# Thermodynamics tutorhour 3

## Gibbs energy

Gibbs energy is defined as: $G = H - TS$

$$\mathrm{d}G = \mathrm{d}H - \mathrm{d}(TS) = \mathrm{d}H - T\mathrm{d}S - \cancel{S\mathrm{d}T}$$

at constant T this becomes: $\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S$

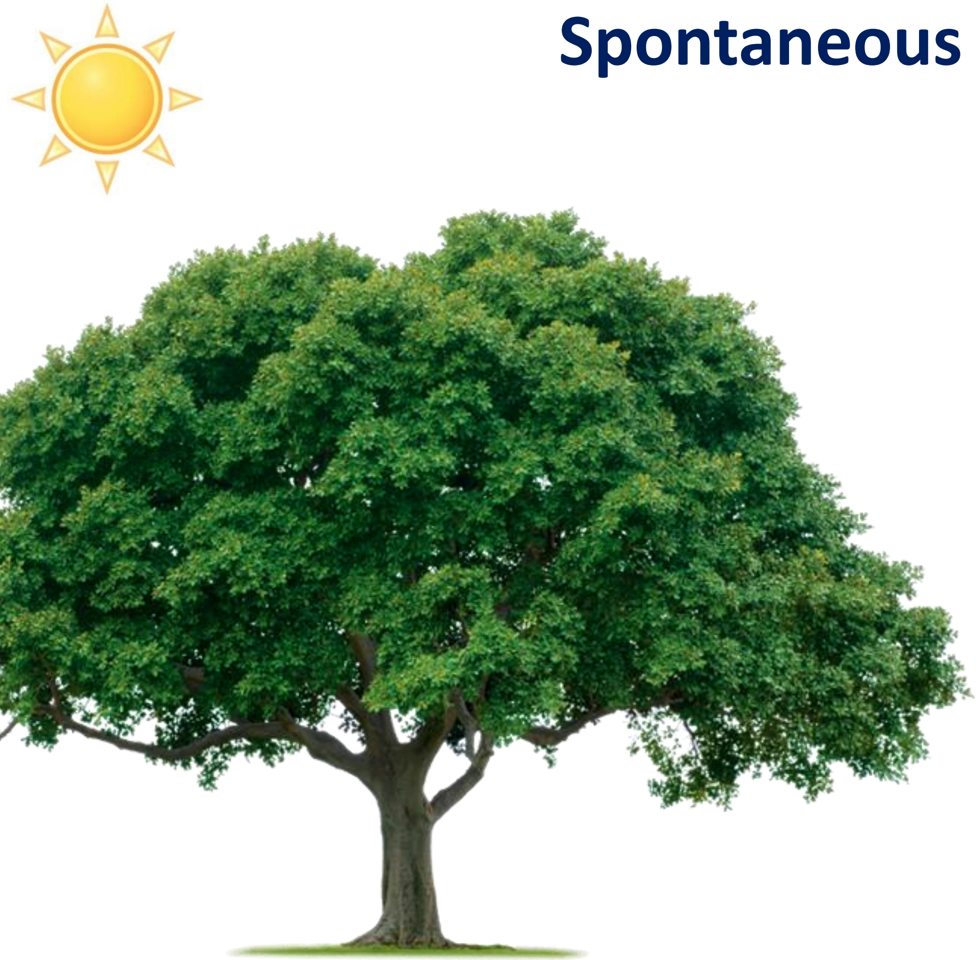
at constant T,p this becomes: $\boxed{\mathrm{d}G = \mathrm{d}Q - T\mathrm{d}S}$

Second Law: $$\mathrm{d}S^{tot} = \mathrm{d}S^{sys} + \mathrm{d}S^{sur} = \left(\mathrm{d}S^{sys} - \frac{\mathrm{d}Q}{T}\right) \geq 0$$

leading to the Clausius inequality: $\mathrm{d}Q - T\mathrm{d}S^{sys} \leq 0$

So when p and T are constant, for a spontaneous process holds: $\mathrm{d}G \leq 0$

