

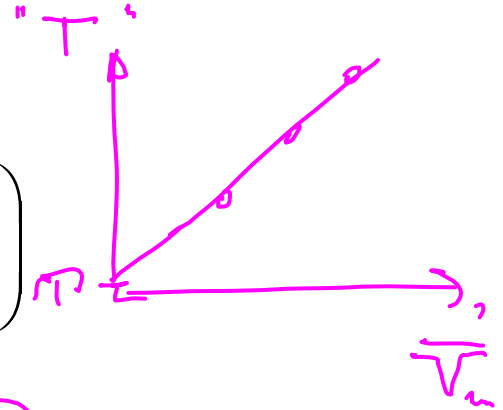
Beschikbare Arbeid

Samenvatting Thermometrie

- 0^{de} hoofdwet: Thermisch evenwicht: thermometer

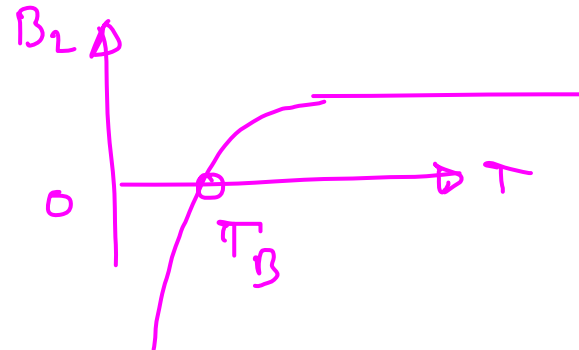
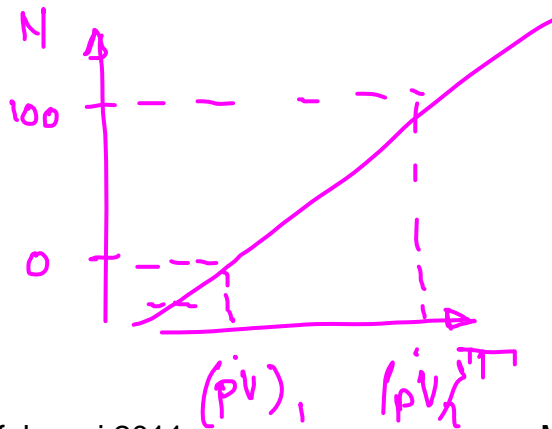
- Niet-ideale gassen

$$p = \frac{RT}{V_m} \left(1 + \frac{B_2}{V_m} + \frac{B_3}{V_m^2} + \dots \right)$$



- te gebruiken als thermometer

$$T = \lim_{V_m \rightarrow \infty} \frac{pV_m}{R}$$



Samenvatting Spontane Processen (1)

2^{de} hoofdwet: processen met

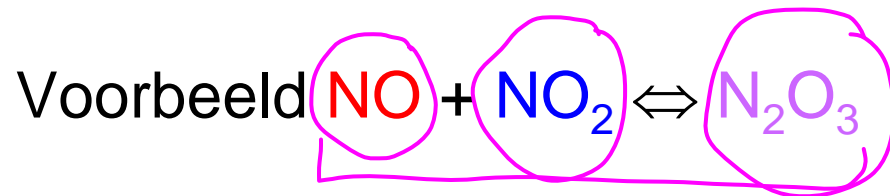
- $\Delta G < 0$: kunnen spontaan verlopen
- $\Delta G = 0$: zijn in (thermodynamisch) evenwicht
- $\Delta G > 0$: kunnen niet verlopen

Samenvatting Spontane Processen (2)

Berekening ΔG

- Additiviteitsregel $\Delta G = \sum_{j=1}^n \beta_j \Delta_f G^\circ_{B_j} - \sum_{j=1}^n \alpha_j \Delta_f G^\circ_{A_j}$
- Temperatuurafwijkingen $\Delta_f G(T, p^\circ) \approx \Delta_f G^\circ(T^\circ, p^\circ) - (T - T^\circ)S^\circ$
- Drukafwijkingen $\Delta_f G(p, T^\circ) \approx \Delta_f G^\circ(p^\circ, T^\circ) + (p - p^\circ)V_m$
 - voor gassen $\Delta_f G_{\text{gas}}(p, T^\circ) \approx \Delta_f G^\circ_{\text{gas}}(p^\circ, T^\circ) + RT^\circ \ln\left(\frac{p}{p^\circ}\right)$
- Mengsels $\Delta_f G_{B \subset A} \approx (1-x)\Delta_f G_A + x\Delta_f G_B + RT\{(1-x)\ln(1-x) + x\ln x\}$

Reactievoortgang



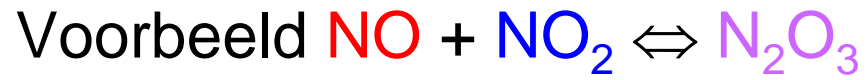
Stoichiometrische coefficients

$$\begin{pmatrix} v_{\text{NO}} \\ v_{\text{NO}_2} \\ v_{\text{N}_2\text{O}_3} \end{pmatrix} = \begin{pmatrix} -1 \\ -1 \\ 1 \end{pmatrix}$$

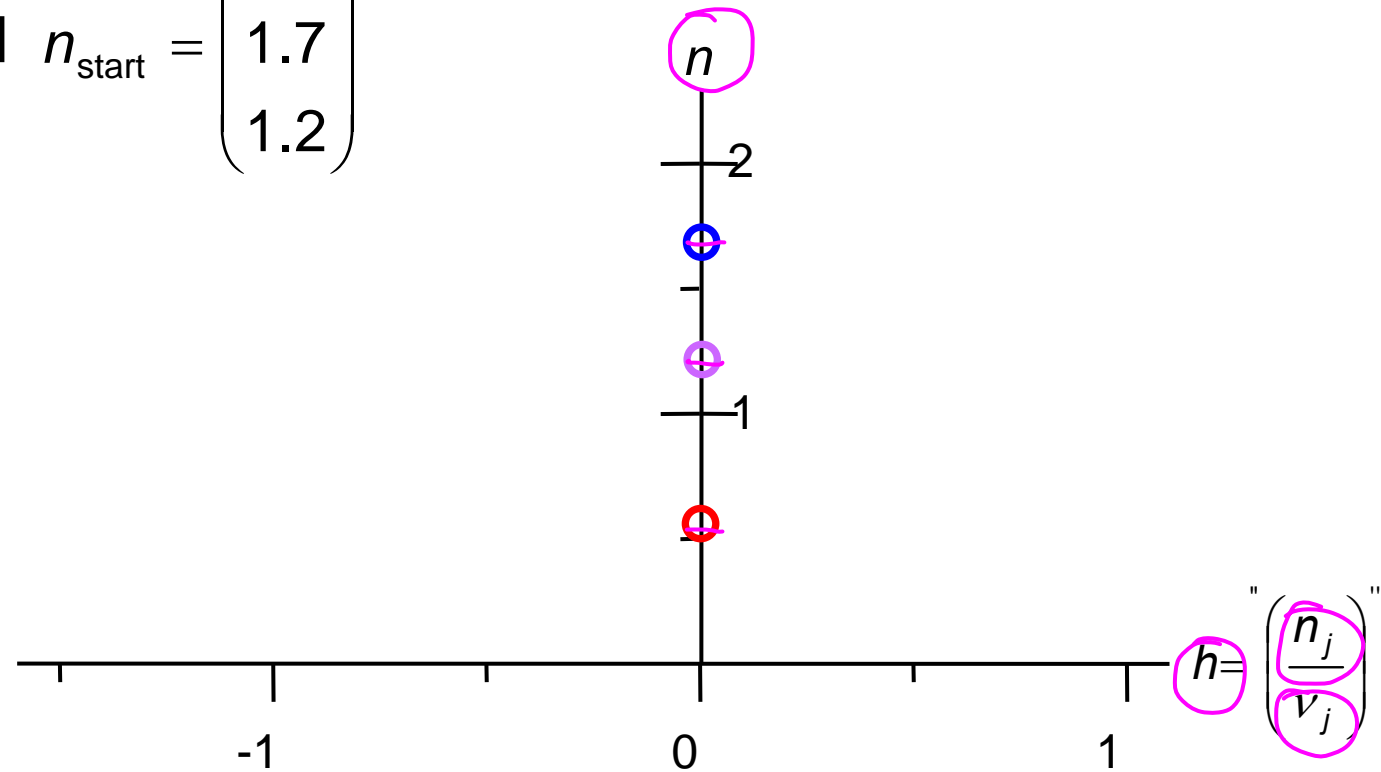
Begintoestand $\begin{pmatrix} n_{\text{NO}} \\ n_{\text{NO}_2} \\ n_{\text{N}_2\text{O}_3} \end{pmatrix} = \begin{pmatrix} 0.6 \\ 1.7 \\ 1.2 \end{pmatrix}$

