

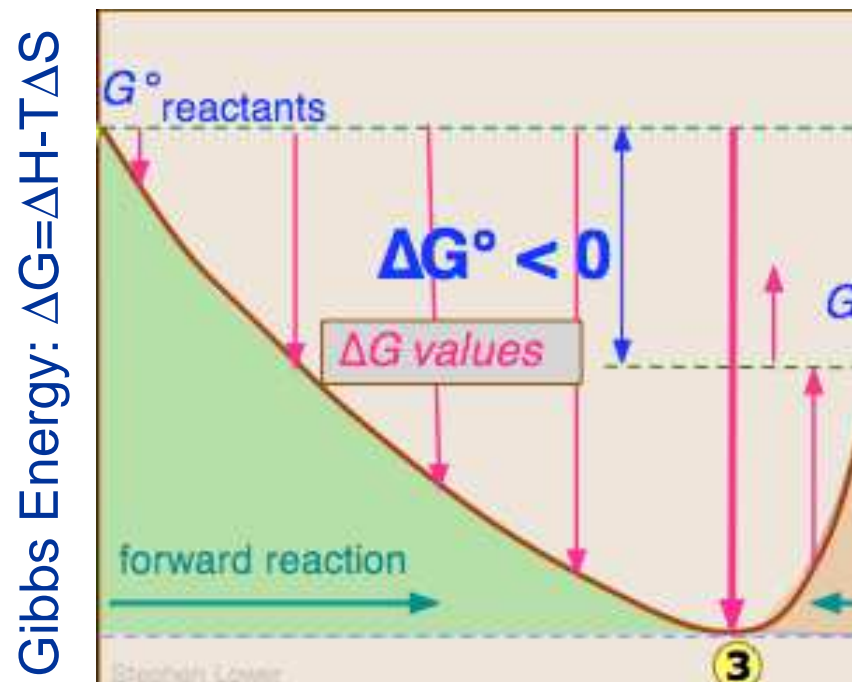
Inleiding Evenwichten

Chemisch evenwicht

Ammoniak synthese: $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$

- Bij welke compositie treedt evenwicht op?
- Hoe hangt dit van de druk en temperatuur af?

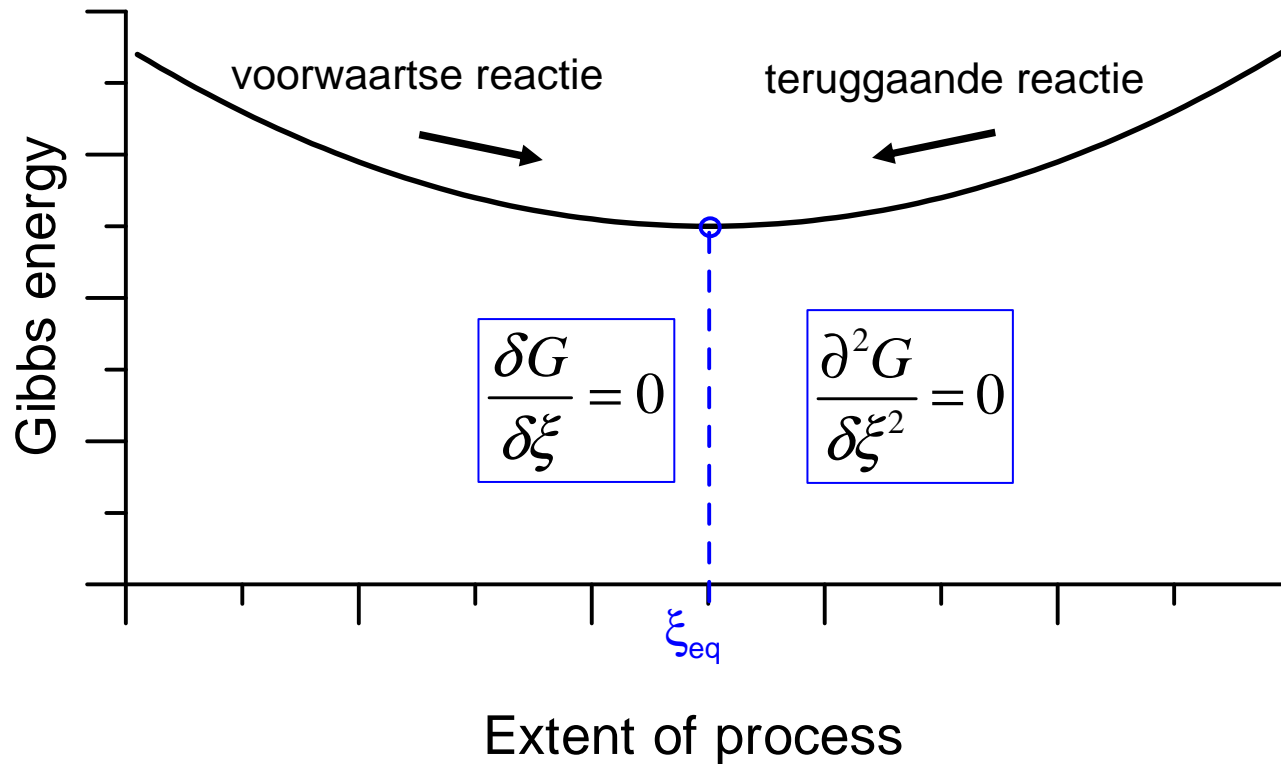
Exotherm
proces $\Rightarrow \Delta H^\circ$
is negatief



Niet alle stikstof
wordt omgezet

Chemisch evenwicht

Evenwicht bij een Gibbs energieminimum



Gibbs reactie-energie

Gibbs energie: $G = \sum_j n_j \mu_j$

Reactievoortgangspaarparameter: $n_j = n_j^o + \nu_j \xi$

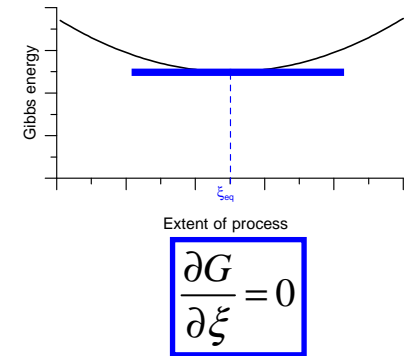
Helling van Gibbs energie:

$$\frac{\partial G}{\partial \xi} = \frac{\partial}{\partial \xi} \left[\sum_j n_j^o \mu_j + \sum_j \nu_j \mu_j \xi \right]$$

$$\frac{\partial G}{\partial \xi} = \sum_j \nu_j \mu_j \equiv \Delta_r G$$

Vergelijk met

- Gibbs energie-verschil $\Delta G = G_B - G_A = \sum_j \beta_j \mu_{j,B} - \sum_j \alpha_j \mu_{j,A}$
- Gibbs vormings-energie $\Delta_f G^\ominus = \Delta_r G^\ominus$