# Spontaneous process?



$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2$

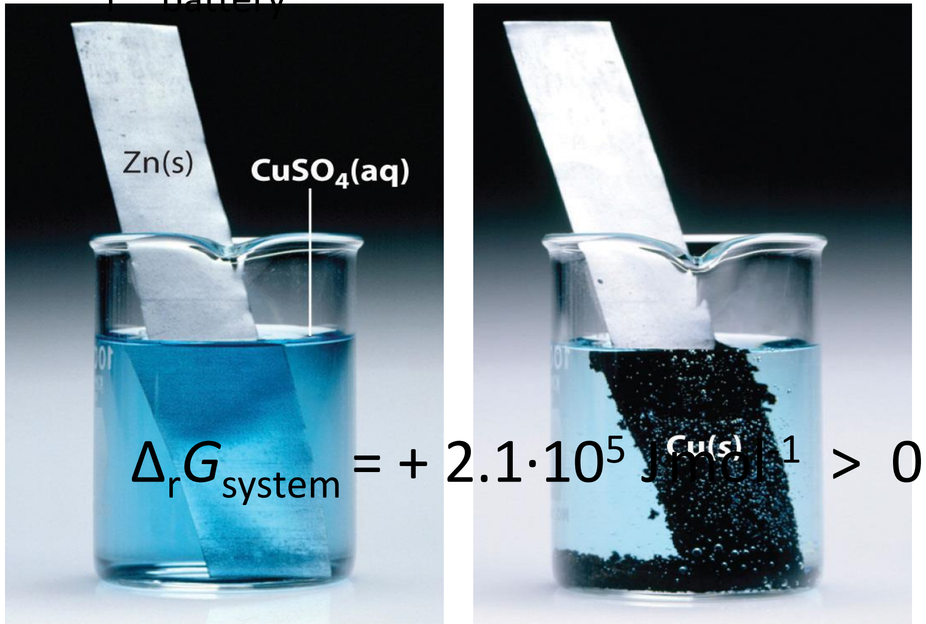
$\Delta_r G = +\,28.3 \cdot 10^5\ \mathrm{J\ mol^{-1}} > 0$

$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O$

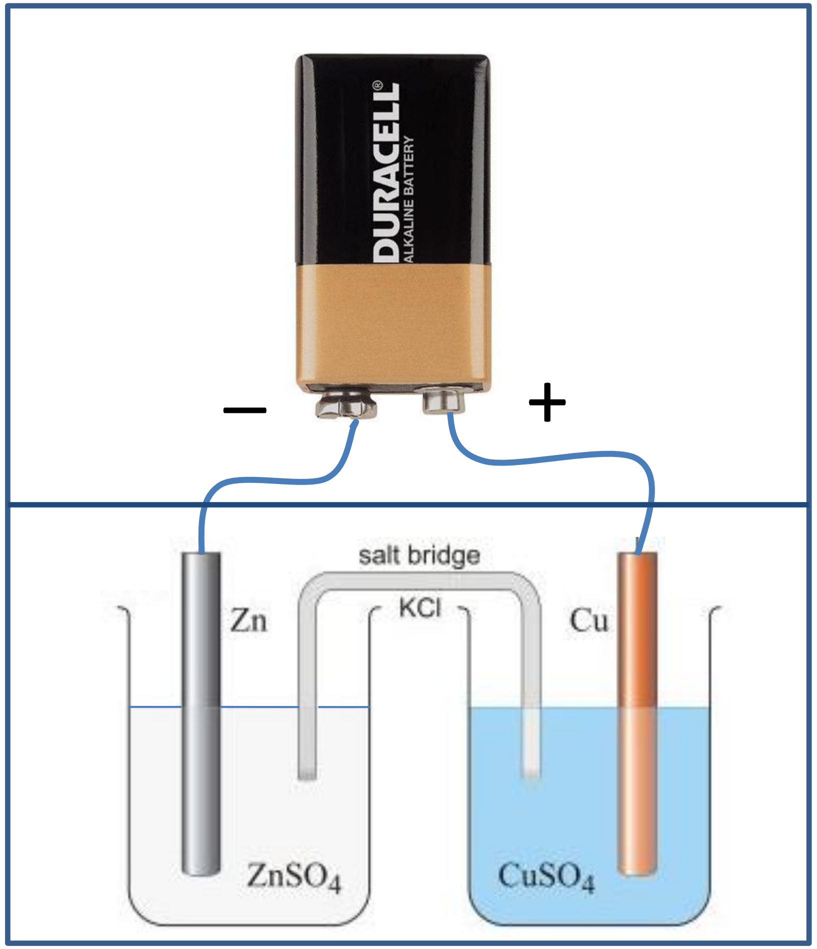
$\Delta_r G = -\,28.3 \cdot 10^5\ \mathrm{J\ mol^{-1}} < 0$

