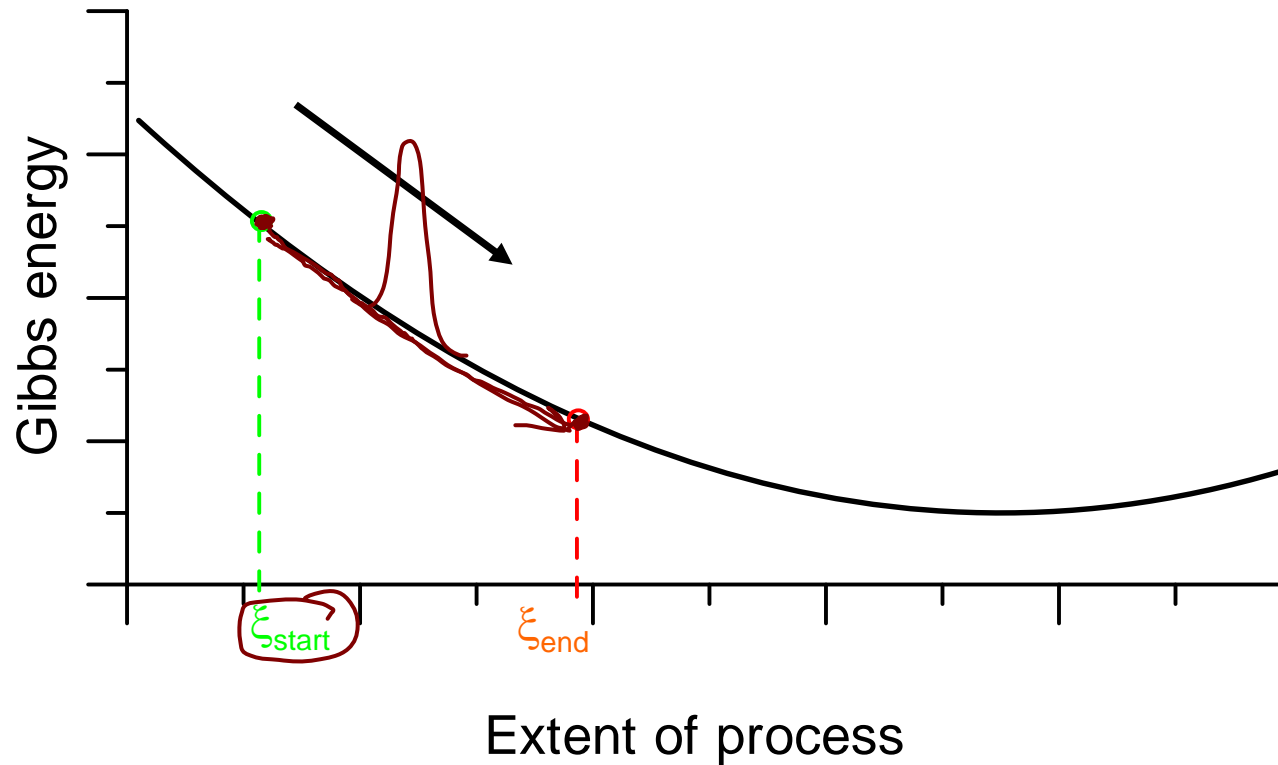


Spontaniteit van Processen

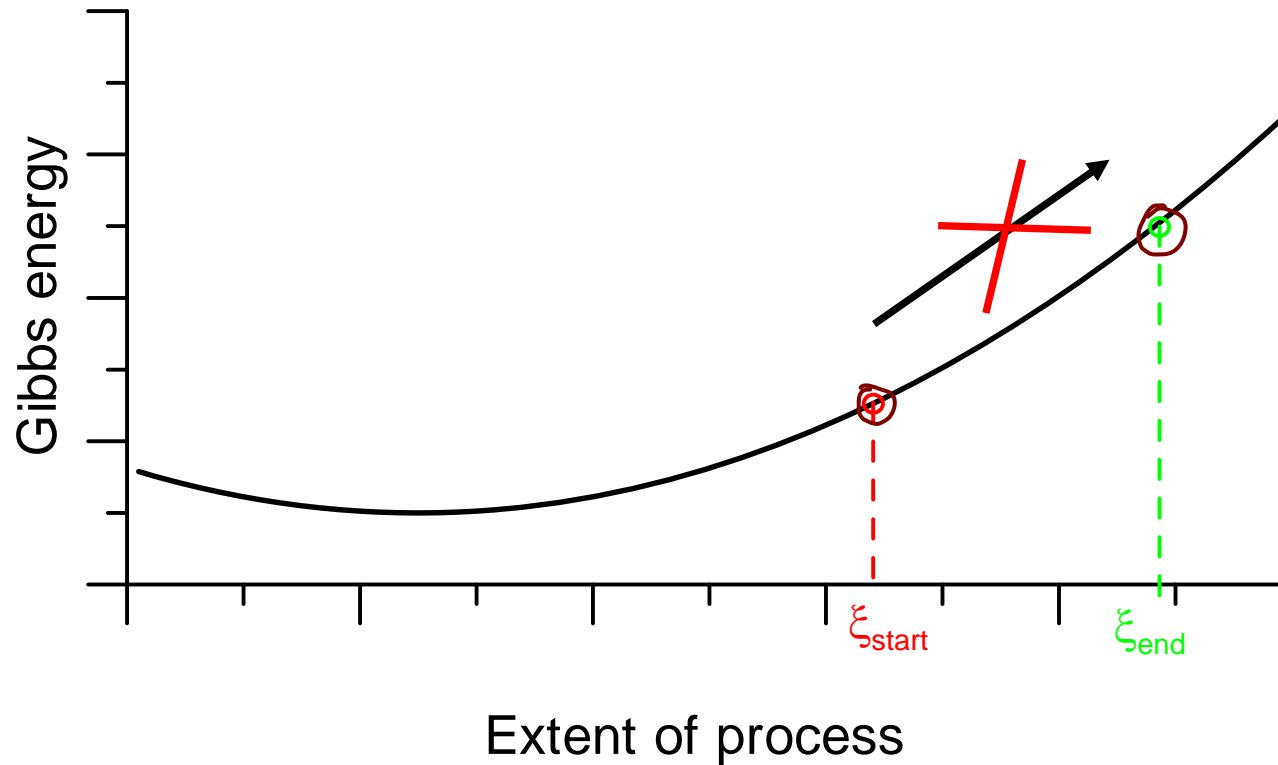
Gibbs energie als voorspeller

Spontaan verloop als Gibbs energie kan afnemen