(Handwritten annotations: a bracket under the vector and the word "start" next to the bottom element, and an arrow pointing to the bottom element of the vector.)

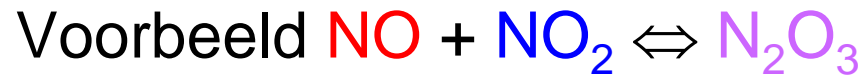
Reactievoortgang



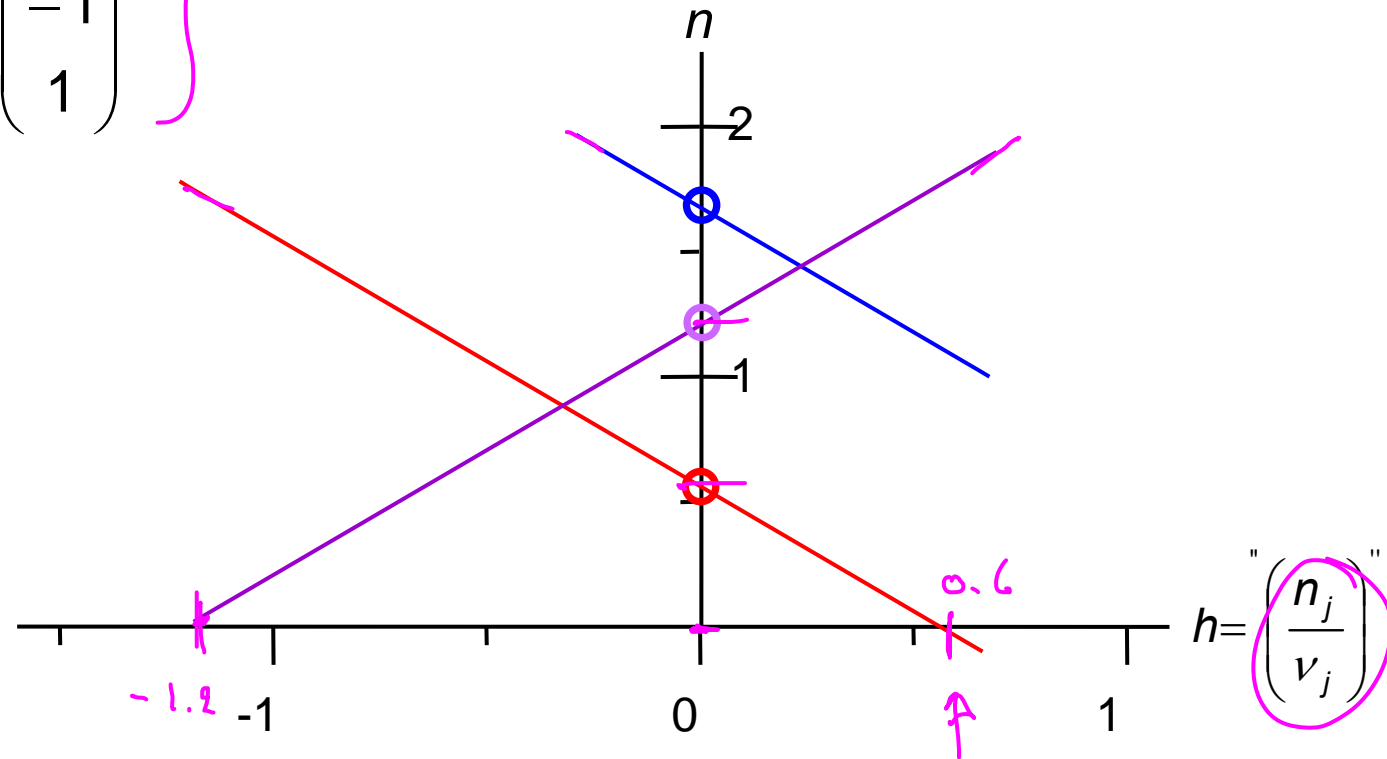
Begintoestand $n_{\text{start}} = \begin{pmatrix} 0.6 \\ 1.7 \\ 1.2 \end{pmatrix}$