# Spontaneous process?

$\Delta_r G_{battery} = -17.4 \cdot 10^5\ \mathrm{J\,mol^{-1}} < 0$



$\Delta_r G_{system} = +2.1 \cdot 10^5\ \mathrm{J\,mol^{-1}} > 0$



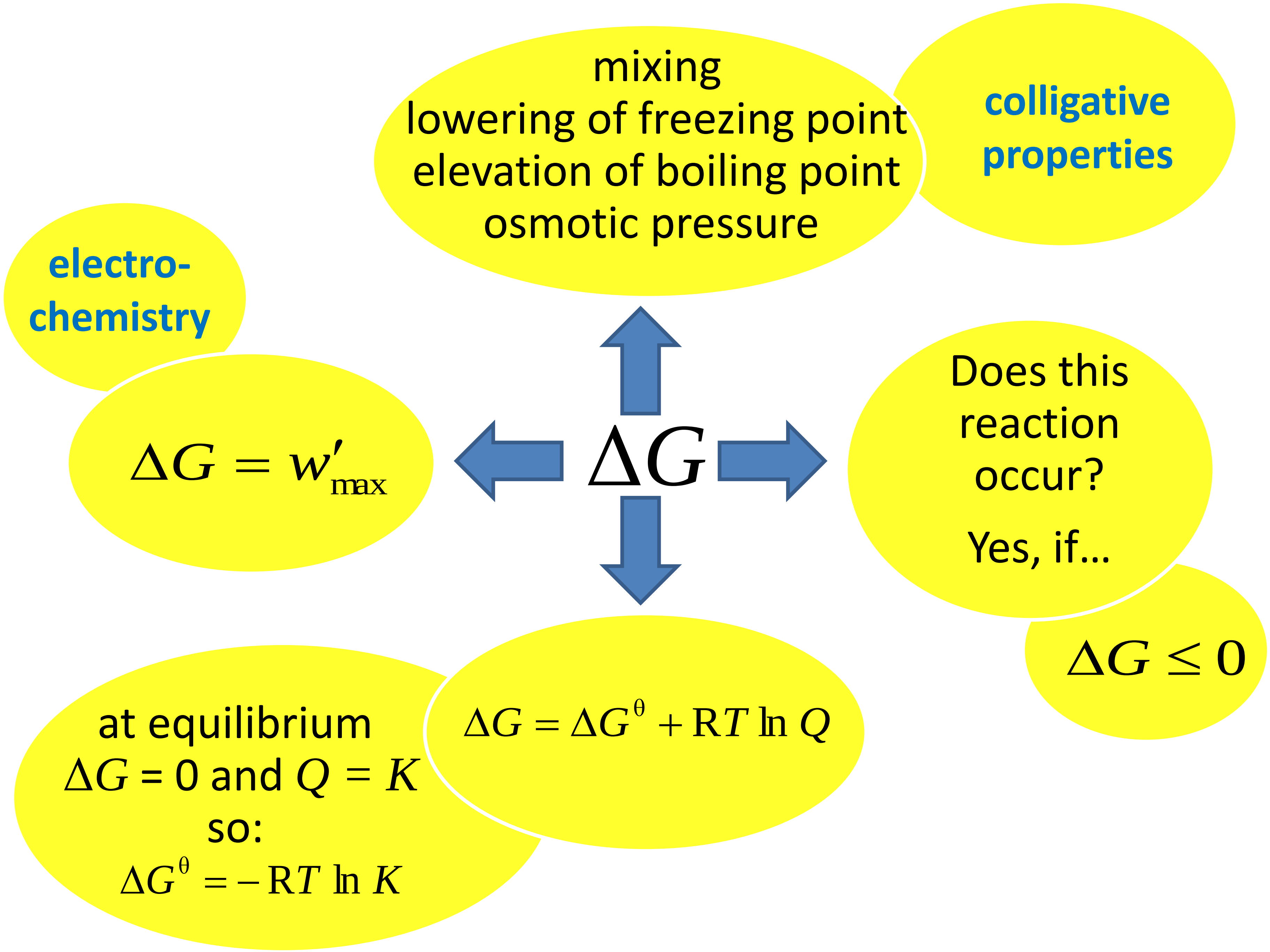
$Zn\ (s) + Cu^{2+} \rightarrow Cu\ (s) + Zn^{2+}$

