthalpy of transition is equal to the energy transferred as heat at constant pressure in the transition. (b) A thermochemical equation is a chemical equation and its associated change in enthalpy. (c) Hess's law states that the standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

(a) Enthalpies of physical change

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta_{vap}H^{\ominus}(373\ \text{K}) = +40.66\ \text{kJ mol}^{-1}$$

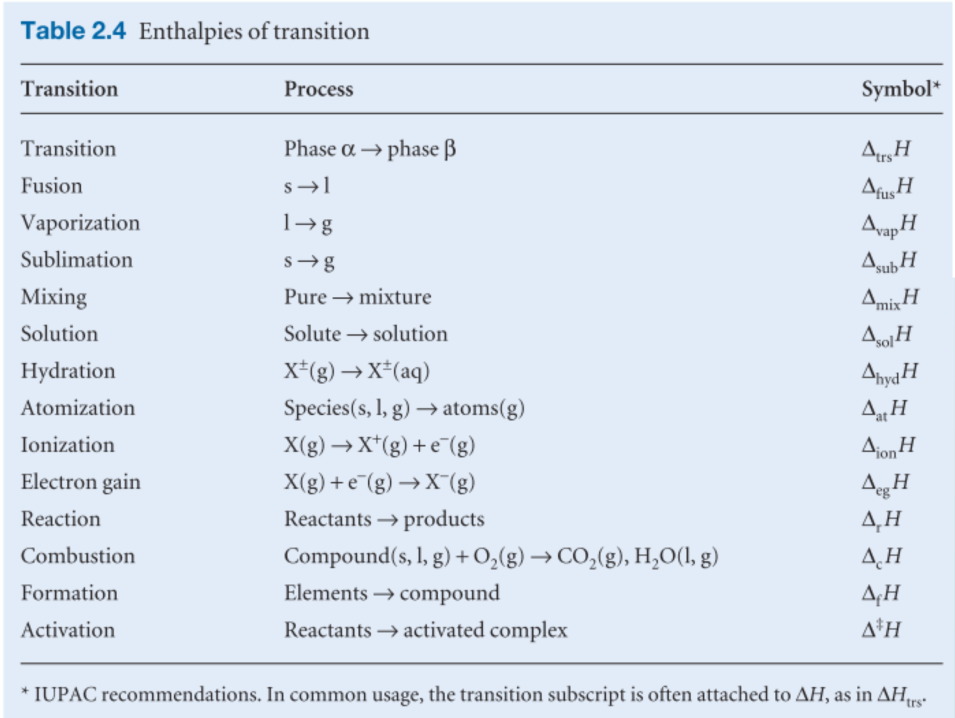
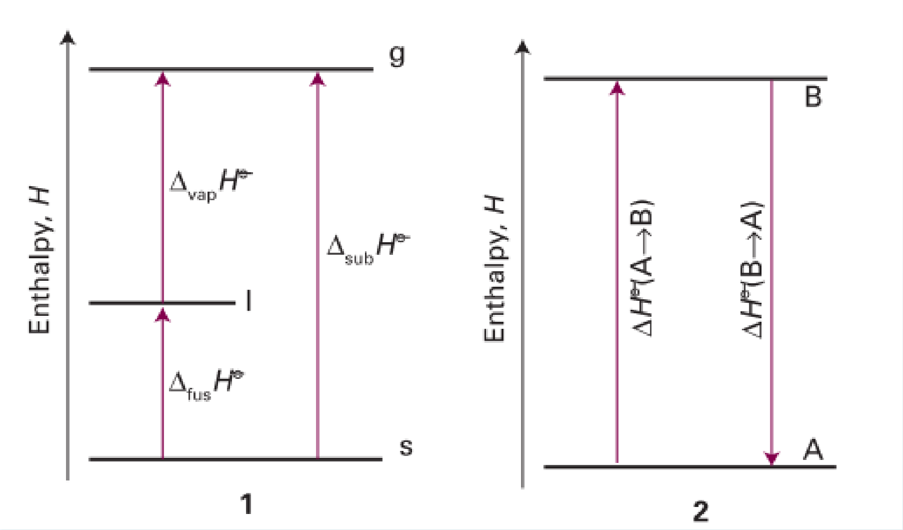


Table 2.4 Enthalpies of transition

Transition	Process	Symbol*
Transition	Phase α → phase β	$\Delta_{trs}H$
Fusion	$s \rightarrow l$	$\Delta_{fus}H$
Vaporization	$l \rightarrow g$	$\Delta_{vap}H$
Sublimation	$s \rightarrow g$	$\Delta_{sub}H$
Mixing	Pure → mixture	$\Delta_{mix}H$
Solution	Solute → solution	$\Delta_{sol}H$
Hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	$\Delta_{hyd}H$
Atomization	Species(s, l, g) → atoms(g)	$\Delta_{at}H$
Ionization	$X(g) \rightarrow X^{+}(g) + e^{-}(g)$	$\Delta_{ion}H$
Electron gain	$X(g) + e^{-}(g) \rightarrow X^{-}(g)$	$\Delta_{eg}H$
Reaction	Reactants → products	$\Delta_{r}H$
Combustion	Compound(s, l, g) + $O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	$\Delta_{c}H$
Formation	Elements → compound	$\Delta_{f}H$
Activation	Reactants → activated complex	$\Delta^{\ddagger}H$

* IUPAC recommendations. In common usage, the transition subscript is often attached to ΔH, as in ΔH_{trs}.



(b) Enthalpies of chemical change

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu H_m^\ominus - \sum_{\text{Reactants}} \nu H_m^\ominus \qquad [2.32]$$

Definition of standard reaction enthalpy

Example 2.5 *Using Hess's law*

The standard reaction enthalpy for the hydrogenation of propene

$$CH_2{=}CHCH_3(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$$

is –124 kJ mol^{-1}. The standard reaction enthalpy for the combustion of propane

$$CH_3CH_2CH_3(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

is –2220 kJ mol^{-1}. Calculate the standard enthalpy of combustion of propene.

Method The skill to develop is the ability to assemble a given thermochemical equation from others. Add or subtract the reactions given, together with any others needed, so as to reproduce the reaction required. Then add or subtract the reaction enthalpies in the same way. Additional data are in Table 2.6.