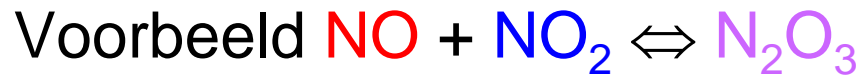
Reactievoortgang



Hellingen $\nu = \begin{pmatrix} -1 \\ -1 \\ 1 \end{pmatrix}$



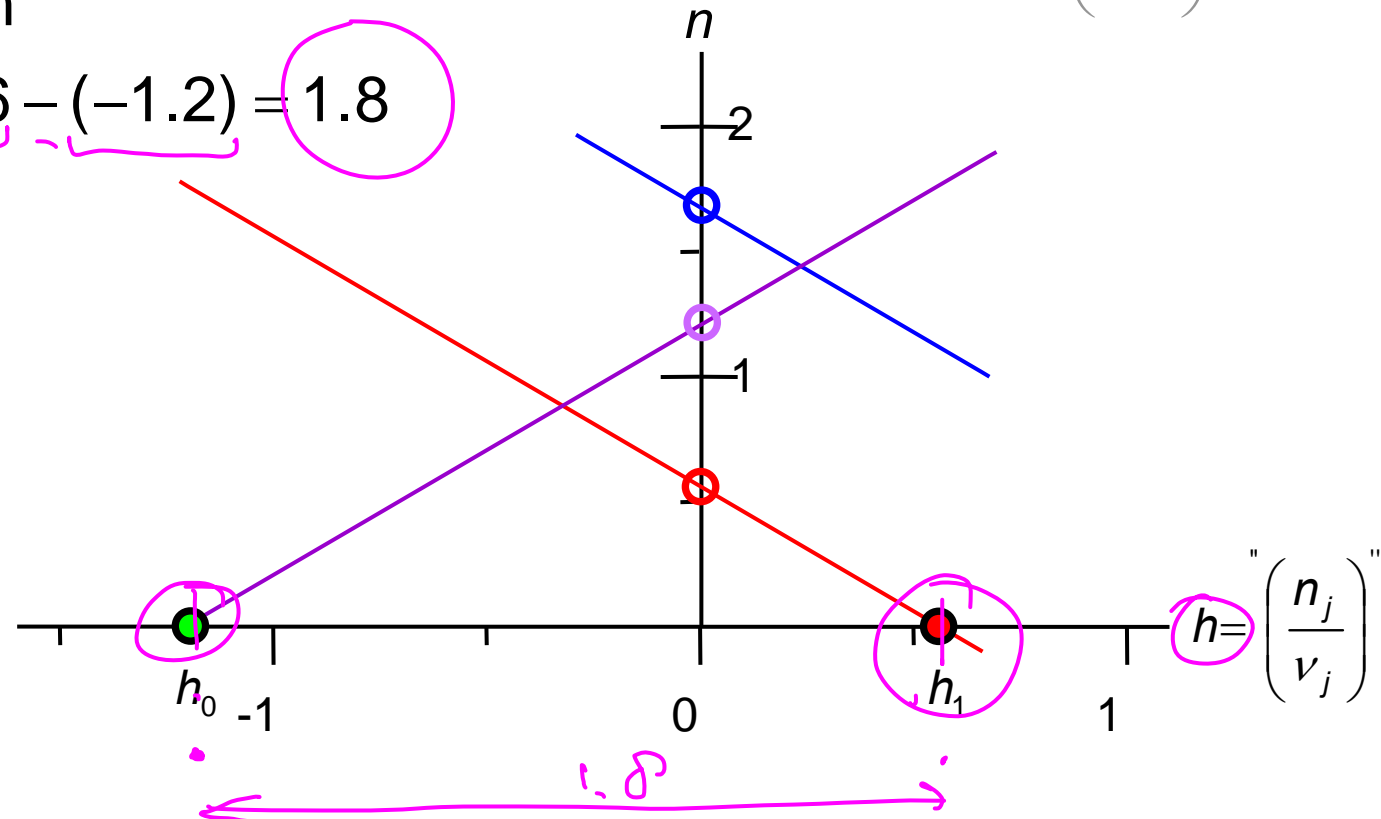
Reactievoortgang



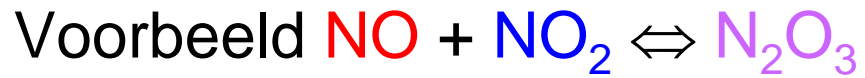
$$n_{\text{start}} = \begin{pmatrix} 0.6 \\ 1.7 \\ 1.2 \end{pmatrix}$$

Asafsnijdingen

$$h_1 - h_0 = 0.6 - (-1.2) = 1.8$$



Reactievoortgang

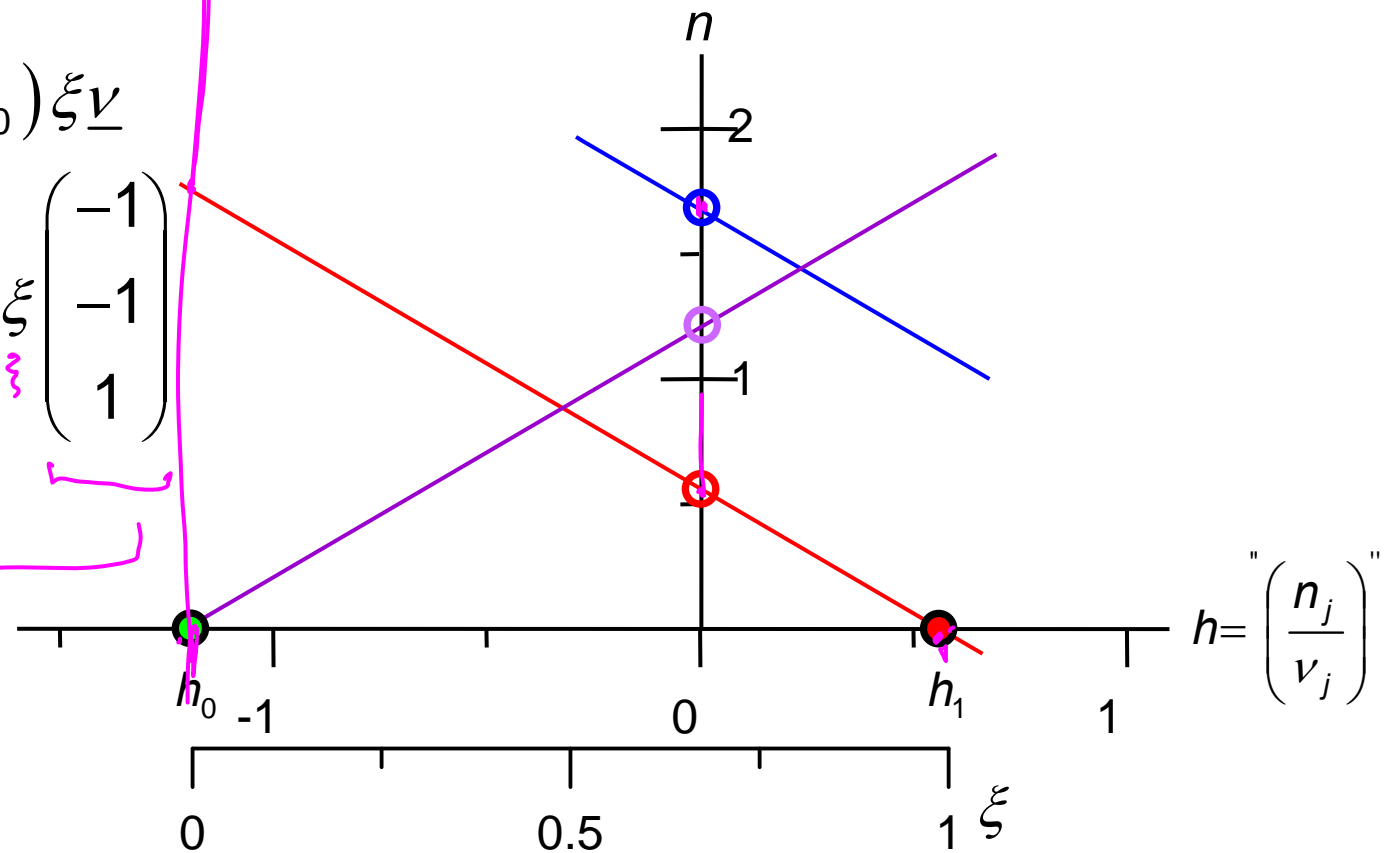


Mol-aantallen

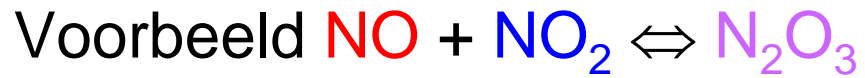
$$\underline{n} = \underline{n}_0 + (h_1 - h_0) \xi \underline{v}$$

$$= \begin{pmatrix} 1.8 \\ 2.0 \\ 0 \end{pmatrix} + 1.8 \xi \begin{pmatrix} -1 \\ -1 \\ 1 \end{pmatrix}$$

(Handwritten annotations: 1.8 and 2.0 are circled in pink. A pink arrow points from 1.8 to the coefficient of the stoichiometric vector. A pink bracket underlines the entire equation.)