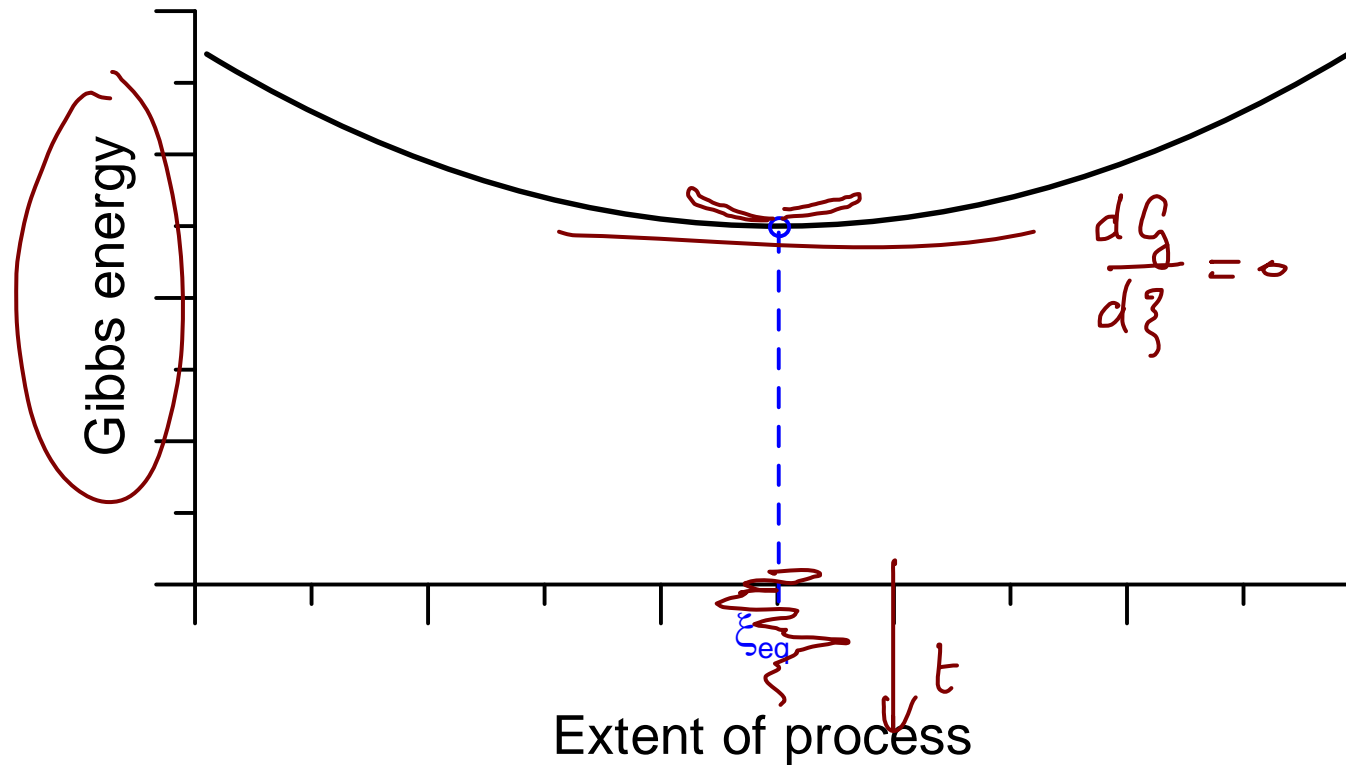
Gibbs energie als voorspeller

Geen spontaan verloop als Gibbs energie toe moet nemen



Gibbs energie als voorspeller

Evenwicht bij een Gibbs energiminimum

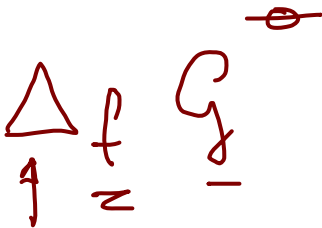


Tabellen voor Gibbs energie

Gegeven voor standaard temperatuur en druk (STP)