Gibbs reactie-energie

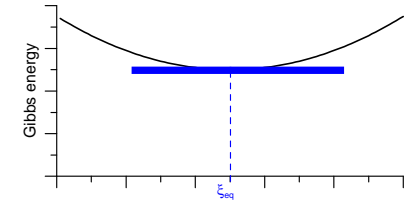
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$$\frac{\partial G}{\partial \xi} = \sum_j \nu_j \mu_j \equiv \Delta_r G$$



$$\frac{\partial G}{\partial \xi} = 0$$

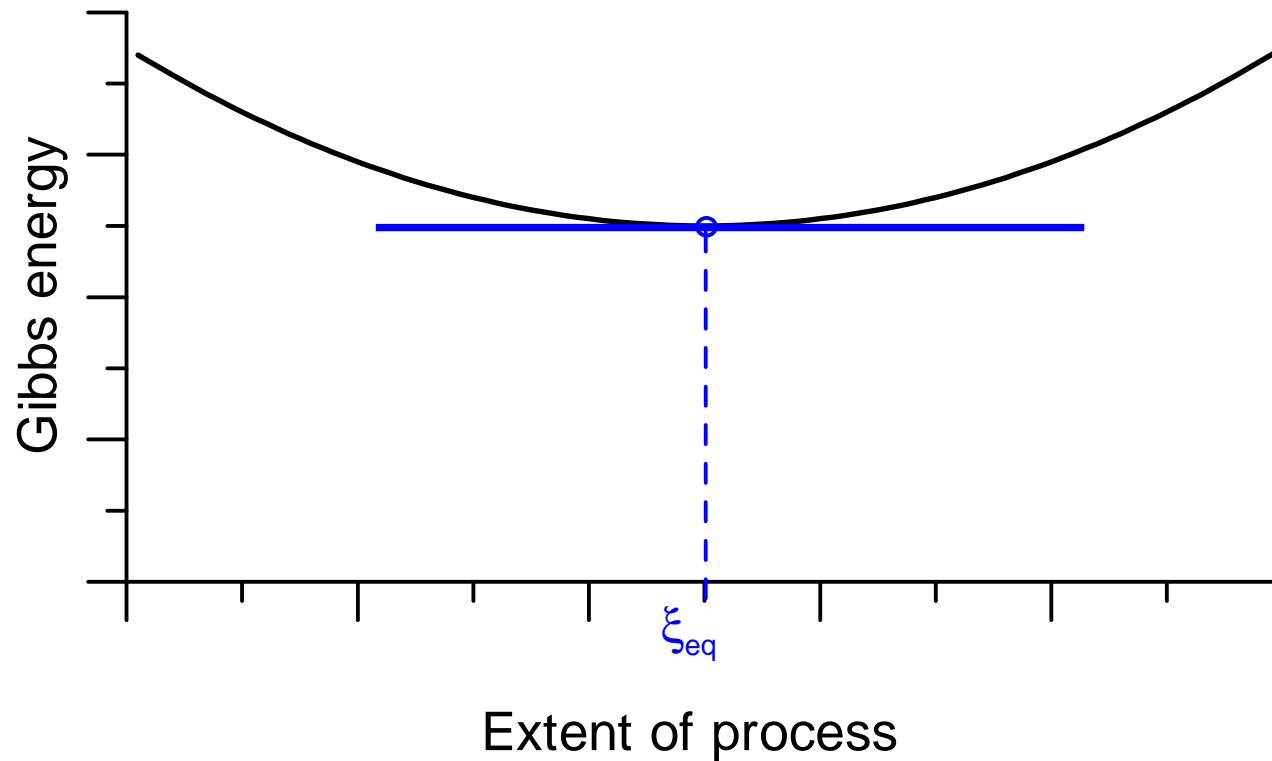


$$\frac{\partial G}{\partial \xi} = \sum_j \nu_j \mu_j = 2\mu_{NH_3} - 3\mu_{H_2} - \mu_{N_2} = \Delta_r G = 0$$

Chemisch evenwicht

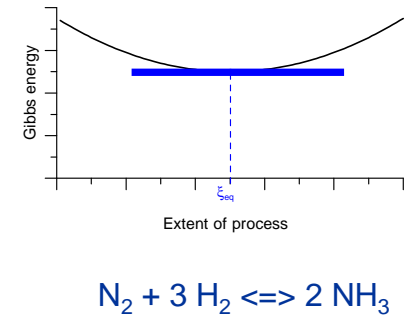
Evenwichtsvoorwaarde:

$$\left(\frac{\partial G}{\partial \xi}\right)_{\text{eq}} = 0 \quad \text{en} \quad \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{\text{eq}} > 0$$



Gassen

Evenwichtsvoorwaarde geeft $\frac{\partial G}{\partial \xi} = \sum_j \nu_j \mu_j \equiv \Delta_r G = 0$



Voor een verdund gas mengsel $\mu_j = \mu_j^\ominus + RT \ln \frac{p_j}{p^\ominus}$

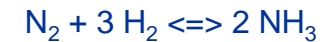
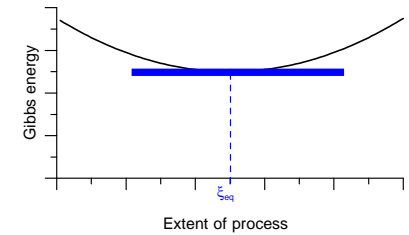
invullen geeft $\Delta_r G = \sum_j \nu_j \mu_j^\ominus + RT \sum_j \nu_j \ln \frac{p_j}{p^\ominus} = 0$

$$RT \sum_j \nu_j \ln \frac{p_j}{p^\ominus} = RT \left[\ln \left(\frac{p_1}{p^\ominus} \right)^{\nu_1} + \ln \left(\frac{p_2}{p^\ominus} \right)^{\nu_2} + \ln \left(\frac{p_2}{p^\ominus} \right)^{\nu_3} + \dots \right]$$

$$RT \sum_j \nu_j \ln \frac{p_j}{p^\ominus} = RT \ln \left[\prod_j \left(\frac{p_j}{p^\ominus} \right)^{\nu_j} \right] = RT \ln K$$