Reactievoortgang



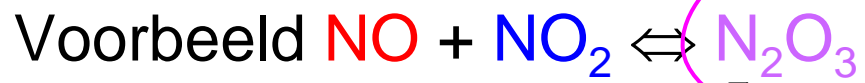
Gibbs energie

$$\Delta_r G(T, p^\ominus) = \underbrace{n}_{\text{circled}} \left\{ \underbrace{\Delta_f \underline{G}^\ominus(T^\ominus, p^\ominus)}_{\text{circled}} - \underbrace{(T - T^\ominus) \underline{S}^\ominus}_{\text{circled}} - RT \ln \left(\frac{\underbrace{n}_{\text{circled}}}{\underbrace{\sum_j n_j}_{\text{circled}}} \right) \right\}$$

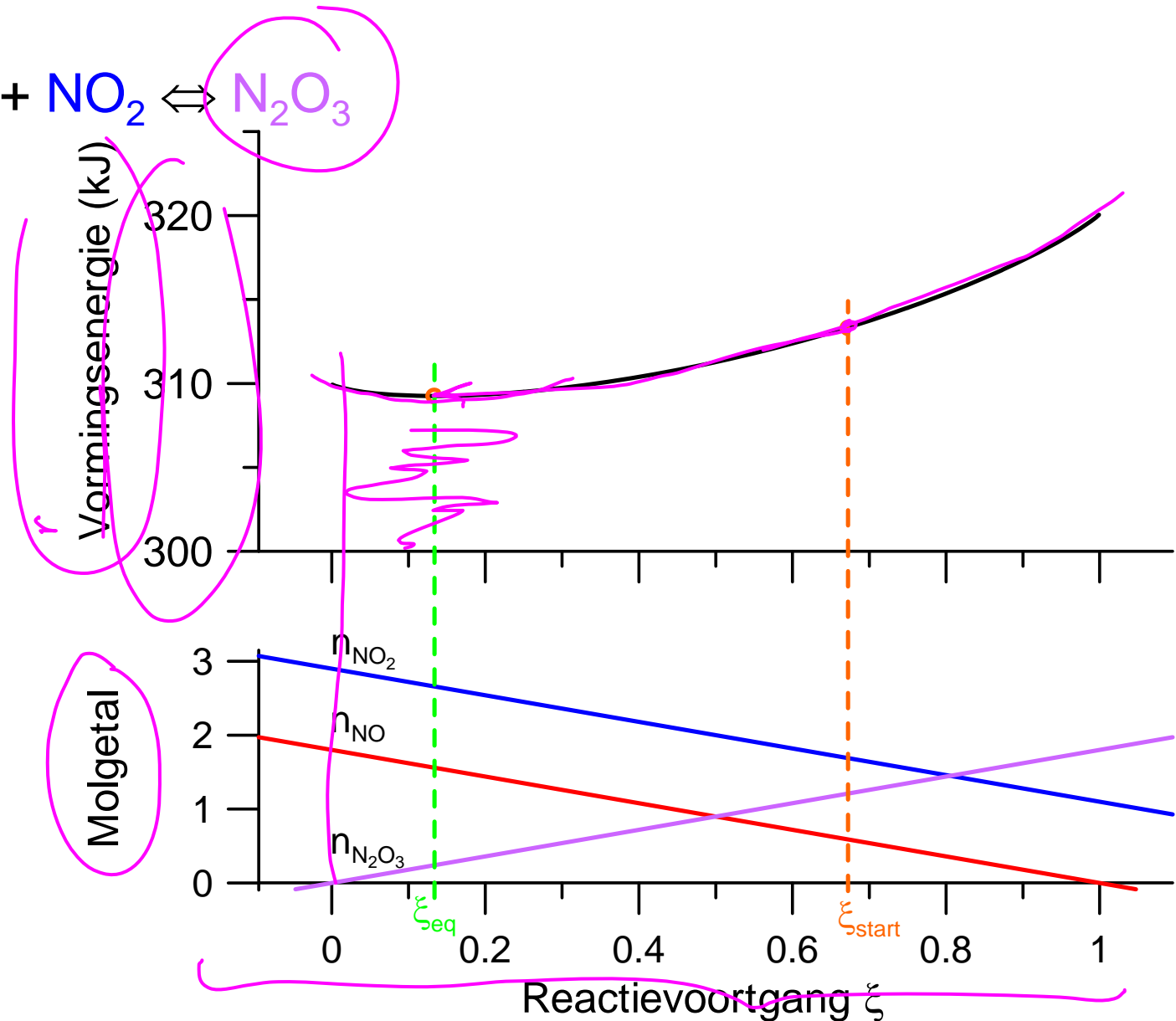
$-RT \ln \frac{P}{p^\ominus}$

$\begin{pmatrix} x_1 P \\ x_2 P \\ \vdots \\ x_n P \end{pmatrix}$

Reactievoortgang



Gibbs energie

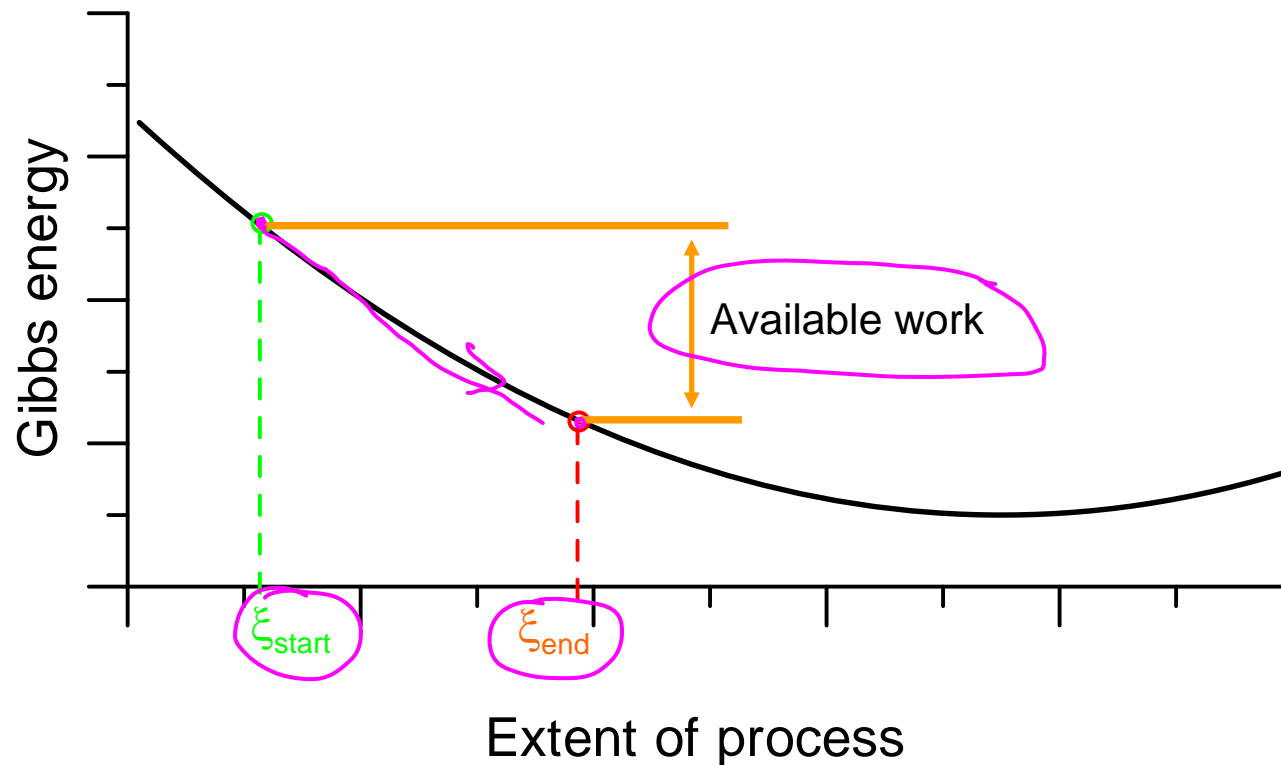


Gibbs energie = Beschikbare Arbeid

(Maximaal) beschikbare arbeid:

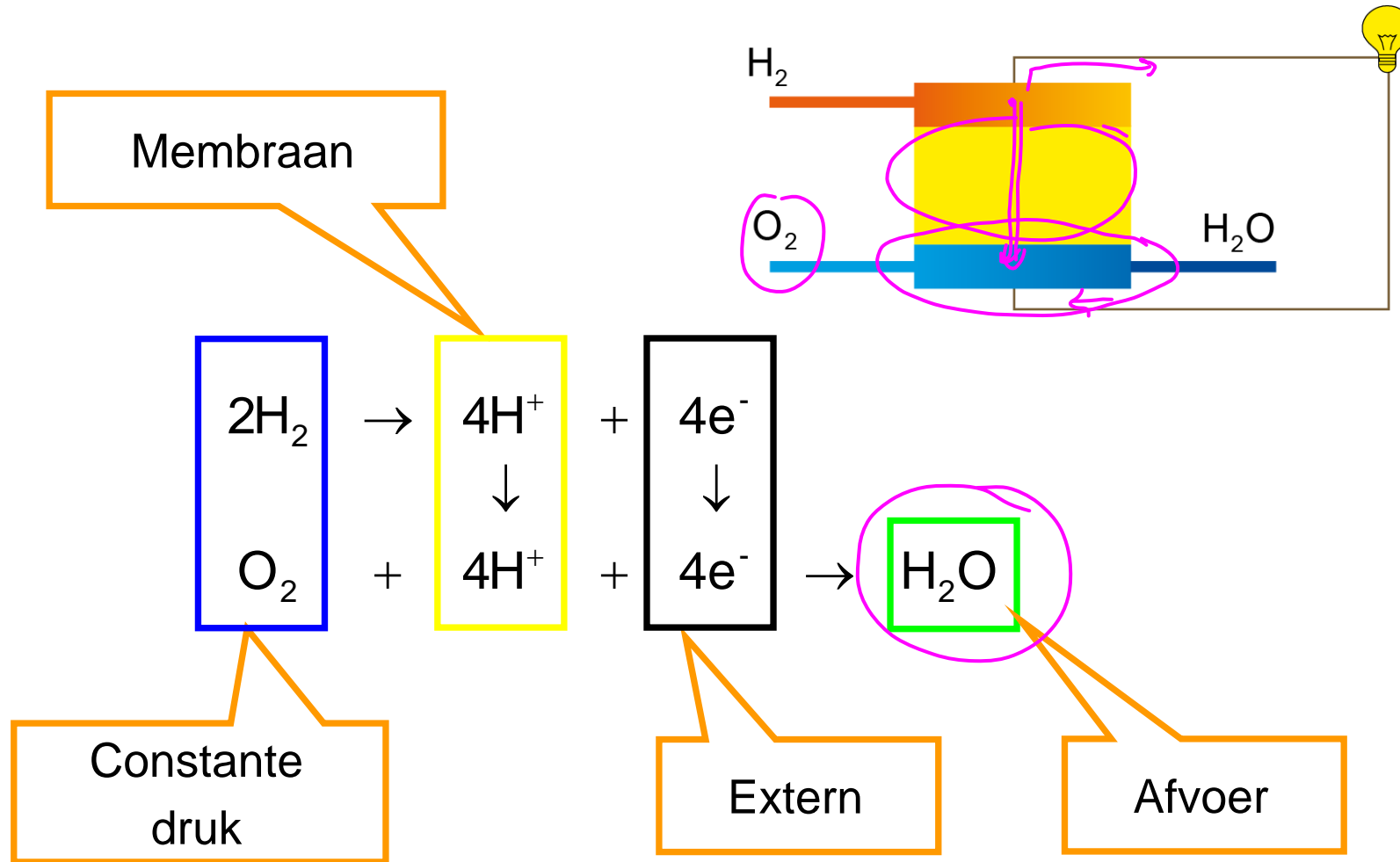
Mechanisch
Elektrisch
Straling
.....

Maar NIET warmte



Beschikbare Arbeid: brandstofcel

Massabalans



Beschikbare Arbeid: brandstofcel

Thermodynamica

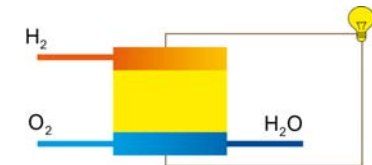
Name	$\Delta_f G^\ominus$ (J/mol)	S^\ominus (J/(Kmol))
H ₂		130.7
O ₂		205.2
H ₂ O	-228,572	188.8

Bij 85 °C en standaarddruk

$$\Delta_r G(358.15 \text{ K}, p^\ominus) = \begin{pmatrix} 0 \\ 0 \\ -228,572 \end{pmatrix} - 60 \begin{pmatrix} 130.7 \\ 205.2 \\ 188.8 \end{pmatrix} \cdot \begin{pmatrix} -1 \\ -\frac{1}{2} \\ 1 \end{pmatrix} \text{ J/mol}$$

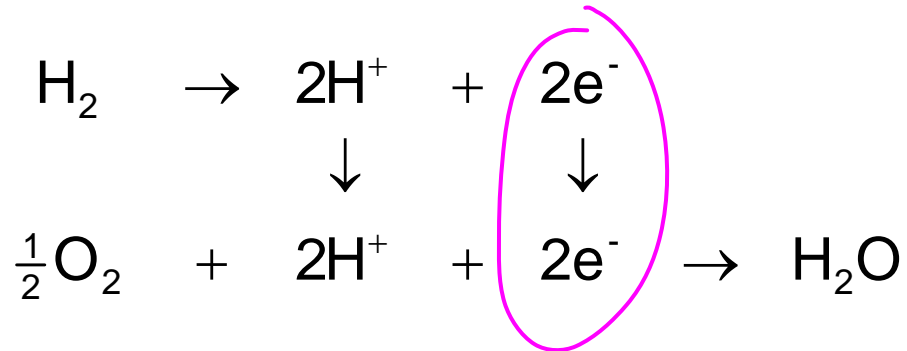
$$= -226 \text{ kJ/mol}$$

Beschikbare arbeid



Beschikbare Arbeid: brandstofcel

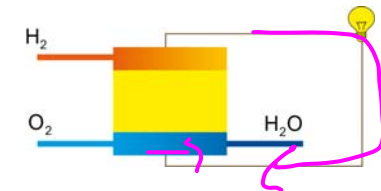
Stationaire reactievoortgang



Tijdsinterval Δt : omzetting $\Delta\xi$

- $\Delta\xi \text{ mol H}_2 + 0.5 \Delta\xi \text{ mol O}_2 \rightarrow \Delta\xi \text{ mol H}_2\text{O}$
- lading $\Delta Q = 2F\Delta\xi$ door extern circuit

Faraday = lading 1 mol elektronen
 $1 F = 96,485 \text{ C}$

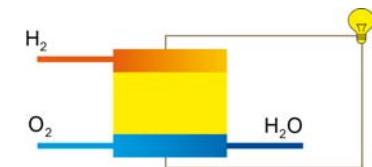


Beschikbare Arbeid: brandstofcel

Stationaire reactievoortgang

Omzetting per tijdseenheid, “reactiesnelheid” $\frac{d\xi}{dt} = \text{constant}$