Answer The combustion reaction we require is

$$C_3H_6(g) + \tfrac{9}{2}O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$$

This reaction can be recreated from the following sum:

	$\Delta_r H^\ominus/(\text{kJ mol}^{-1})$
$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$	–124
$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$	–2220
$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$	+286
$C_3H_6(g) + \tfrac{9}{2}O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$	–2058

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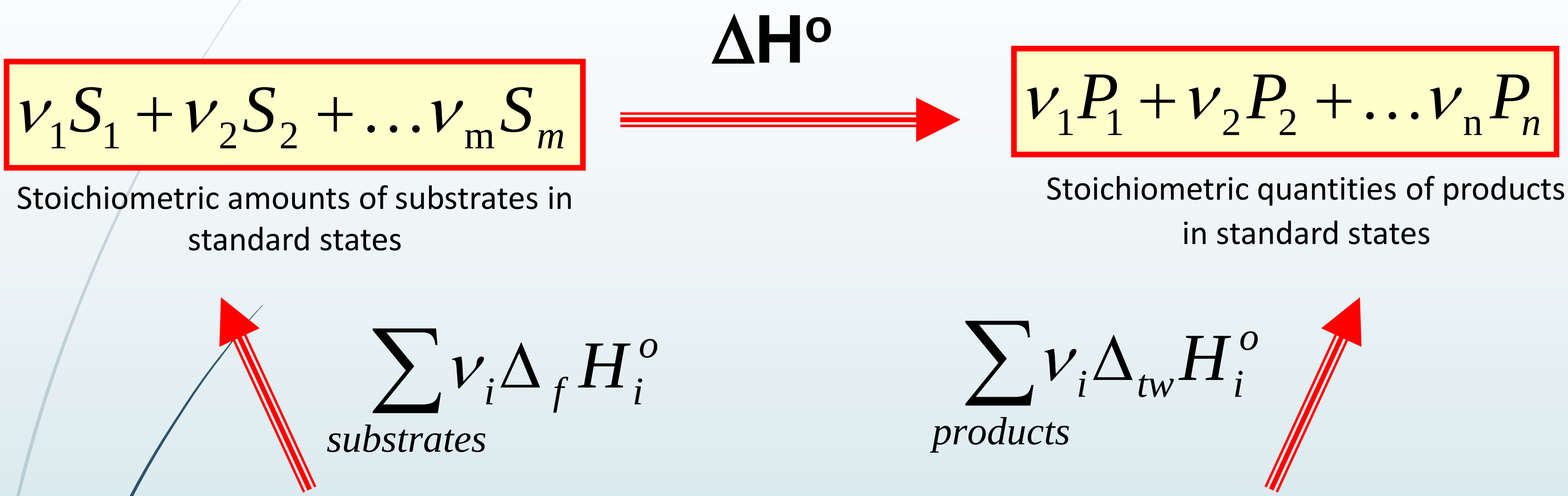
Standard enthalpy of formation $\Delta_f H^o$



$$\nu_1 S_1 + \nu_2 S_2 + \ldots \nu_m S_m \xrightarrow{\Delta H^o} \nu_1 P_1 + \nu_2 P_2 + \ldots \nu_n P_n$$

Stoichiometric amounts of substrates in standard states

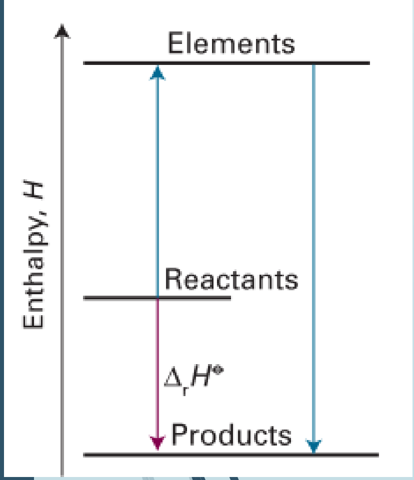
Stoichiometric quantities of products in standard states

$$\sum_{substrates} \nu_i \Delta_f H_i^o$$

$$\sum_{products} \nu_i \Delta_{tw} H_i^o$$

$$\boxed{\Delta H^o = \sum_{products} \nu_i \Delta_f H_i^o - \sum_{substrates} \nu_i \Delta_f H_i^o}$$

$$\boxed{\Delta H^o = \sum_{reagents} \nu_i \Delta_f H_i^o}$$



subscript „f” stands for formation

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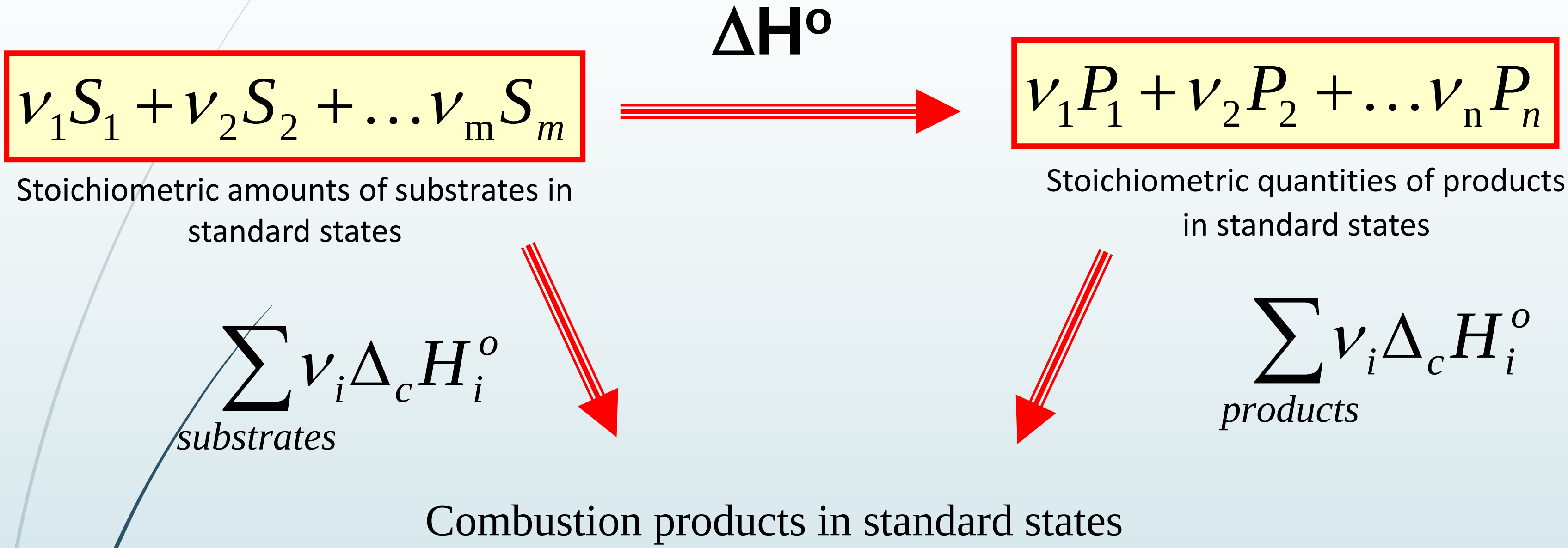
Standard enthalpy of combustion $\Delta_c H^o$...