Gassen

$$\frac{\partial G}{\partial \xi} = \sum_j \nu_j \mu_j \equiv \Delta_r G = 0$$



$$\Delta_r G = \sum_j \nu_j \mu_j^\ominus + RT \sum_j \nu_j \ln \frac{p_j}{p^\ominus} = 0$$

$$\Delta_r G = \Delta_r G^\ominus + RT \sum_j \nu_j \ln \frac{p_j}{p^\ominus} = 0$$

$$\Delta_r G^\ominus = -RT \ln K$$

$$\prod_j \left(\frac{p_j}{p^\ominus} \right)^{\nu_j} = K = e^{-\Delta_r G^\ominus / (RT)}$$

Hangt niet af van druk
wel van temperatuur

Gibbs reactie-energie

Form	$\Delta_{f,298}G^\ominus$ (kJ/mol)	S_{298}^\ominus (J/(K mol))
N ₂	0	191.6
H ₂	0	130.7
NH ₃	-16.4	192.8
H ₂ O	-228.6	188.8

Vb: ammonia synthese: $\text{N}_2 + 3 \text{H}_2 \leftrightarrow 2 \text{NH}_3$

Bij 298 K:

$$\Delta G_r = \begin{pmatrix} -1 \\ -3 \\ +2 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ -16.4 \end{pmatrix} \text{ kJ/mol} = -32.8 \text{ kJ/mol}$$

$$-S = \left(\frac{\partial G}{\partial T} \right)_{p,n}$$

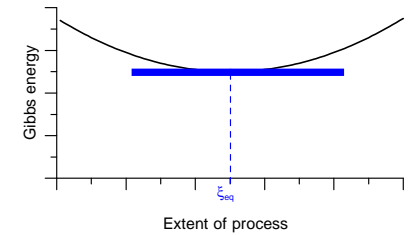
en bij 323 K:

$$\Delta G_r = \begin{pmatrix} -1 \\ -3 \\ +2 \end{pmatrix} \cdot \left[\begin{pmatrix} 0 \\ 0 \\ -16.4 \end{pmatrix} \times 1000 - (T - T^\circ) \begin{pmatrix} 191.6 \\ 130.7 \\ 193.8 \end{pmatrix} \right]$$

$$\Delta G_r = [(-32.8 \times 1000) - (25 \times -198.1)] = -27.9 \text{ kJ/mol}$$

Gassen: T-afhankelijkheid

Voorbeeld: ammonia synthese: $\text{N}_2 + 3 \text{H}_2 \leftrightarrow 2 \text{NH}_3$



Evenwichtsconstante $K = \frac{x_{\text{NH}_3}^2}{x_{\text{N}_2} x_{\text{H}_2}^3}$ voor $p = p^\ominus$

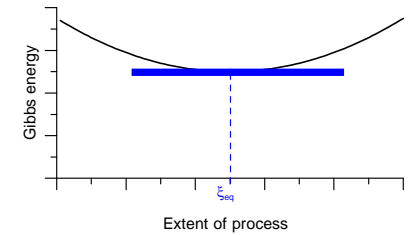
voor 298 K:
$$K_{298} = e^{-\frac{\Delta_r G^\ominus}{RT}} = e^{\frac{-32.8 \times 10^3}{8.3 \times 298}} = 5.7 \times 10^5$$

en voor 323 K:
$$K_{323} = e^{-\frac{\Delta_r G^\ominus}{RT}} = e^{\frac{-27.9 \times 10^3}{8.3 \times 323}} = 3.2 \times 10^4$$

Let op: volume verandert !

Gassen: p-afhankelijkheid

Voorbeeld: ammonia synthese: $\text{N}_2 + 3 \text{H}_2 \leftrightarrow 2 \text{NH}_3$



Als de totale druk $p \neq p^\ominus$ blijft K constant, echter:

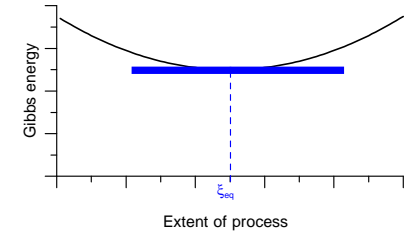
$$\prod_j \left(\frac{p_j}{p^\ominus} \right)^{\nu_j} = K = e^{-\Delta_r G^\ominus / (RT)}$$

$$K = \frac{\left(\frac{p_{\text{NH}_3}}{p^\ominus} \right)^2}{\left(\frac{p_{\text{N}_2}}{p^\ominus} \right) \left(\frac{p_{\text{H}_2}}{p^\ominus} \right)^3} = \frac{1}{\left(\frac{p}{p^\ominus} \right)^2} \frac{\left(\frac{p_{\text{NH}_3}}{p} \right)^2}{\left(\frac{p_{\text{N}_2}}{p} \right) \left(\frac{p_{\text{H}_2}}{p} \right)^3} = \left(\frac{p^\ominus}{p} \right)^2 \frac{x_{\text{NH}_3}^2}{x_{\text{N}_2} x_{\text{H}_2}^3}$$

Principe van Le Chatelier:

Een systeem dat uit evenwicht verstoord wordt reageert zodanig dat het evenwicht hersteld wordt.

Oplossingen



Evenwichtsvoorwaarde $\Delta_r G = 0$

Voor een verdunde oplossing $\mu_j = \mu_j^\ominus + RT \ln a_j \approx \mu_j^\ominus + RT \ln x_j$

invullen geeft
$$\Delta_r G = \sum_j \nu_j \mu_j^\ominus + RT \sum_j \nu_j \ln a_j = 0$$