Elektrische stroom $I = \frac{dQ}{dt} = \nu_e F \frac{d\xi}{dt} = \text{constant}$



Beschikbare Arbeid: brandstofcel

Stationaire reactievoortgang

Elektrische spanning

Geleverd elektrisch vermogen $P_{el} = EI = v_e E F \frac{d\xi}{dt} = \text{constant}$

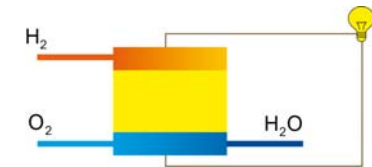
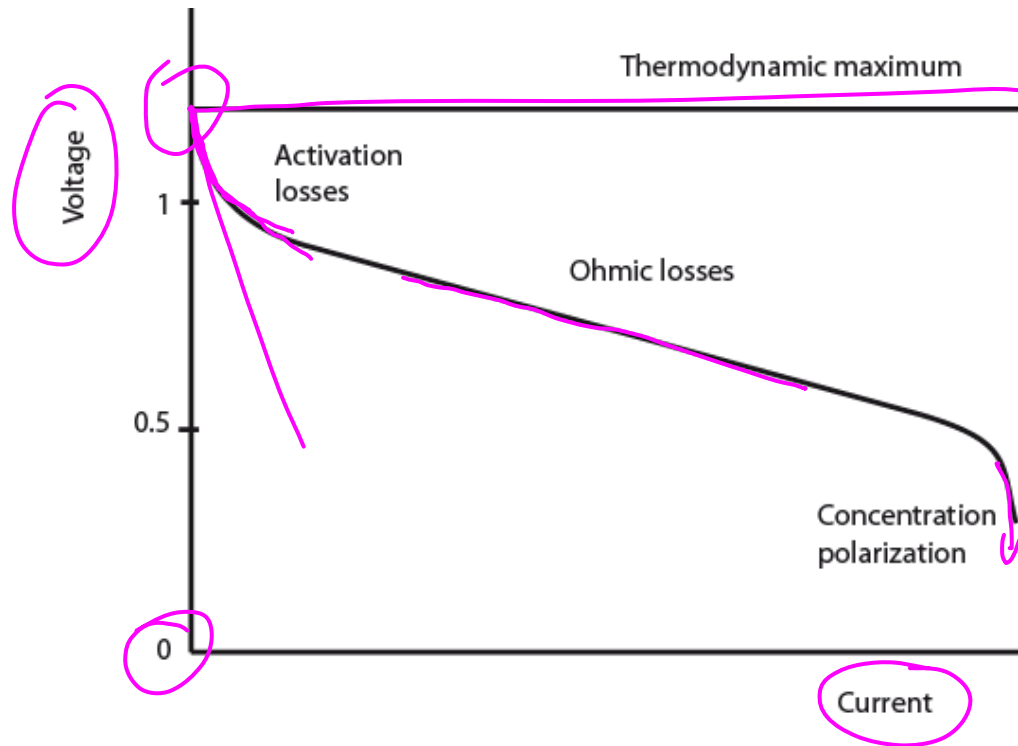
Geproduceerd chemisch vermogen $P_{chem} = \frac{d\Delta G}{dt} = \frac{d\xi}{dt} \Delta_r G$

2^{de} hoofdwet $P_{el} \leq P_{chem} \Rightarrow E \leq \frac{|\Delta_r G|}{v_e F} = \frac{226 \cdot 10^3}{2 \times 96485} \text{ V} = 1.17 \text{ V}$



Beschikbare Arbeit: brandstofcel

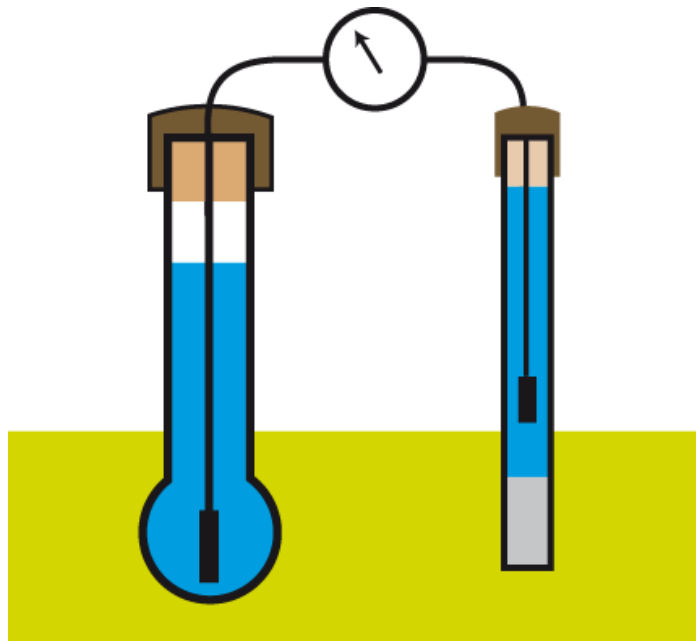
Standaard brandstofcel



Gibbs energie: elektrochemische cel

Elektrische spanning \Rightarrow maat voor chemische energie

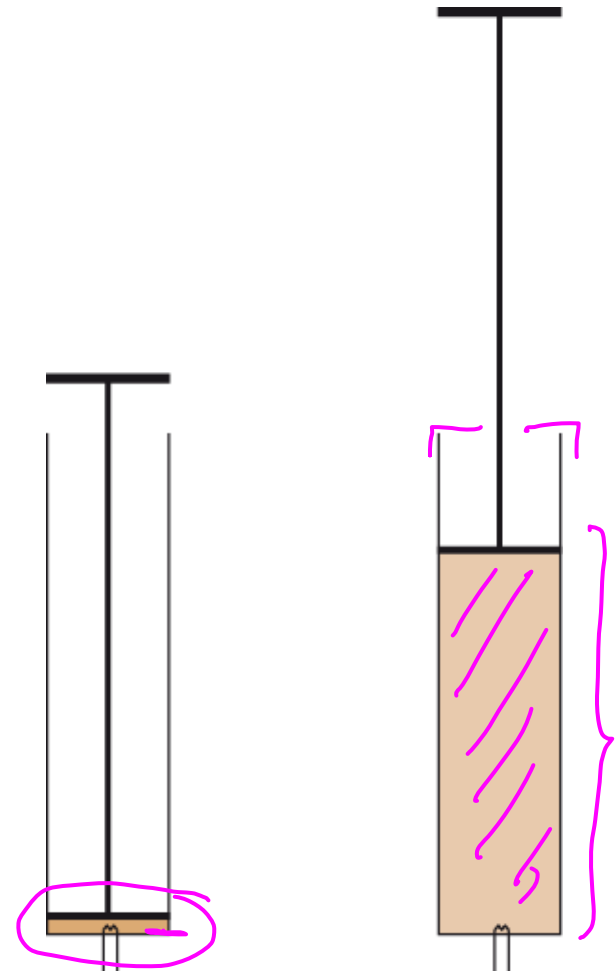
$$\Delta_r G = \lim_{I \rightarrow 0} v_e FE$$