$$\nu_1 S_1 + \nu_2 S_2 + \ldots \nu_m S_m \xrightarrow{\Delta H^o} \nu_1 P_1 + \nu_2 P_2 + \ldots \nu_n P_n$$

Stoichiometric amounts of substrates in standard states

Stoichiometric quantities of products in standard states

$$\sum_{substrates} \nu_i \Delta_c H_i^o$$

$$\sum_{products} \nu_i \Delta_c H_i^o$$

Combustion products in standard states

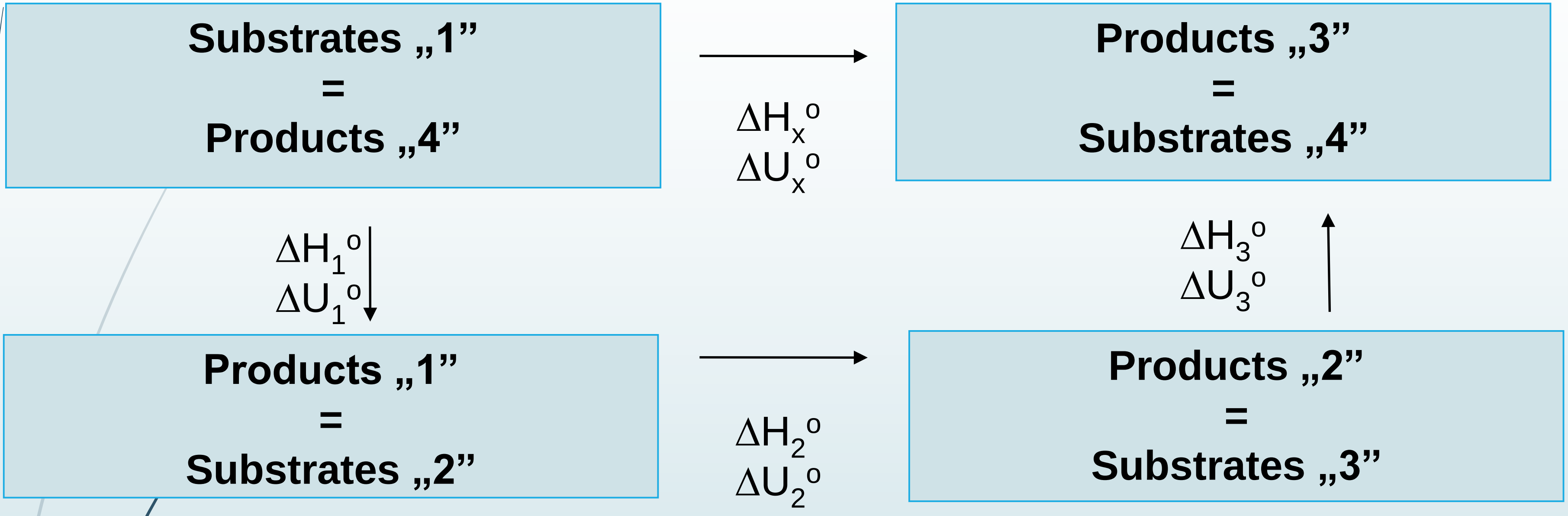
$$\boxed{\Delta H^o = \sum_{substrates} \nu_i \Delta_c H_i^o - \sum_{products} \nu_i \Delta_c H_i^o}$$

$$\boxed{\Delta H^o = -\sum_{reagents} \nu_i \Delta_c H_i^o}$$

THERMAL EFFECT OF CYCLIC REACTIONS

The Third Law of Thermochemistry

The enthalpy of any process can be replaced by a set of other reactions (thermochemical equations = algebraic equations)



Substrates „1” = Products „4”

ΔH_x^o ΔU_x^o

Products „3” = Substrates „4”

ΔH_1^o ΔU_1^o

ΔH_3^o ΔU_3^o

Products „1” = Substrates „2”

ΔH_2^o ΔU_2^o

Products „2” = Substrates „3”

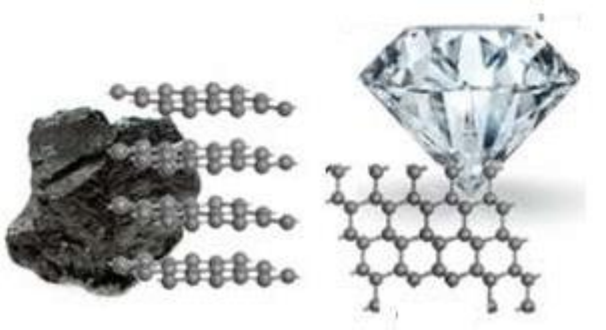
For any thermodynamic cycle:

$$\sum_i \Delta H_i = 0 \qquad \sum_i \Delta U_i = 0$$

$$\Delta H_x = \Delta H_1 + \Delta H_2 + \Delta H_3 \qquad \Delta U_x = \Delta U_1 + \Delta U_2 + \Delta U_3$$

EXAMPLES OF CALCULATION OF THERMAL EFFECTS

requires P>20GPa =200Katm



Example:

Energetics of making a diamond from pencil lead.