$$\Delta_r G = \Delta_r G^\ominus + RT \sum_j \nu_j \ln a_j = 0$$

“activiteit”
 $\lim_{x \rightarrow 0} a_j = x_j$

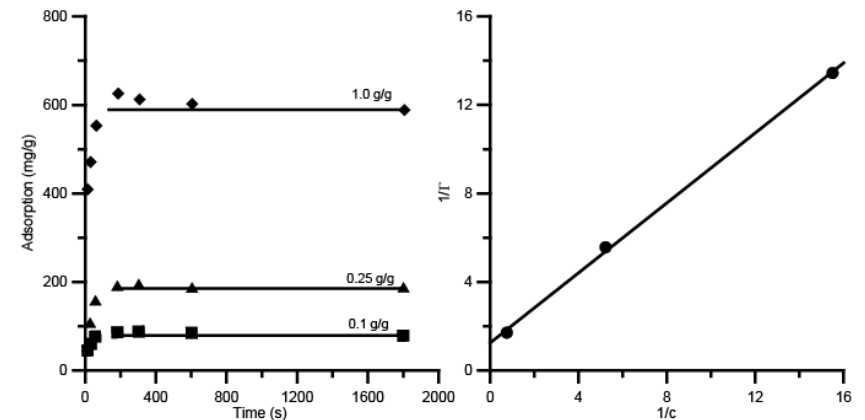
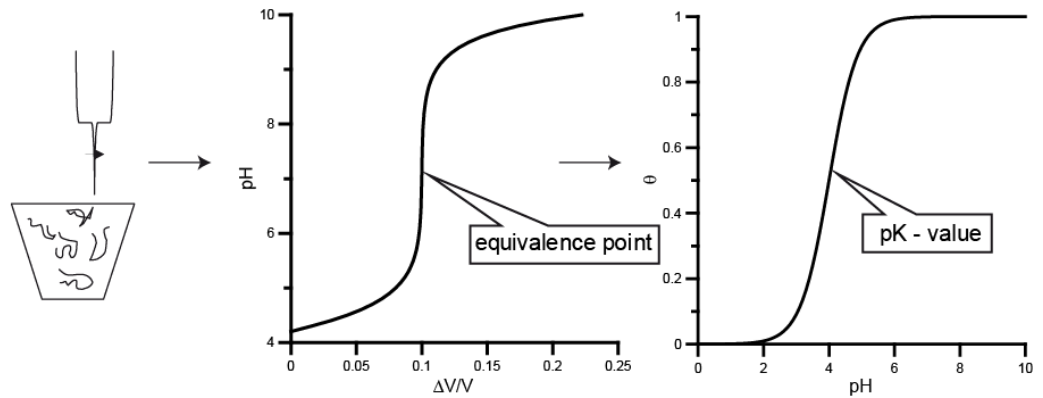
hieruit volgt voor de evenwichtsconstante

$$\prod_j a_j^{\nu_j} = K = e^{-\Delta_r G^\ominus / (RT)}$$

Oplossingen

Voorbeelden

- Oplosbaarheidsproducten
- Bindings-isothermen
– titratiecurves
- Adsorptie-isothermen
- Partitionering
- Associatie-evenwichten



Oplosbaarheidsproduct

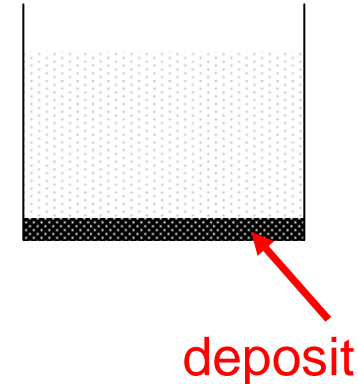
Voorbeeld $\text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \leftrightarrow \text{AgCl} (\text{s})$

Evenwichtsconstante

$$K = \frac{a(\text{Ag}^+)a(\text{Cl}^-)}{\cancel{a(\text{AgCl})}} \approx x_{\text{Ag}^+} x_{\text{Cl}^-} = x^2$$

“solubility”

$$s = \sqrt{K_{sp}} = \sqrt{1.77 \times 10^{-10}} \approx 1.33 \times 10^{-5}$$



Compound	Formula	K_{sp}
Radium iodate	$\text{Ra}(\text{IO}_3)_2$	$1.16 \cdot 10^{-9}$
Radium sulfate	RaSO_4	$3.66 \cdot 10^{-11}$
Rubidium perchlorate	RbClO_4	$3.00 \cdot 10^{-3}$
Scandium fluoride	ScF_3	$5.81 \cdot 10^{-24}$
Scandium hydroxide	$\text{Sc}(\text{OH})_3$	$2.22 \cdot 10^{-31}$
Silver(I) acetate	AgCH_3COO	$1.94 \cdot 10^{-3}$
Silver(I) arsenate	Ag_3AsO_4	$1.03 \cdot 10^{-22}$
Silver(I) bromate	AgBrO_3	$5.38 \cdot 10^{-5}$
Silver(I) bromide	AgBr	$5.35 \cdot 10^{-13}$
Silver(I) carbonate	Ag_2CO_3	$8.46 \cdot 10^{-12}$
Silver(I) chloride	AgCl	$1.77 \cdot 10^{-10}$
Silver(I) chromate	Ag_2CrO_4	$1.12 \cdot 10^{-12}$

Evenwichtsconstante: temperatuureffect

Evenwichtsconstante

$$\ln K = -\frac{\Delta_r G^\ominus}{RT}$$

Gibbs – Helmholtz relatie

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

Van 't Hoff relatie

$$\ln K = -\frac{\Delta_r H^\ominus}{R} \frac{1}{T} + \frac{\Delta_r S^\ominus}{R}$$



