

3 Physical meaning and relevance of TD potentials

→ Enthalpy $H = U + pV = H(S, p, n_k)$

- most important in thermochemistry
- Measurement of enthalpy changes for processes taking place under standard conditions:

The standard state of a substance at a specified T is its pure form at $p = 1 \text{ bar} = 10^5 \text{ Pa}$

physical changes like

fusion solid \rightarrow liquid

for water
 $\Delta_{\text{fus}} H^\ominus (273\text{K}) = +6.01 \frac{\text{kJ}}{\text{mol}}$

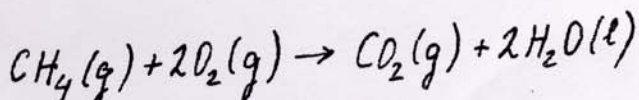
vaporization liquid \rightarrow gas

$$\Delta_{\text{vap}} H^\ominus (373\text{K}) = +40.66 \frac{\text{kJ}}{\text{mol}}$$

mixing, sublimation cf. Tables 2.3 ... 2.4 PWA p. 56, 57

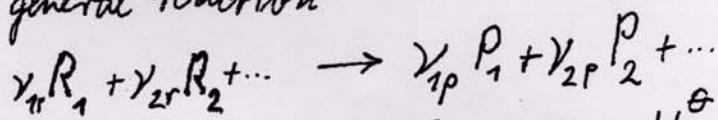
chemical changes like

combustion



$$\Delta_c H^\ominus = -890 \text{ kJ/mol}$$

general reaction



$$\Delta_r H^\ominus = \sum_{\text{products}} \nu_{kp} H_{kp}^\ominus - \sum_{\text{reactants}} \nu_{kr} H_{kr}^\ominus$$

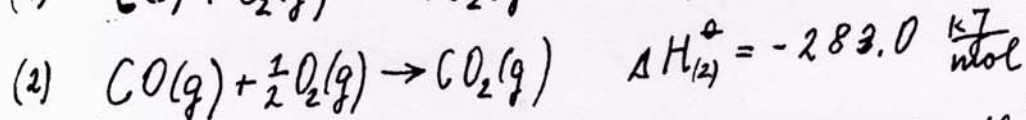
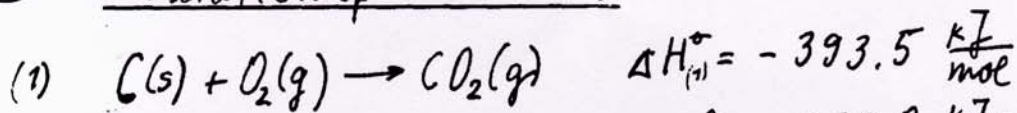
stoichiometric coefficients ν_k

standard reaction enthalpy $\Delta_r H^\ominus$

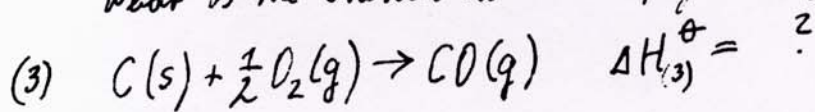
Hess's law

The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction can be divided.

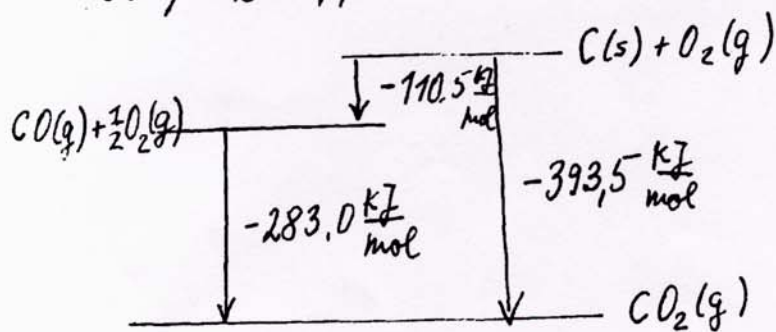
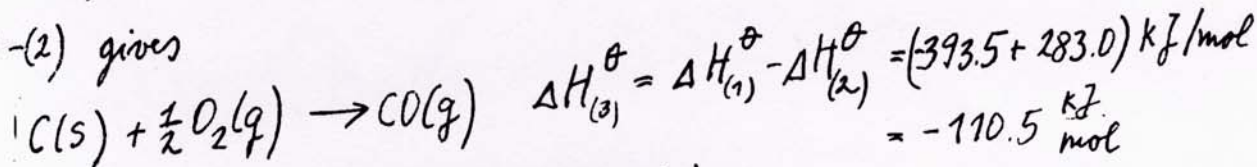
⑧ Illustration of Hess's law