We are looking for

$$\mathbf{C_{(g)} \rightarrow C_{(d)}} \quad \Delta H=?$$

We know:

$$C_{(g)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H°298K = -393.51 \text{ kJ/mol}$$
$$C_{(d)} + O_2(g) \rightarrow CO_2(g) \qquad \Delta H°298K = -395.40 \text{ kJ/mol}$$

$$\Delta H = (H(CO_2) – H(C_{(gt)}) – H(O_2) - (H(CO_2) – H(C_{(d)}) – H(O_2)$$

$$\Delta H = H(C_{(g)}) – H(C_{(d)}) = -393.51+395.40= 1.89 \text{kJ/mol}$$

EXAMPLES OF CALCULATING THERMAL EFFECTS

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Write the expression for heat of reaction at constant pressure

$$SO_{2(g)} + 1/2O_{2(g)} = SO_{3(g)}$$

$$\Delta U = Q_V = \sum n_i \Delta U_i \ _{(prod)} - \sum n_i \Delta U_i \ _{(substr)}$$

$$\Delta H = Q_p = \sum n_i \Delta H_i \ _{(prod)} - \sum n_i \Delta H_i \ _{(substr)}$$

$$\boxed{\Delta H = \Delta H_{SO_3} - \left(\frac{1}{2} \Delta H_{O_2} + \Delta H_{SO_2} \right)}$$

The energy effect of a reaction is the sum of the enthalpy of formation

Example

Calculate the standard enthalpy change for the hydrogenation of benzene:

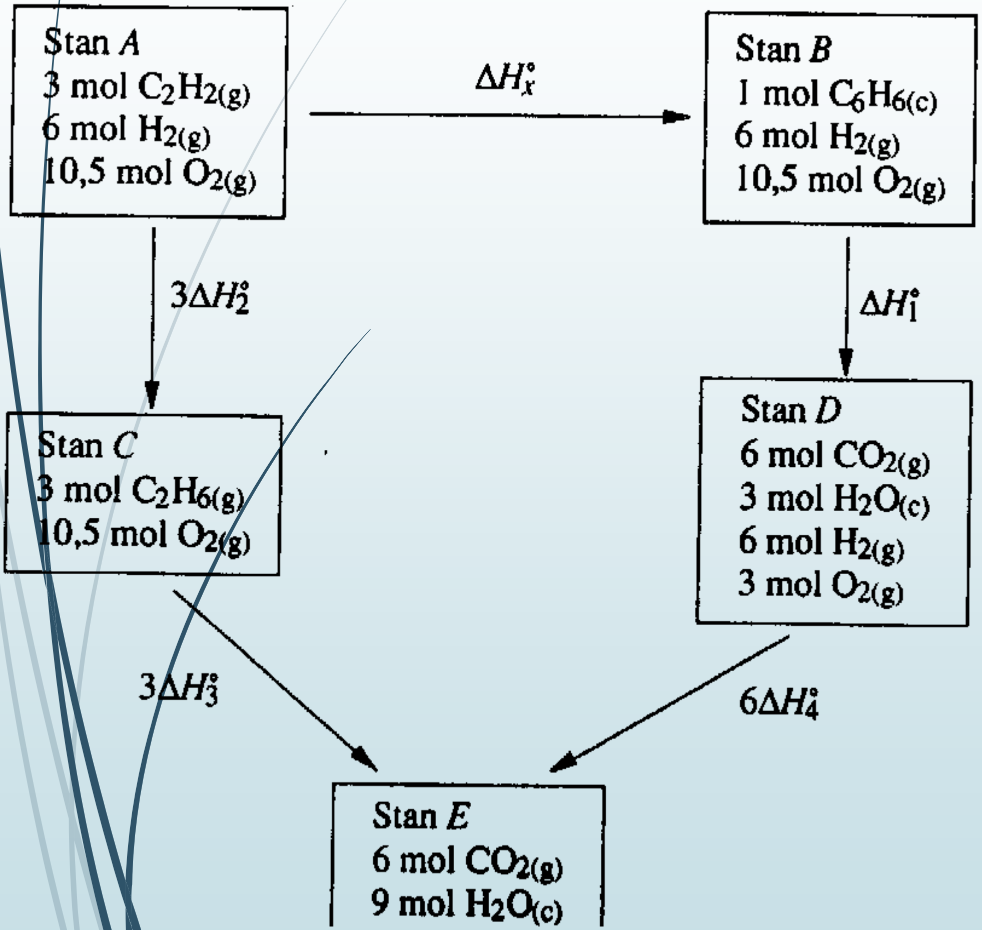
$$C_6H_{6(c)} + 3H_{2(g)} = C_6H_{12(c)}$$

It is necessary to know thermochemical data,

e.g. standard enthalpies of formation of reactants:

$$\Delta H^o_{298} = \Delta H^0_{298\,(C_6H_{12})} - \Delta H^0_{298\,(C_6H_6)} - 3\Delta H^0_{298\,(H_2)}$$

Calculate the enthalpy of formation of liquid benzene from gaseous acetylene.



We have standard enthalpies for the following reactions

$$C_6H_{6(c)} + 7{,}5O_{2(g)} \rightarrow 6CO_{2(g)} + 3H_2O_{(c)}$$
$$C_2H_{2(g)} + 2H_{2(g)} = C_2H_{6(g)}$$
$$C_2H_{6(g)} + 3{,}5O_{2(g)} = 2CO_{2(g)} + 3H_2O_{(c)}$$
$$H_{2(g)} + 0{,}5O_{2(g)} = H_2O_{(c)}$$

$$\Delta H_1^\circ = -3269{,}80\ \text{kJ}\cdot\text{mol}^{-1}$$
$$\Delta H_2^\circ = -310{,}62\ \text{kJ}\cdot\text{mol}^{-1}$$
$$\Delta H_3^\circ = -1560{,}92\ \text{kJ}\cdot\text{mol}^{-1}$$
$$\Delta H_4^\circ = -286{,}03\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_x = 3\Delta H_2 + 3\Delta H_3 - 6\Delta H_4 - \Delta H_1$$

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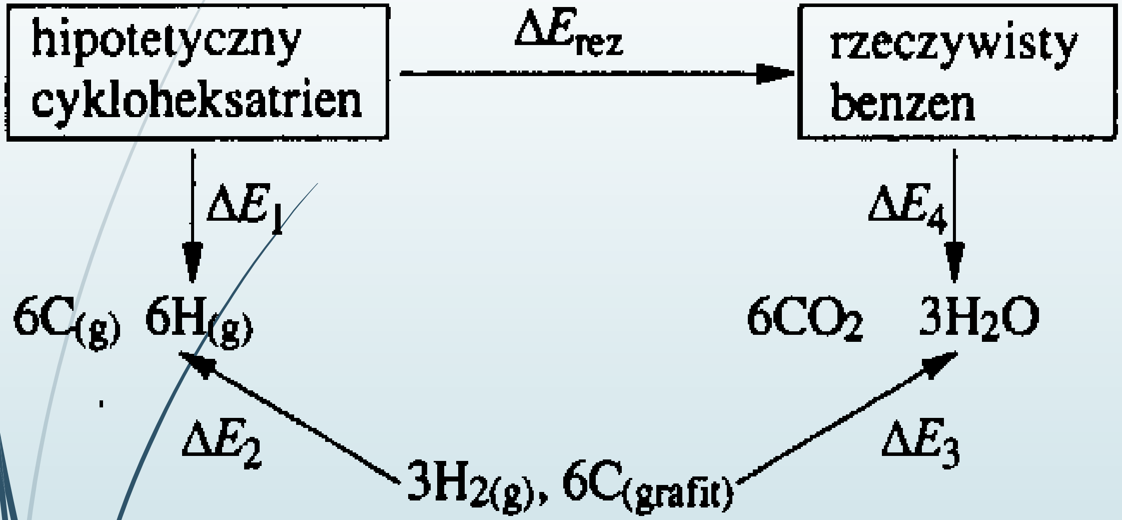
Estimate the resonance energy of benzene knowing the standard combustion enthalpies of: graphite (ΔH_1), hydrogen (ΔH_2), benzene (ΔH_3)