J. H. van 't Hoff (1852 – 1911)

Evenwichtsconstante: temperatuureffect

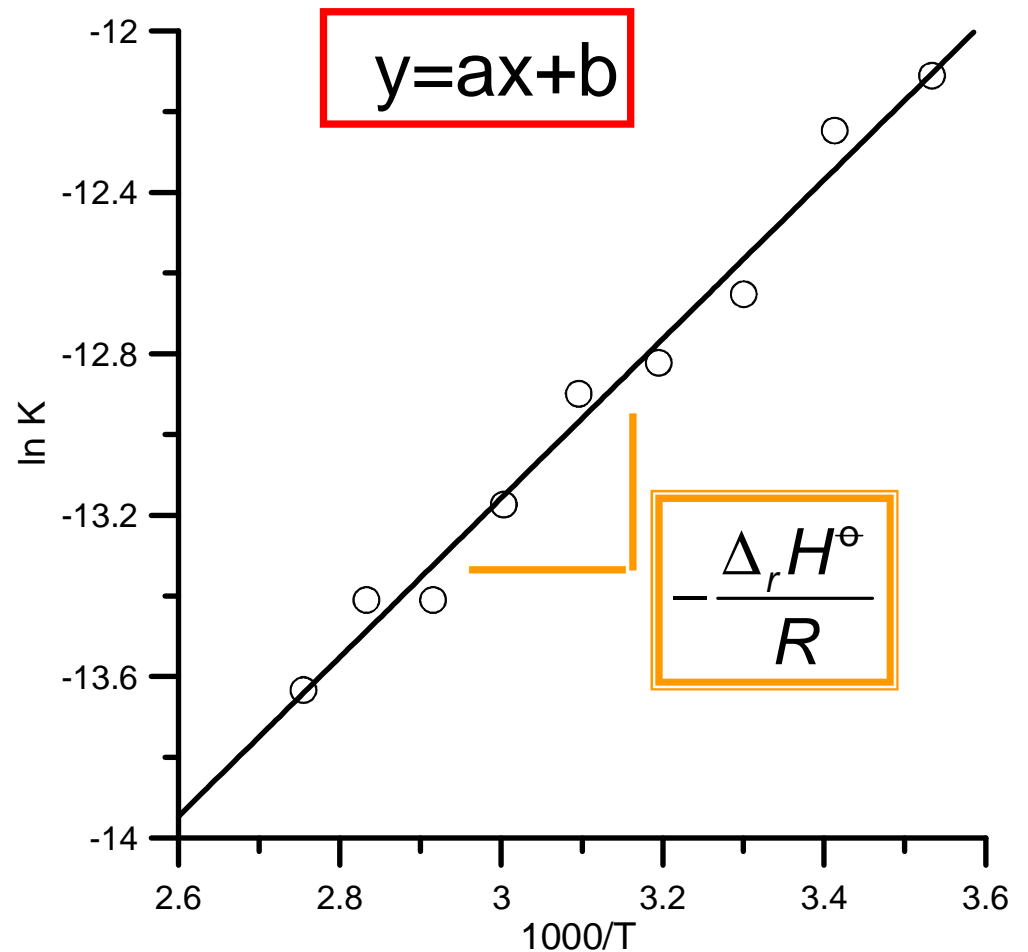
Voorbeeld: oplosbaarheidsproduct $\text{Ca}(\text{OH})_2$

Uit grafiek

- helling: 1970 K
- y-asafsnijding: -19.1

Daarmee

$$\ln K = -\frac{\Delta_r H^\ominus}{R} \frac{1}{T} + \frac{\Delta_r S^\ominus}{R}$$



Evenwichtsconstante: temperatuureffect

Voorbeeld: oplosbaarheidsproduct $\text{Ca}(\text{OH})_2$

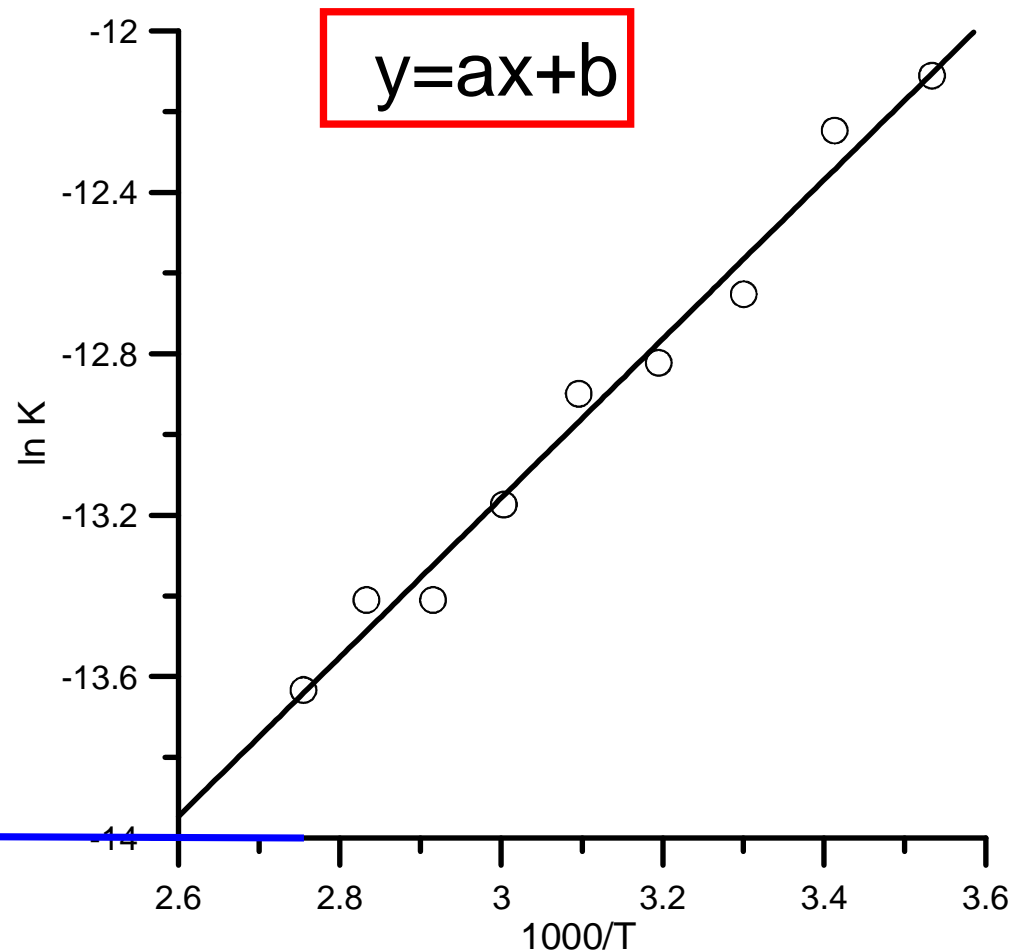
Uit grafiek

- helling: 1970 K
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Daarmee

$$\ln K = -\frac{\Delta_r H^\ominus}{R} \frac{1}{T} + \frac{\Delta_r S^\ominus}{R}$$