$\Delta_r G_{total} = -15.3 \cdot 10^5\ \mathrm{J\,mol^{-1}} < 0$

$\Delta_r G = -2.1 \cdot 10^5\ \mathrm{J\,mol^{-1}} < 0$

$Zn^{2+} + Cu\ (s) \rightarrow Cu^{2+} + Zn\ (s)$

$\Delta_r G = +2.1 \cdot 10^5\ \mathrm{J\,mol^{-1}} > 0$



$$\Delta G$$

mixing
lowering of freezing point
elevation of boiling point
osmotic pressure

**colligative properties**

Does this reaction occur?

Yes, if…

$$\Delta G \leq 0$$

$$\Delta G = \Delta G^{\theta} + \mathrm{R}T \ln Q$$

at equilibrium
$\Delta G$ = 0 and $Q$ = $K$
so:

$$\Delta G^{\theta} = -\mathrm{R}T \ln K$$

$$\Delta G = w'_{\mathrm{max}}$$

**electro-chemistry**

# Activity instead of concentration

- Activity (symbol a) is a measure of the *"effective concentration"* of a species in a mixture

- The difference between activity and other measures of composition arises because molecules in non-ideal gases or solutions **interact** with each other, either to attract or to repel each other.

  i.e ion – ion and ion – water interactions

- Used to explain discrepancies between **ideal** solutions and **real** solutions (same for mixtures of gases)

- Activity of a **gas**: use the ratio of the effective pressure to the standard state pressure

$$a_{gas} = \frac{P}{P^{\theta}}$$

$a_{gas}$ *is a ratio with* ***no units.***

- Activity of a **solute in solution**: use ratio of effective concentration to the standard state of solute concentration ($C^{\theta}$ = 1 mole solute / kg solvent = 1 molal):

$$a_{solute} = \frac{C}{C^{\theta}}$$

$a_{solute}$ is a ratio with **no units.**

- The activity of **pure substances** in condensed phases (solid or liquids): $a = 1$

- **Relation** between activity and concentration: $a = \gamma\,[\text{compound}]$

$\gamma$: *activity coefficient*

- The **lower the concentration** of all solute particles in the solution, the closer the value of $\gamma$ for each solute approaches 1, resulting in the approximation: $a = [\text{compound}]$