Hypothetical cyclohexatriene

Real benzene



$$\Delta E_1 = 3E_{C-C} + 3E_{C=C} + 6E_{C-H}$$

$$\Delta E_2 = 3E_{H-H} + 6\Delta E_{subl.}(\text{grafit})$$

$$\Delta E_3 = 6\Delta H_{spal}(\text{grafit}) + 3\Delta H_{spal}(H_2)$$

$$\Delta E_4 = \Delta H_{spal}(C_6H_{6(g)})$$

$$\Delta E_{rez} = \Delta E_1 - \Delta E_2 + \Delta E_3 - \Delta E_4$$

Estimation of the C-H bond energy knowing the standard combustion enthalpies: methane (ΔH_1), hydrogen (ΔH_2), graphite (ΔH_3)

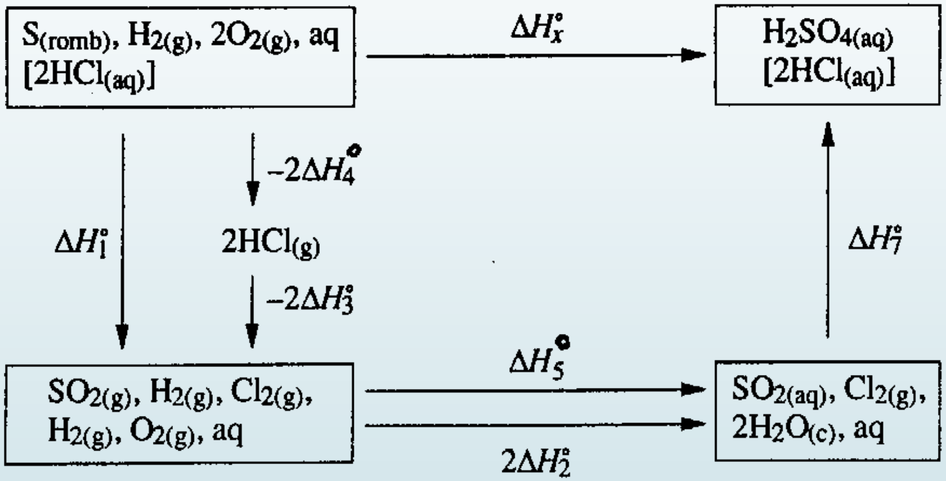
$$\begin{tikzcd}
CH_{4(g)}(2O_{2(g)}) \arrow[r, "4E_{C-H}"] \arrow[d, "\Delta H_1"] & C_{(g)} + & 4H_{(g)}(2O_{2(g)}) \\
CO_{2(g)} + 2H_2O_{(c)} & C_{grafit} \arrow[l, shift right, "2\Delta H_2^\circ"'] \arrow[l, shift left, "\Delta H_3^\circ"'] \arrow[u, "\Delta H_4^\circ"'] & 2H_{2(g)}(2O_{2(g)} \arrow[u, "2E_{H-H}"']
\end{tikzcd}$$

$$4\Delta H_{C-H} = \Delta H_1 - 2\Delta H_2 - \Delta H_3 + \Delta H_4 + 2\Delta H_{H-H}$$

Calculate the standard enthalpy of formation of a liquid electrolyte in aqueous solution.

$$SO_{2(aq)} + Cl_{2(g)} + 2H_2O_{(aq)} = H_2SO_{4(aq)} + 2HCl_{(aq)} + \Delta H_7$$

Data: standard enthalpies of combustion: sulfur in oxygen (ΔH_1), hydrogen in oxygen (ΔH_2), hydrogen in chlorine (ΔH_3), standard enthalpies of dissolution: gaseous hydrogen chloride (ΔH_4), gaseous SO2 (ΔH_5), liquid sulfuric acid (ΔH_6), standard enthalpy of reaction (ΔH_7):