← Asafsnijding bij $\ln K = 0!$

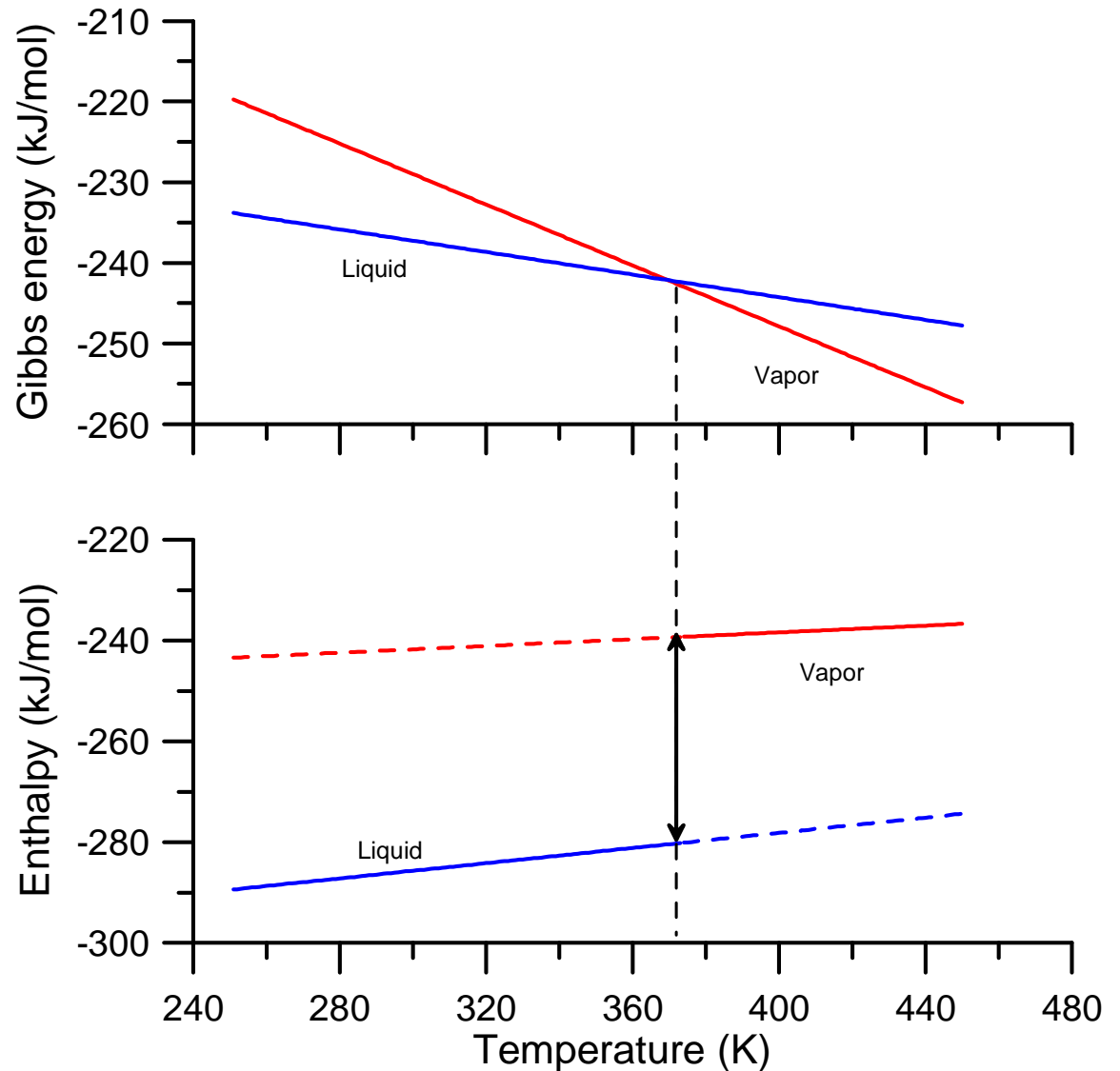


Fasenevenwichten

Voorbeeld: water

Sprong in:

- Molair volume
 - $V_m(l) \approx 18 \text{ cm}^3$
 - $V_m(g) \approx 25 \text{ dm}^3$
- Enthalpie
- Entropie
- NIET Gibbs energie



Sprongwaarden

Gibbs energie gelijk $G_v(T_{\text{vap}}, p_{\text{vap}}) = G_l(T_{\text{vap}}, p_{\text{vap}})$

Gibbs-Helmholtz relatie $H_v - T_{\text{vap}} S_v = H_l - T_{\text{vap}} S_l$

Reorganiseren $\Delta_{\text{vap}} H^\ominus = T_{\text{vap}} \Delta_{\text{vap}} S^\ominus$

Regel van Trouton: $\Delta_{\text{vap}} S^\ominus \approx 85 \text{ J}/(\text{K mol})$

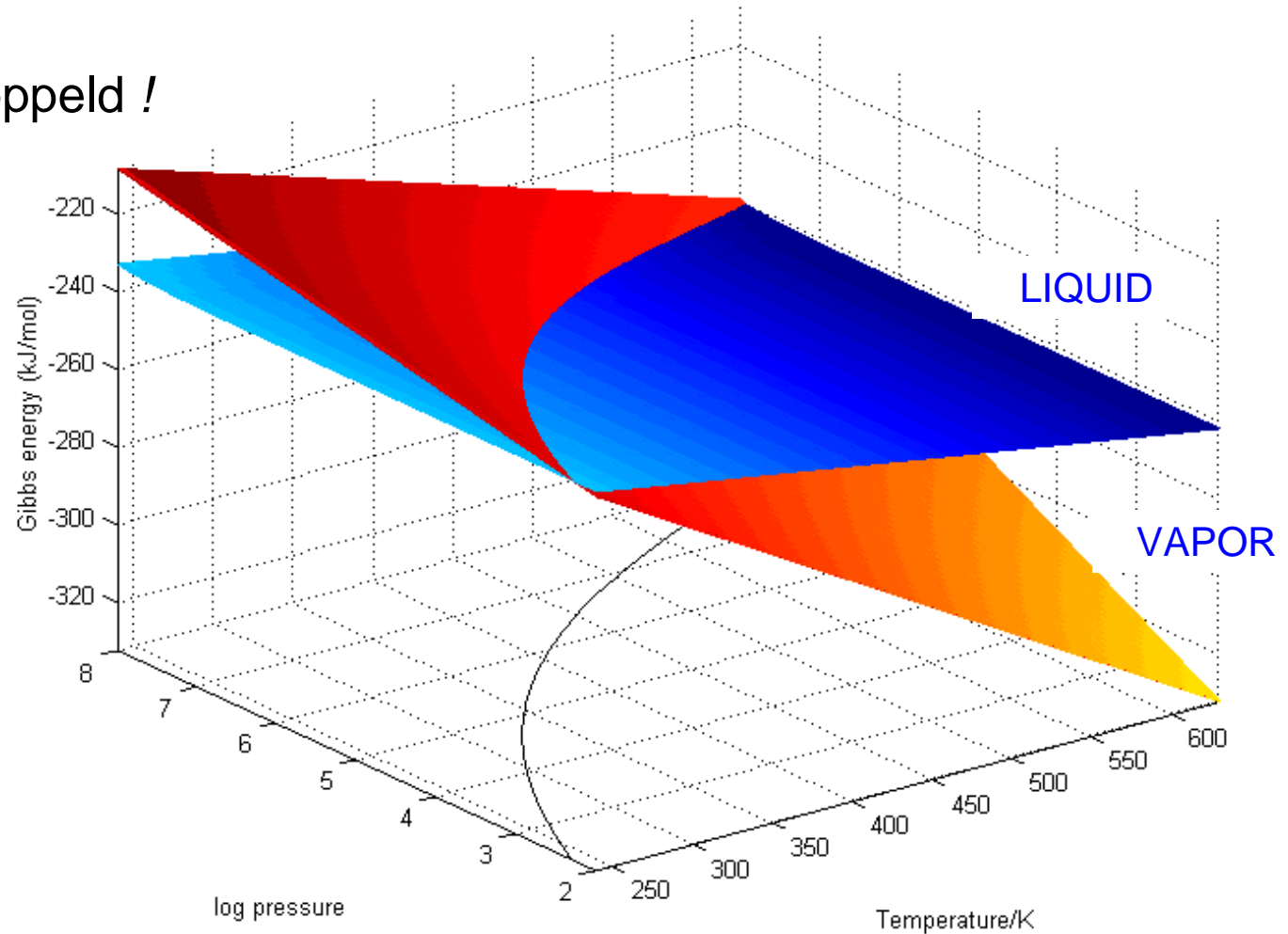
Wat veroorzaakt de afwijkingen?