298.15 K

10^5 Pa of 1 Bar

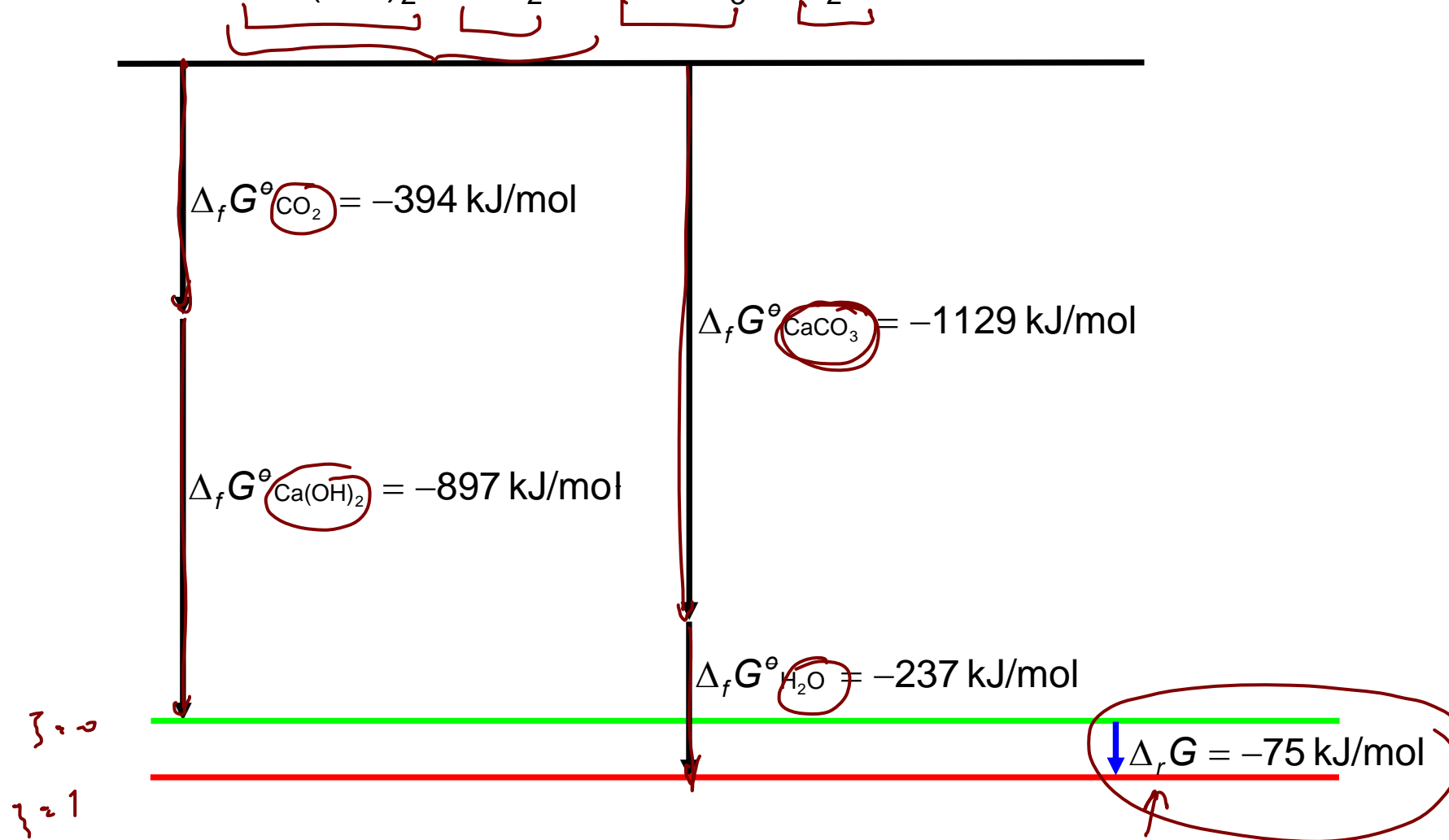


Gibbs vormingsenergie

Molecular formula	Name	Crystal				Liquid				Gas			
		$\Delta_f H^\circ$ kJ/mol	$\Delta_f G^\circ$ kJ/mol	S° J/mol K	C_p J/mol K	$\Delta_f H^\circ$ kJ/mol	$\Delta_f G^\circ$ kJ/mol	S° J/mol K	C_p J/mol K	$\Delta_f H^\circ$ kJ/mol	$\Delta_f G^\circ$ kJ/mol	S° J/mol K	C_p J/mol K
BF ₃ H ₃ P	Trihydro(phosphorus trifluoride)boron									-854.0			
BF ₄ Na	Sodium tetrafluoroborate	-1844.7	-1750.1	145.3	120.3								
BH	Borane(1)									442.7	412.7	171.8	29.2
BHO ₂	Metaboric acid (β , monoclinic)	-794.3	-723.4	38.0						-561.9	-551.0	240.1	42.2
BH ₃	Borane(3)									89.2	93.3	188.2	36.0
BH ₃ O ₃	Boric acid	-1094.3	-968.9	90.0	86.1					-994.1			
BH ₄ K	Potassium borohydride	-227.4	-160.3	106.3	96.1								
BH ₄ Li	Lithium borohydride	-190.8	-125.0	75.9	82.6								
BH ₄ Na	Sodium borohydride	-188.6	-123.9	101.3	86.8								
BI ₃	Boron triiodide									71.1	20.7	349.2	70.8