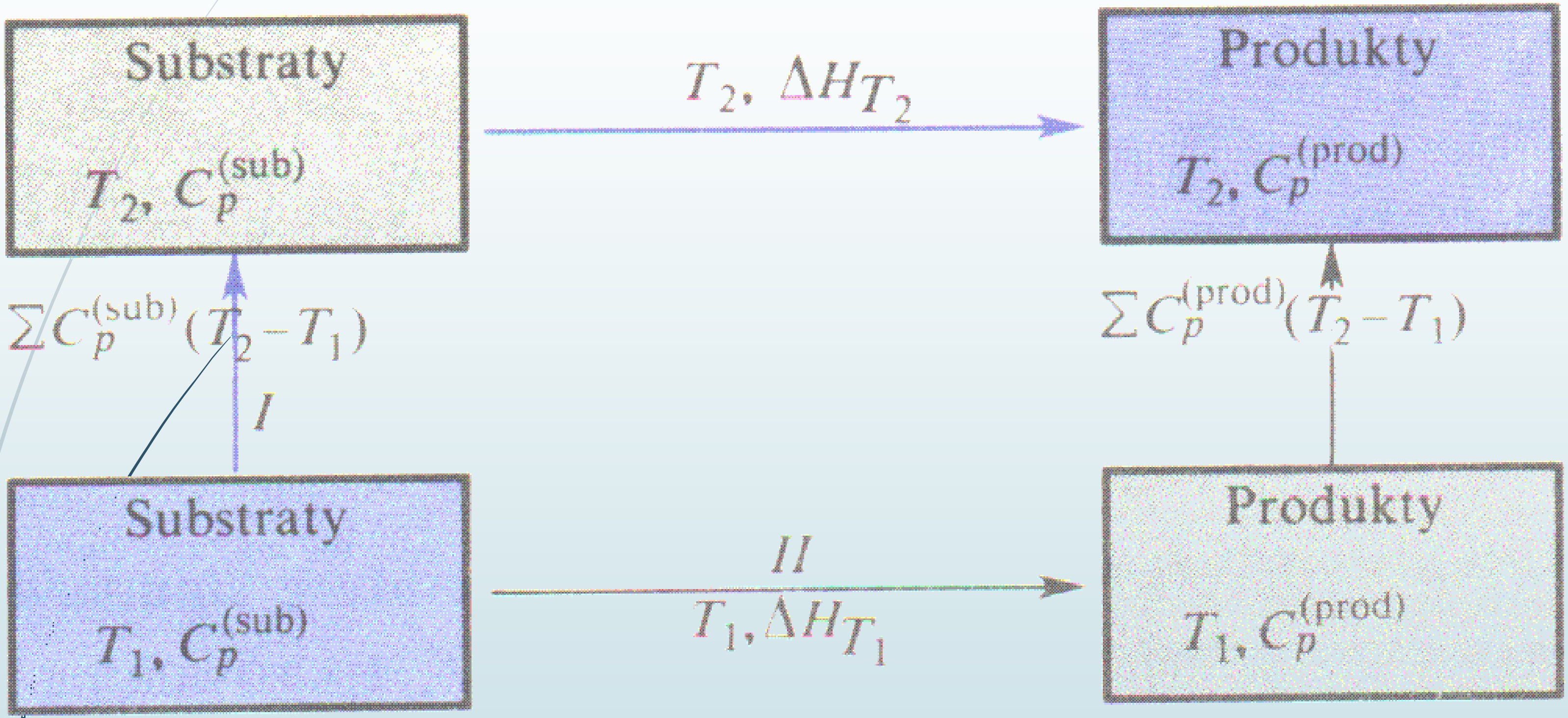


$$S_{romb} + H_{2(g)} + 2O_{2(g)} + aq = H_2SO_{4(aq)}$$

$$\Delta H_x = \Delta H_1 - 2\Delta H_4 - 2\Delta H_3 + \Delta H_5 + 2\Delta H_2 + \Delta H_7$$

Kirchhoff's law

DEPENDENCE OF HEAT ON TEMPERATURE



Reaction paths
Method I – heating the substrates and carrying out the reaction
Method II – carrying out the reaction and heating the products

Mathematical formulation of KIRCHHOFF's law

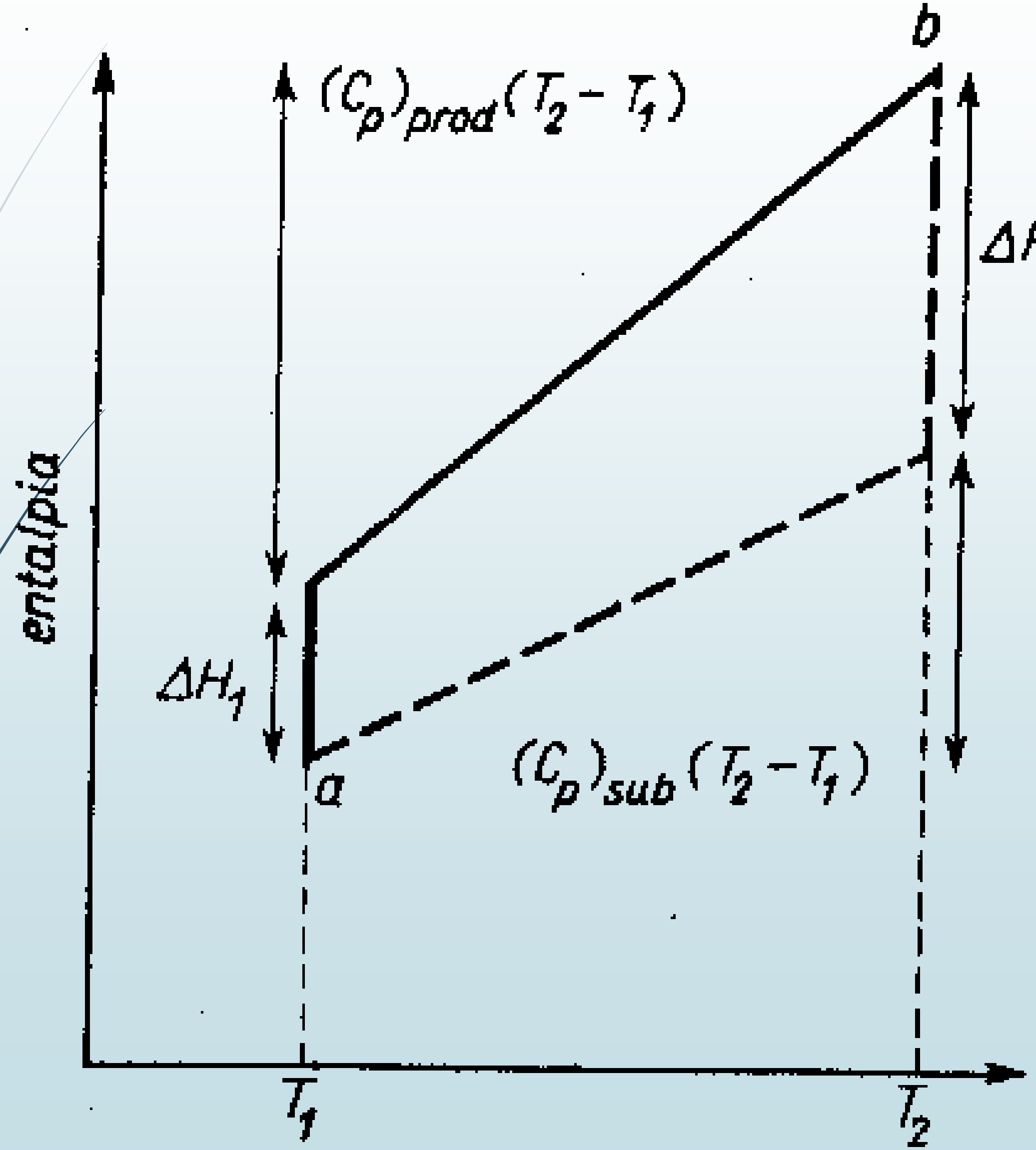
$$\left(\frac{\partial \Delta U_r^o}{\partial T}\right)_V = \left(\frac{\partial C_V}{\partial \xi}\right)_V = \sum_i v_i C_{V,i}^o$$

$$\boxed{\Delta U_{r,T_2} = \Delta U_{r,T_1} + \int_{T_1}^{T_2} \sum v_i C_{V,i}\, dT}$$

$$\left(\frac{\partial \Delta H_r^o}{\partial T}\right)_p = \left(\frac{\partial C_p}{\partial \xi}\right)_p = \sum_i v_i C_{p,i}^o$$

$$\boxed{\Delta H_{r,T_2} = \Delta H_{r,T_1} + \int_{T_1}^{T_2} \sum v_i C_{p,i}\, dT}$$