component	$\Delta_{\text{vap}} H^\ominus$ kJ/mol	T_{vap}^\ominus (°C)	$\Delta_{\text{vap}} S^\ominus$ J/ (K mol)
water	40.7	100.0	109.1
methane	8.18	-161.5	73.2
ethanol	35.2	65.0	104.1
benzene	30.7	80.1	87.2
CS ₂	26.7	46.3	83.7

Fasenlijnen

Vloeistof-damp evenwicht

- p en T gekoppeld !



Fasenlijnen

Punt op fasenlijn

$$G_v(T_{\text{vap}}, p_{\text{vap}}) = G_l(T_{\text{vap}}, p_{\text{vap}})$$

Verschuiving LANGS fasenlijn

$$G_v(T_{\text{vap}} + dT, p_{\text{vap}} + dp) = G_l(T_{\text{vap}} + dT, p_{\text{vap}} + dp)$$

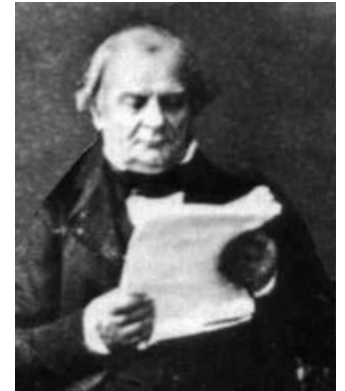
Expanderen

$$\cancel{G_v(T_{\text{vap}}, p_{\text{vap}})} - S_v^\ominus dT + V_{m,v} dp = \cancel{G_l(T_{\text{vap}}, p_{\text{vap}})} - S_l^\ominus dT + V_{m,l} dp$$

Reorganiseren: Vergelijking van Clapeyron

$$\boxed{\frac{dp}{dT} = \frac{\Delta_{\text{vap}} S^\ominus}{\Delta_{\text{vap}} V}} \xrightarrow{\text{GH-relatie}} \boxed{\frac{dp}{dT} = \frac{\Delta_{\text{vap}} H^\ominus}{T_{\text{vap}} \Delta_{\text{vap}} V}}$$

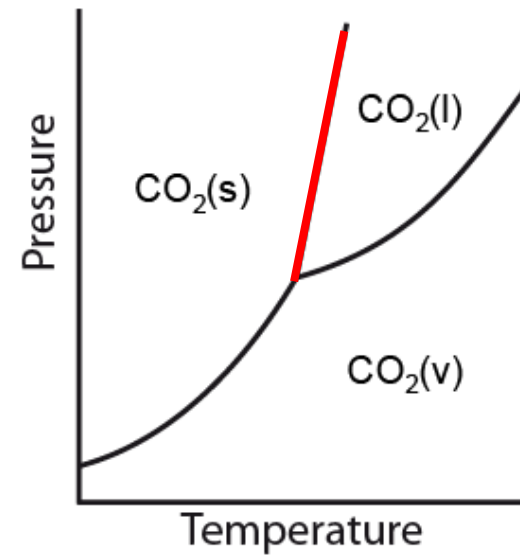
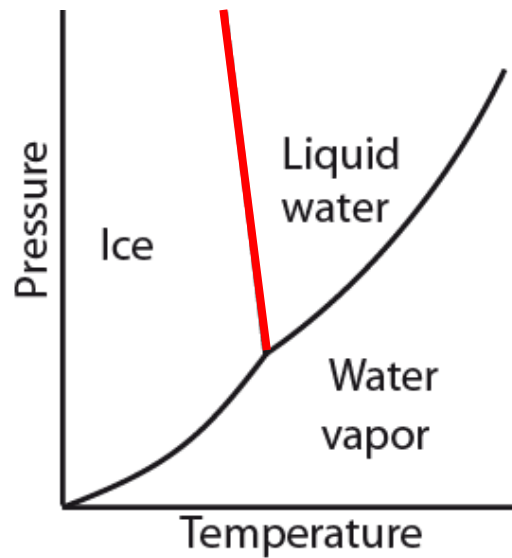
Also works for melting etc.