Beschikbare Arbeid: buskruit

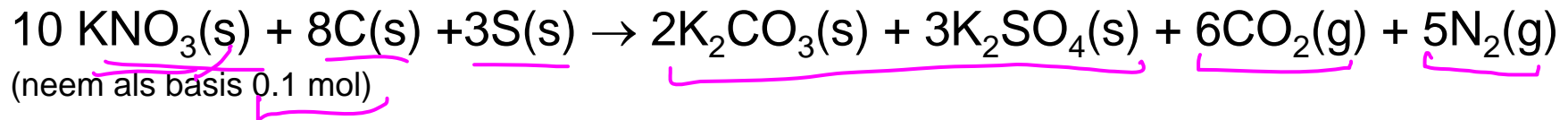
(Gedachten) experiment

- Fietspomp met bodempje buskruit
- Ontsteek buskruit
- Wacht tot afgekoeld
- Meet volumevergroting



Beschikbare Arbeid: buskruit

Reactie

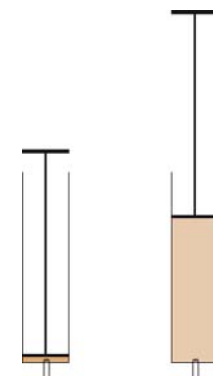


Bereken volumeverandering:

Na detonatie is er 1.1 mol gas bij STP geproduceerd

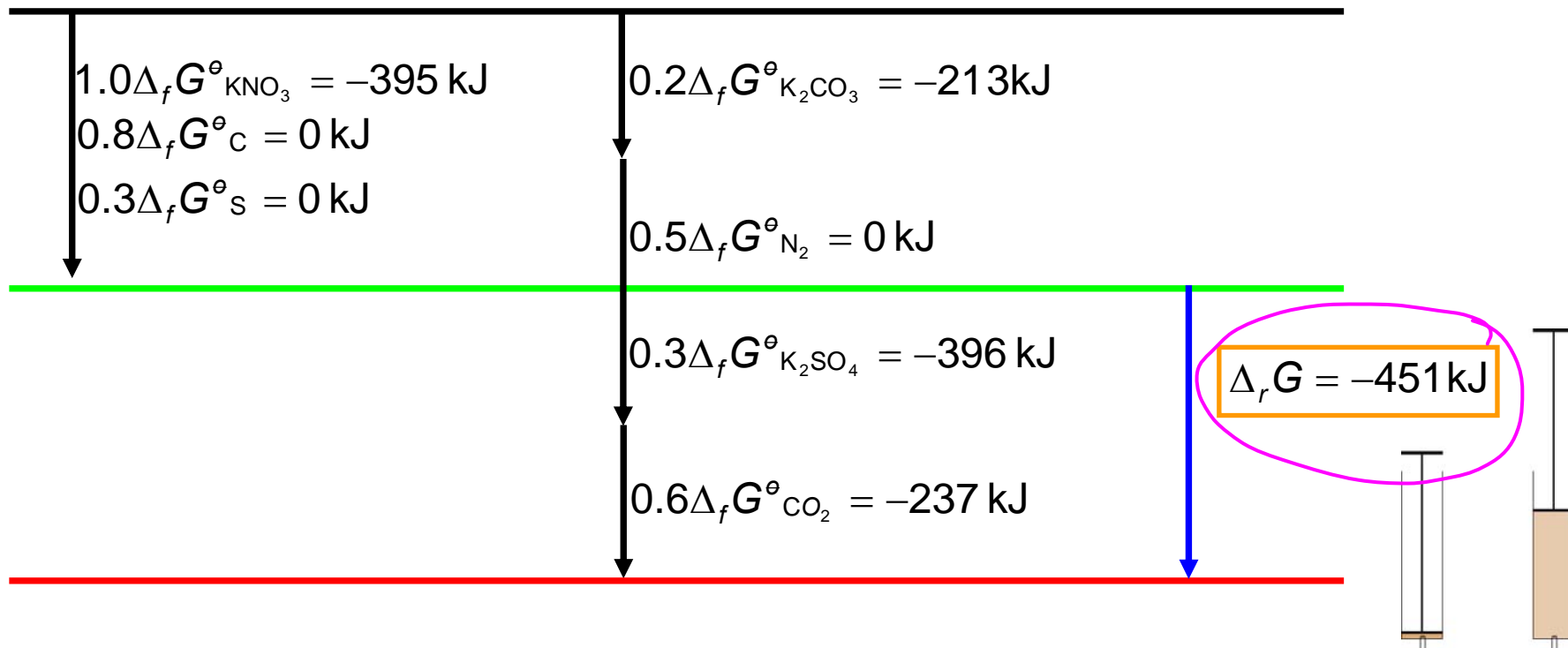
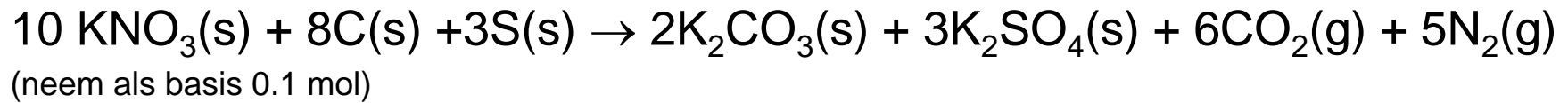
$$\text{Volumeverandering } \Delta V \approx \frac{nRT}{p} = \frac{1.1 \times 8.3 \times 298}{10^5} \approx 27 \text{ L}$$

$$\text{Geleverde arbeid } p\Delta V \approx 10^5 \times 27 \cdot 10^{-3} \text{ J} = 2.7 \text{ kJ}$$



Beschikbare Arbeid: buskruit

Reactie



Beschikbare Arbeid: buskruit

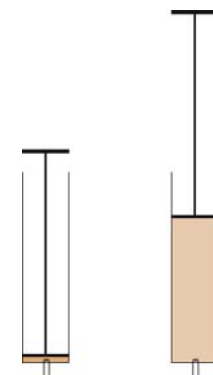
Samenvattend

Beschikbare arbeid: 451 kJ

Geleverde arbeid (na afkoeling): 2.7 kJ

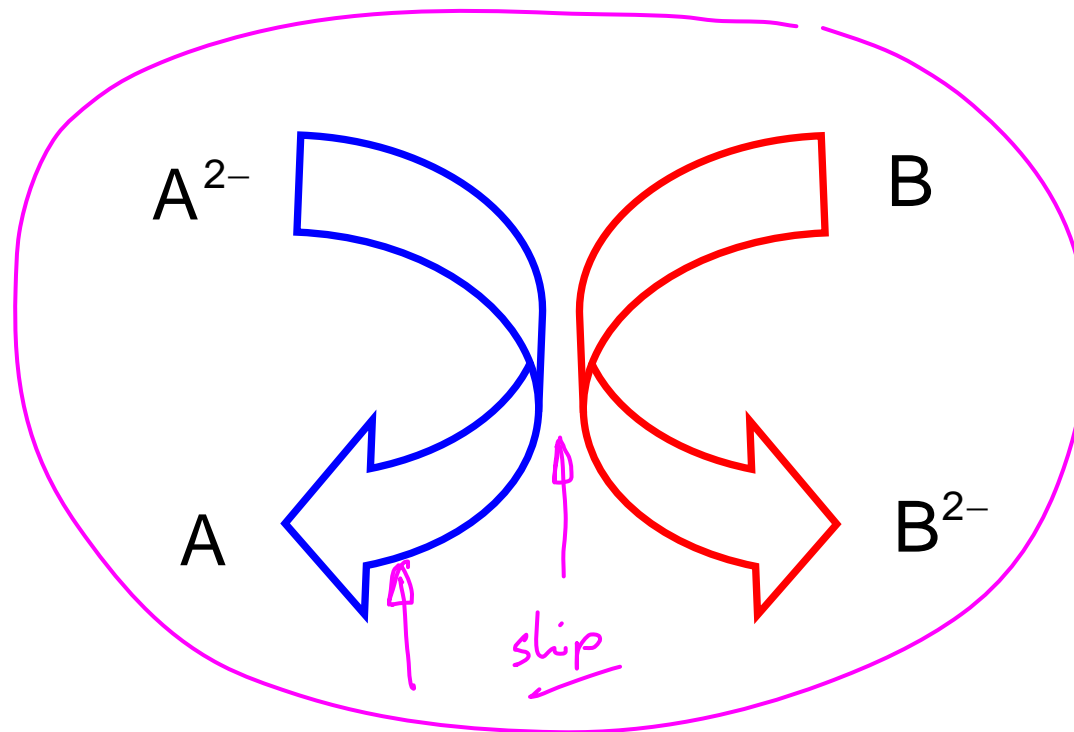
Rest is verloren gegaan geen efficiënt proces,

maar is dat alle arbeid die er uit te krijgen is ...?