## Question 1

a) Equilibrium: $\Delta_r G = \Delta_r G^{\ominus}_{298K} + RT \ln K = 0 \quad \Rightarrow \quad \Delta_r G^{\ominus}_{298K} = -RT \ln K$

$\ln K = \Delta_r G^{\ominus}_{298K} / (-RT) = (-68.3 \cdot 10^3) / (-8.3145 \cdot 298) = 27.565$

$K = 9.4 \cdot 10^{11}$ (at **298 K**)

b) We assume that $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ are temperature-independent: $\Delta_r H^{\ominus}_{400K} = \Delta_r H^{\ominus}_{298K} \quad \Rightarrow$

$\Delta_r G^{\ominus}_{400K} = \Delta_r H^{\ominus}_{298K} - T\Delta_r S^{\ominus}_{298K} = -63.99 \cdot 10^3 - (400 \cdot 14.4) = -69.75 \cdot 10^3$ J/mol

Equilibrium: $\Delta_r G = \Delta_r G^{\ominus}_{400K} + RT \ln K = 0 \quad \Rightarrow \quad \Delta_r G^{\ominus}_{400K} = -RT \ln K$

$\ln K = \Delta_r G^{\ominus}_{400K} / (-RT) = (-69.75 \cdot 10^3) / (-8.3145 \cdot 400) = 20.97$

$K = 1.3 \cdot 10^{9}$ (at **400 K**)

## Question 2

| **molefraction $x$** | **HI** | **$H_2$** | **$I_2$** |
|---|---|---|---|
| start | 1.00 | 0 | 0 |
| change | -0.228 | +0.114 | +0.114 |
| equilibrium | 0.772 | +0.114 | +0.114 |

a) Equilibrium, so $\Delta_r G = 0$

b) $$K = \frac{\frac{p_{H_2}}{p^{\theta}} \cdot \frac{p_{I_2}}{p^{\theta}}}{\left(\frac{p_{HI}}{p^{\theta}}\right)^2} = \frac{x_{H_2} \cdot x_{I_2}}{(x_{HI})^2} = \frac{0.114 \cdot 0.114}{(0.772)^2} = 0.0218$$

c) Equilibrium: $\Delta_r G = \Delta_r G^{\ominus} + RT \ln K = 0 \quad \Rightarrow \quad \Delta_r G^{\ominus} = -RT \ln K$

$\Delta_r G^{\ominus} = -8.3145 \cdot 1000 \cdot \ln 0.0218 = 31.8$ kJ/mol

## Question 3

a) $Q = \frac{\frac{p_{N_2O_4}}{p^\theta}}{\left(\frac{p_{NO_2}}{p^\theta}\right)^2} = \frac{\frac{2.0}{1.0}}{\left(\frac{6.0}{1.0}\right)^2} = 0.0566$

$\Delta_r G = \Delta_r G^\ominus{}_{298K} + RT \ln Q$

$\Delta_r G = -4.73 \cdot 10^3 + 8.3145 \cdot 298 \cdot \ln 0.0566 = -11.89 \cdot 10^3$ J/mol

b) $\Delta_r G$ is negative, no equilibrium, reaction proceeds spontaneously to the right.

## Question 4

Assumptions:

- $\Delta_r H^\ominus$ is independent of temperature
- $\Delta_r S^\ominus$ is independent of temperature
- Decomposition starts when $K = Q = 1$
- Decomposition starts when $\Delta_r G = 0$

$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$

$0 = \Delta_r G^\ominus + 0 \quad => \quad \Delta_r G^\ominus = 0$

$\Delta_r G^\ominus = \Delta_r H^\ominus_{298K} - T\Delta_r S^\ominus_{298K} \quad => \quad \Delta_r H^\ominus_{298K} = T\Delta_r S^\ominus_{298K}$

$$T = \frac{\Delta_r H^\ominus_{298K}}{\Delta_r S^\ominus_{298K}} = \frac{299 \cdot 10^3}{753} = 397\ K$$