Benoît Clapeyron
(1799 – 1864)

Fasenlijnen

Voorbeeld: water en CO₂



$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}} S^{\ominus}}{\Delta_{\text{vap}} V}$$

Fasenlijnen

Clapeyron vergelijking
$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}} H^\ominus}{T_{\text{vap}} \Delta_{\text{vap}} V}$$

Voor gassen
$$\Delta_{\text{vap}} V = V_{m,v} - V_{m,l} \approx V_{m,v} \approx \frac{RT_{\text{vap}}}{p_{\text{vap}}}$$

waarmee
$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}} H^\ominus p_{\text{vap}}}{RT_{\text{vap}}^2}$$

Vergelijking van Clausius-Clapeyron
$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}} H^\ominus}{RT_{\text{vap}}^2}$$

in de praktijk
$$\ln \frac{p}{p_{\text{ref}}} = -\frac{\Delta_{\text{vap}} H^\ominus}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right)$$

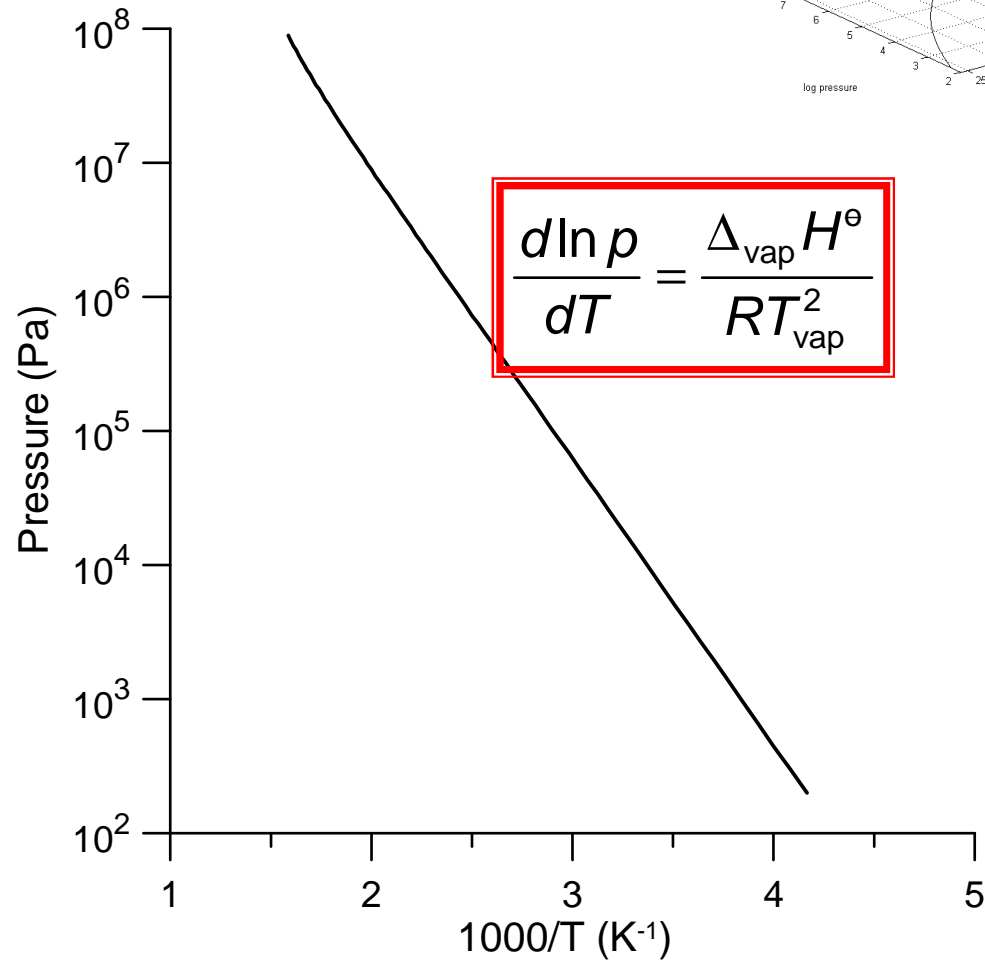
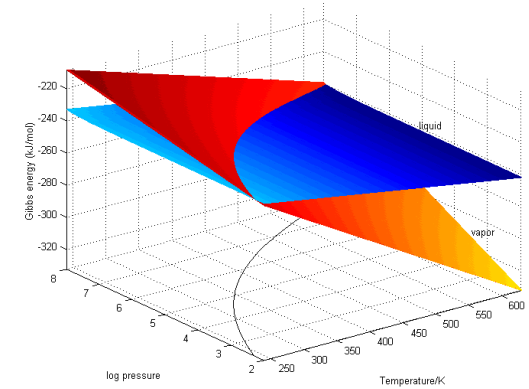


Rudolf Clausius
(1822 – 1888)

Fasenlijnen

Clausius-Clapeyron vergelijking

vb: water-waterdamp



Molair volume bij fasenovergang

Volumesprong, bijvoorbeeld $V_{m,l} \rightarrow V_{m,v}$: factor 1000 !

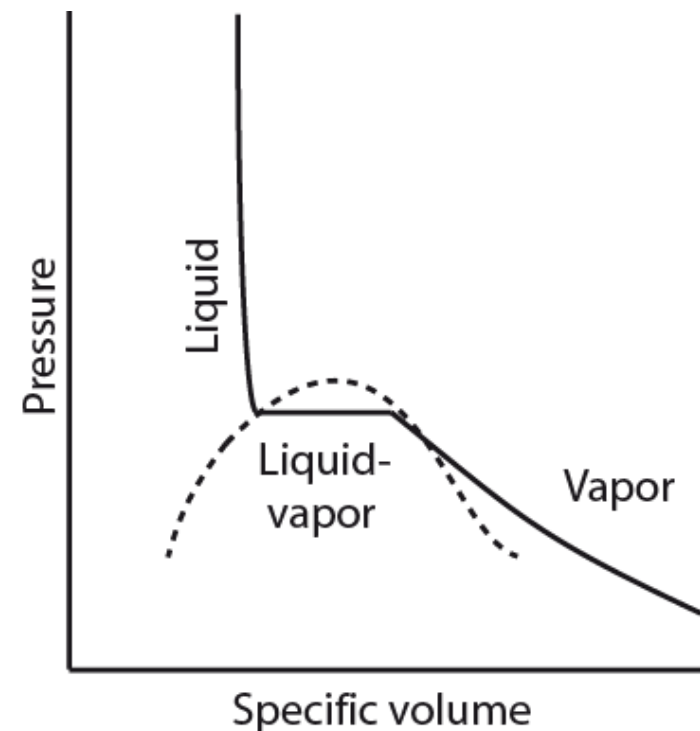
p en T gekoppeld: V vrij te kiezen tijdens fasenovergang!

Kies een volume V tussen $V_{m,l}$ en $V_{m,v}$

$$\begin{cases} 1 &= x_l + x_v \\ V &= x_l V_{m,l} + x_v V_{m,v} \end{cases}$$

oplossing

$$x_l = \frac{V - V_{m,v}}{V_{m,l} - V_{m,v}}$$



Er is geen arbeid nodig om het volume te veranderen!