Graphical interpretation of KIRCHHOFF's law

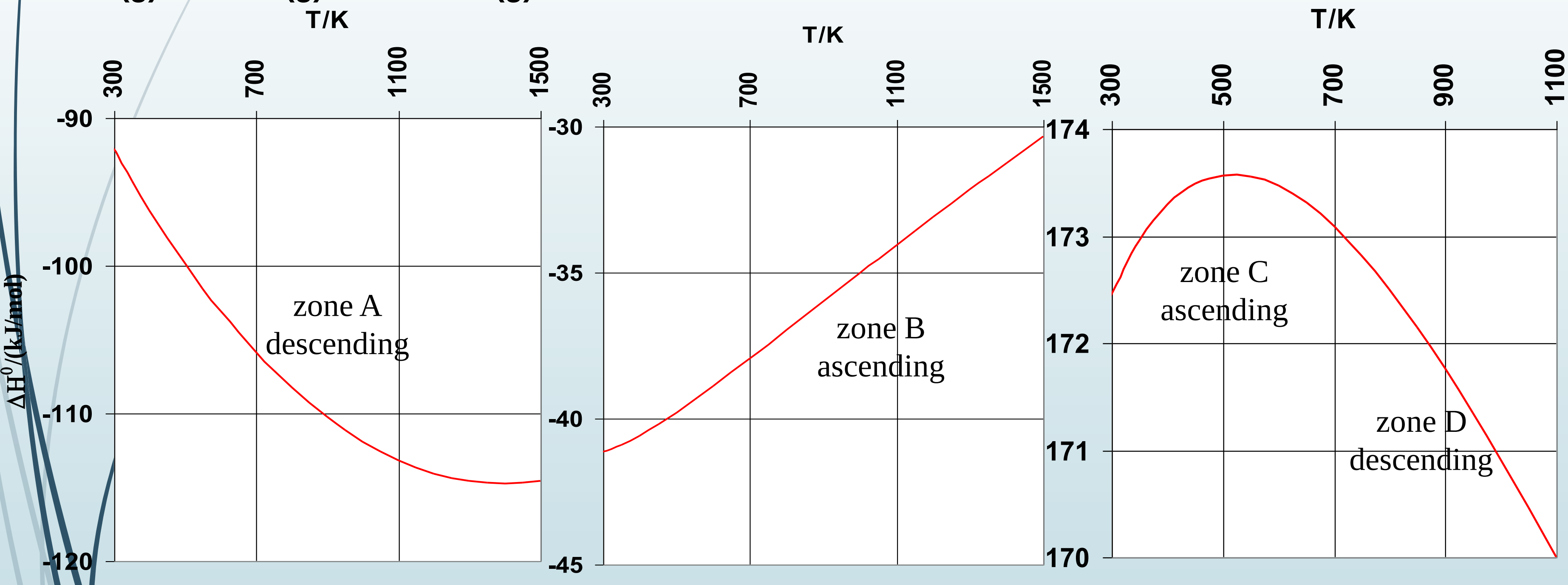


$$C_p = a + b \cdot T + c \cdot T^{-2}$$

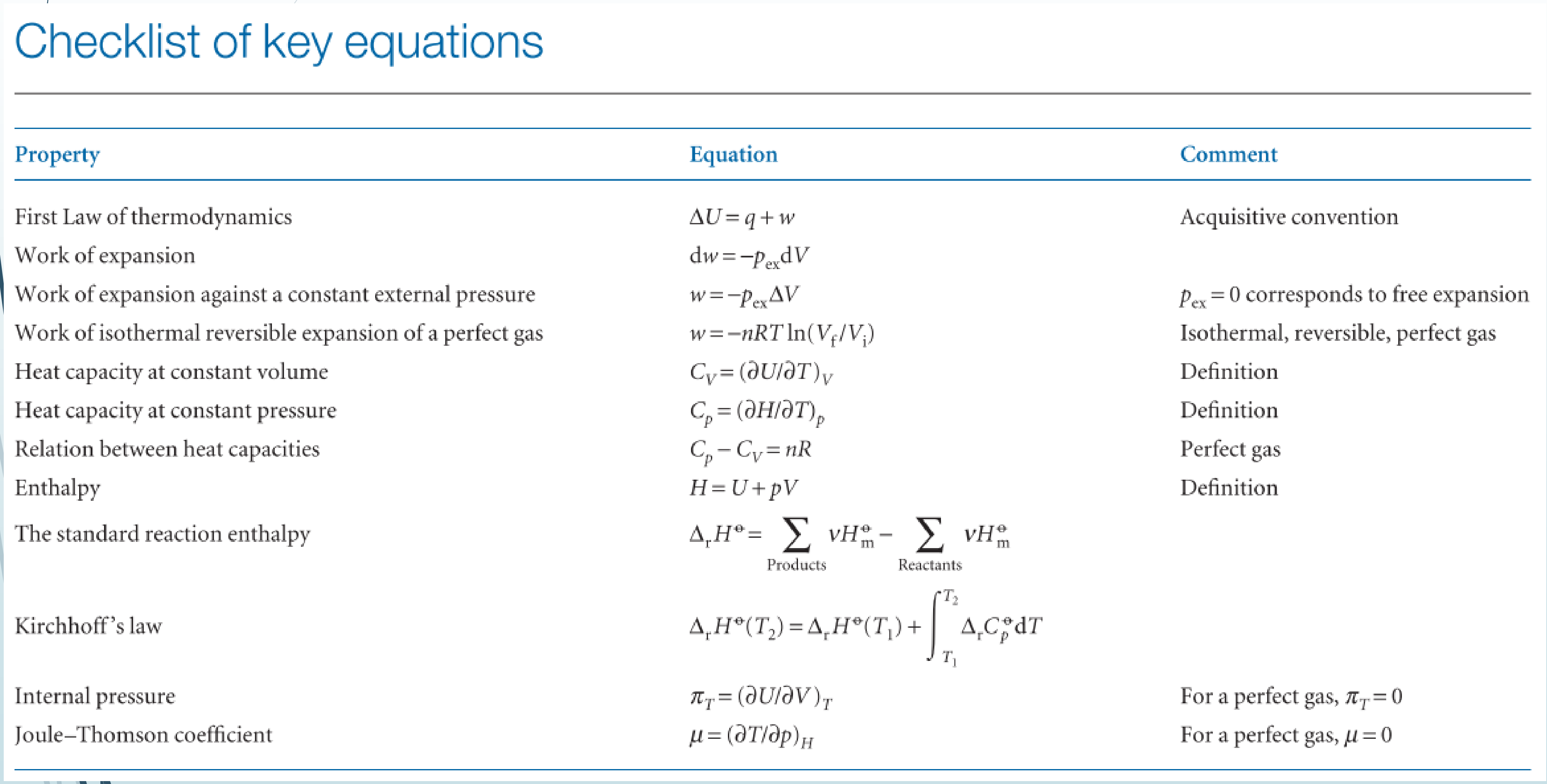
An example of the effect of temperature on the energtics of a reaction ΔHº(T):