— What is the standard enthalpy change for the reaction



(1) - (2) gives



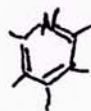
→ Standard enthalpy of formation

of a substance, $\Delta_f H^\ominus$, is the standard reaction enthalpy for the formation of the compound from its elements in their reference states (the most stable state at the specified T and $p=1 \text{ bar}$).

$$\Delta_r H^\ominus = \sum_{\text{products}} \nu_k \Delta_f H_k^\ominus - \sum_{\text{reactants}} \nu_k \Delta_f H_k^\ominus$$

③ Note: There is no TD exact way of expressing $\Delta_f H^\ominus$ in terms of contributions from individual chemical bonds!

Kirchhoff's law



At const. pressure T_2

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

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

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

((molar quantities),
"m")

$$\Delta C_p^\ominus \equiv \sum_{\text{products}} \nu_k C_{p,m}^\ominus - \sum_{\text{Reactants}} \nu_k C_{p,m}^\ominus$$

((Illustration in PWA book p. 63)) example: heat of combustion of H_2 to H_2O at 1500K

(10) Helmholtz energy

$$A \equiv U - TS = TS - pV + G - TS = G - pV$$

$$dA = -SdT - pdV + \sum_k \mu_k dn_k \quad A = A(T, V, n_k)$$

most important for processes at const. T and V

a) surroundings Criterion for spontaneity



at $T = \text{const}$
(heat reservoir)

heat transferred
to the environment

In the system are going on irreversible (spontaneous) processes, if

$$dS + dS_{\text{env.}} > 0$$

$$dS_{\text{env.}} = \frac{\delta Q_{\text{env.}}}{T} = -\frac{dU}{T}$$

U = internal energy of the system
(Because $V = \text{const.}$ no work is done upon the system.)

$$dS + dS_{\text{env.}} = dS - \frac{dU}{T} = \frac{TdS - dU}{T} = -\frac{dA}{T} > 0$$

i.e. irreversible processes in the system if $dA < 0$.

At equilibrium, A is at minimum end of lecture

b) The change in the Helmholtz energy is equal to the maximum work accompanying the process: $\delta W_{\text{max}} = \Delta A$

Proof: $\delta W = dU - \delta Q$ (1. law) $\delta Q \leq TdS$ (2. law)

$$\delta W_{\text{max}} = dU - TdS = dA \quad (\text{for isothermal processes})$$

$A =$ "maximum work function" or "free energy" (energy for work)

11) Gibbs energy

$$G \equiv H - TS$$

$$dG = -SdT + Vdp + \sum_k \mu_k dn_k \quad G = G(p, T, n_k)$$

most important for processes at const. p and T

a) Criterion for spontaneous reactions (at const p and T)

$$dS + dS_{env} > 0$$

$$dS_{env} = \frac{\delta Q_{env}}{T} = -\frac{dH}{T} \quad \leftarrow \text{enthalpy change of the system (at } p = \text{const.)}$$

$$dS - \frac{dH}{T} = -\frac{dH - TdS}{T} = -\frac{dG}{T} > 0$$

$dG < 0$ irreversible (spontaneous) process

At equilibrium, G is at a minimum.

b) Maximum non-expansion work $\delta W_{add, max}$

At const. T and p , the maximum additional (non-expansion) work, is given by dG

Proof: $H = U + pV \quad dH = \delta Q + \delta W + d(pV)$

$$dG = dH - TdS - SdT = \delta Q + \delta W + d(pV) - TdS - SdT$$

$$dT = 0 \text{ (isoth. change)}$$

When the change is reversible $\delta W = \delta W_{rev}$ and $\delta Q = TdS$,

i.e. for a reversible isothermal process

$$dG = \delta W_{rev} + d(pV) = -pdV + \delta W_{add, rev} + pdV + Vdp$$

$$\text{i.e. } dG = \delta W_{add, rev} = \delta W_{add, max}$$