Beschikbare Arbeid: gekoppelde reacties

Voorbeeld: Redox reactie

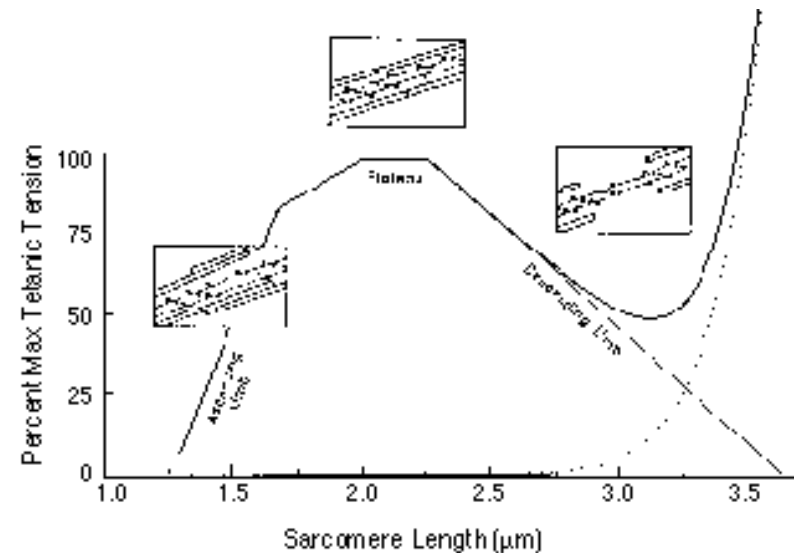


Totale Gibbs energie verschil: som van delen

Beschikbare Arbeid: spierkracht

Arbeid spier:

- Uitwijking sarcomeer 0.5 μm
- Spanning 46 N/mm²
- Schatting arbeid 10 $\mu\text{J}/\text{mm}^2$

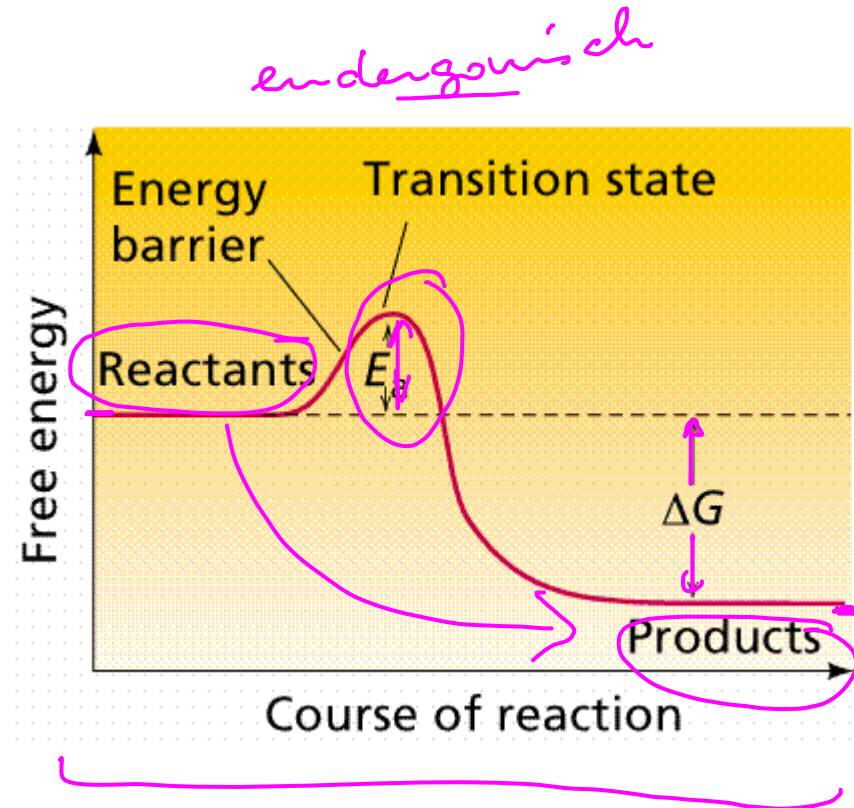
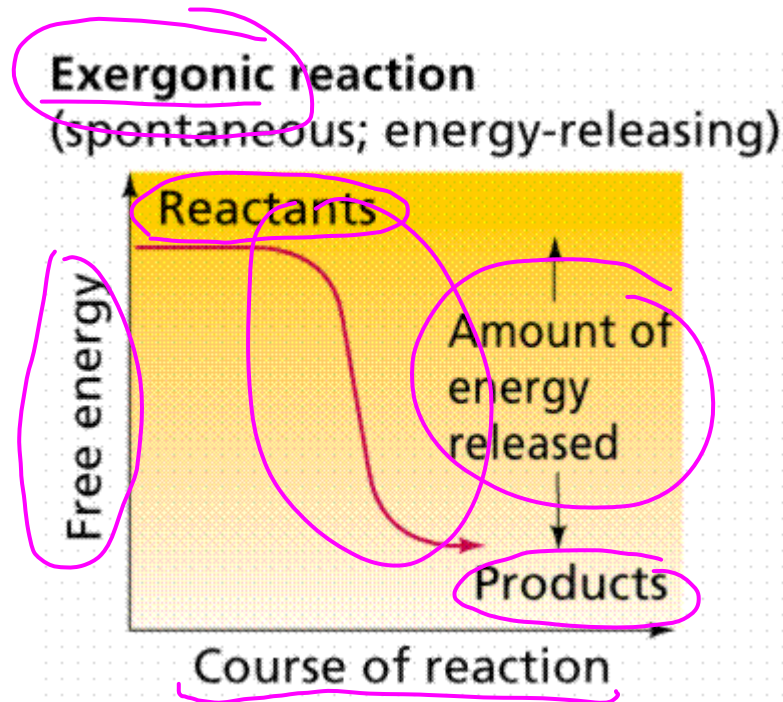


Bron: ATP \rightarrow ADP omzetting: $\Delta G \approx 3.4 \text{ kJ/mol}$

Minimaal benodigd $2 \cdot 10^{15}$ omzettingen / mm^2

Beschikbare Arbeit

Foutje op internet ...



Time-energy graphs of an exergonic reaction (top) and endergonic reaction (bottom). Images from Purves et al., Life: The Science of Biology, 4th Edition, by Sinauer Associates (www.sinauer.com) and WH Freeman (www.whfreeman.com), used with permission.