$N_{2(g)} + 3H_{2(g)} = 2\ NH_{3(g)}$

$C_{(s)} + CO_{2(g)} = 2\ CO_{(g)}$



$CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)}$



Checklist of key equations

Property	Equation	Comment
First Law of thermodynamics	$\Delta U = q + w$	Acquisitive convention
Work of expansion	$\mathrm{d}w = -p_{\mathrm{ex}}\mathrm{d}V$	
Work of expansion against a constant external pressure	$w = -p_{\mathrm{ex}}\Delta V$	$p_{\mathrm{ex}} = 0$ corresponds to free expansion
Work of isothermal reversible expansion of a perfect gas	$w = -nRT\ln(V_{\mathrm{f}}/V_{\mathrm{i}})$	Isothermal, reversible, perfect gas
Heat capacity at constant volume	$C_V = (\partial U/\partial T)_V$	Definition
Heat capacity at constant pressure	$C_p = (\partial H/\partial T)_p$	Definition
Relation between heat capacities	$C_p - C_V = nR$	Perfect gas
Enthalpy	$H = U + pV$	Definition
The standard reaction enthalpy	$\Delta_{\mathrm{r}}H^\ominus = \sum_{\mathrm{Products}} \nu H_{\mathrm{m}}^\ominus - \sum_{\mathrm{Reactants}} \nu H_{\mathrm{m}}^\ominus$	
Kirchhoff's law	$\Delta_{\mathrm{r}}H^\ominus(T_2) = \Delta_{\mathrm{r}}H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_{\mathrm{r}}C_p^\ominus \mathrm{d}T$	
Internal pressure	$\pi_T = (\partial U/\partial V)_T$	For a perfect gas, $\pi_T = 0$
Joule–Thomson coefficient	$\mu = (\partial T/\partial p)_H$	For a perfect gas, $\mu = 0$

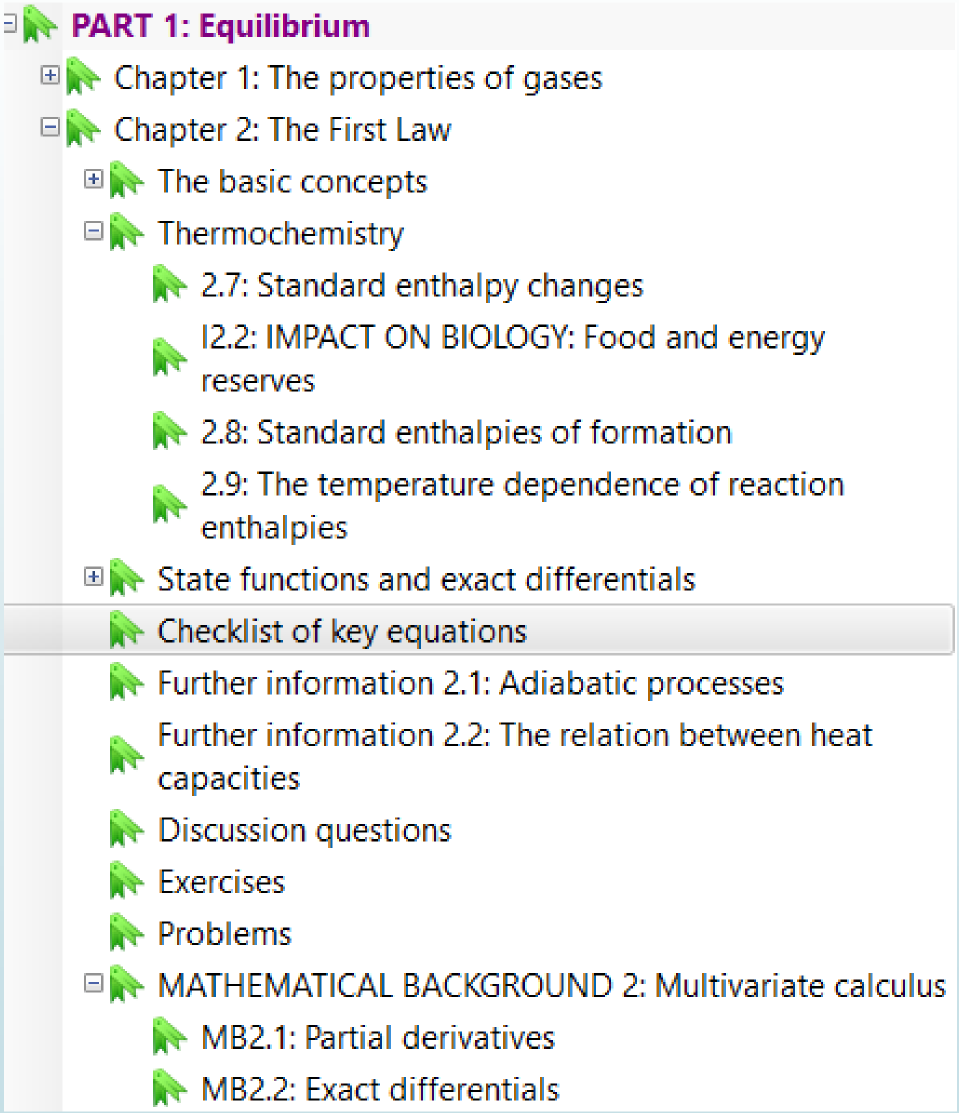
Further information

Further information 2.1 *Adiabatic processes*

Further information 2.2 *The relation between heat capacities*

Exercises

Problems*



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