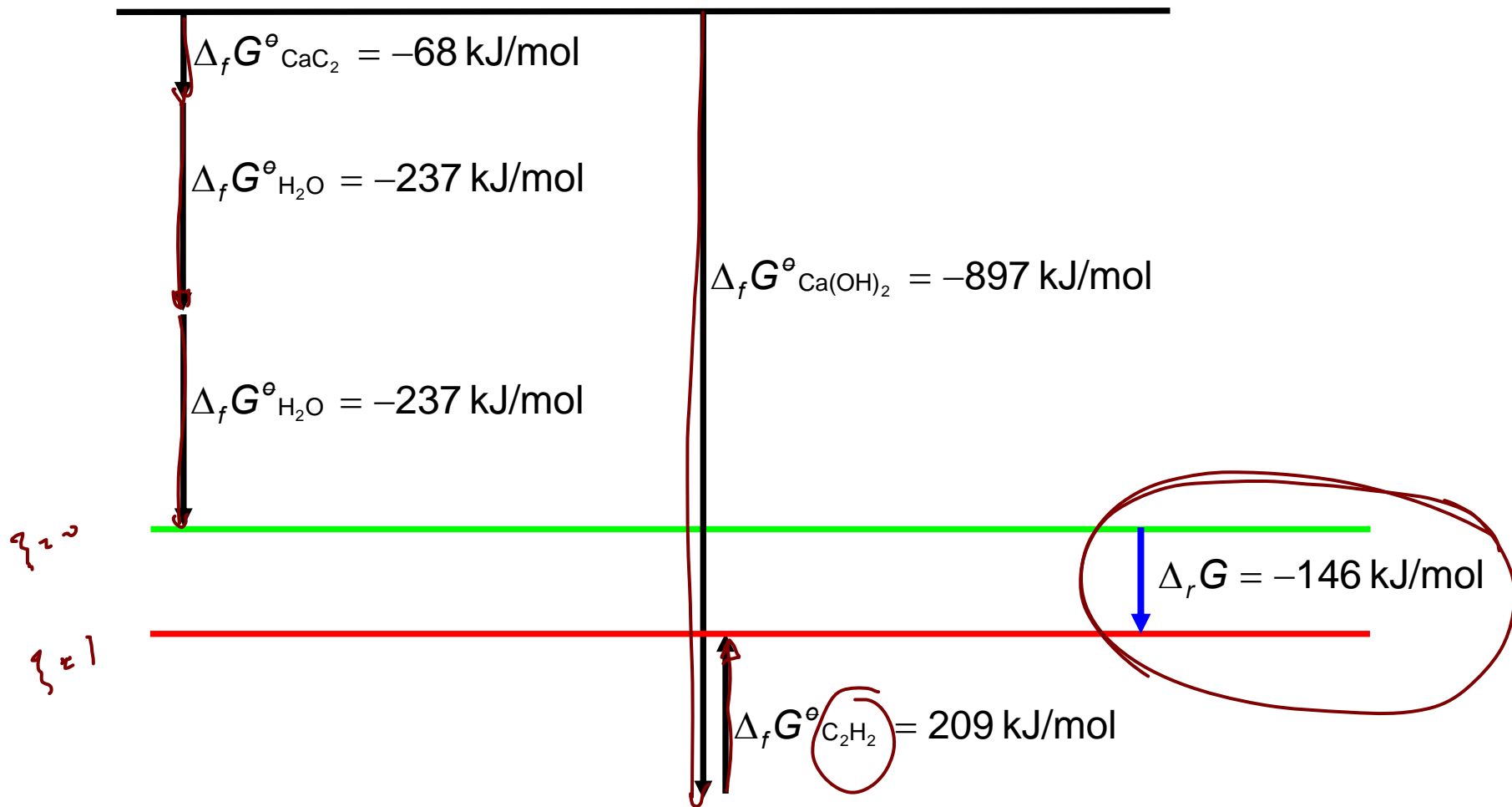
Gibbs energie is additief

Voorbeeld: $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$: uitharden cement



Gibbs energie is additief

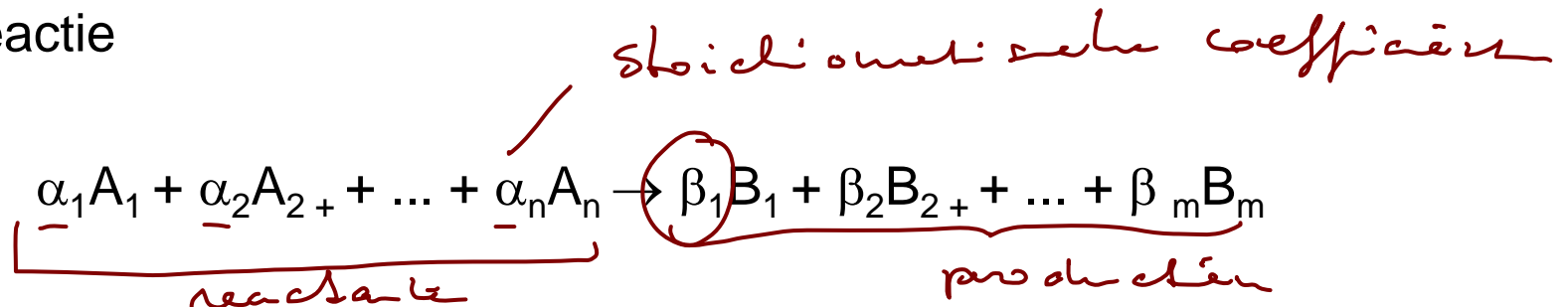
Voorbeeld: $\text{CaC}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$: productie acetyleen



Gibbs energie is additief

Regel:

Voor een reactie



wordt het Gibbs energieverval berekend volgens

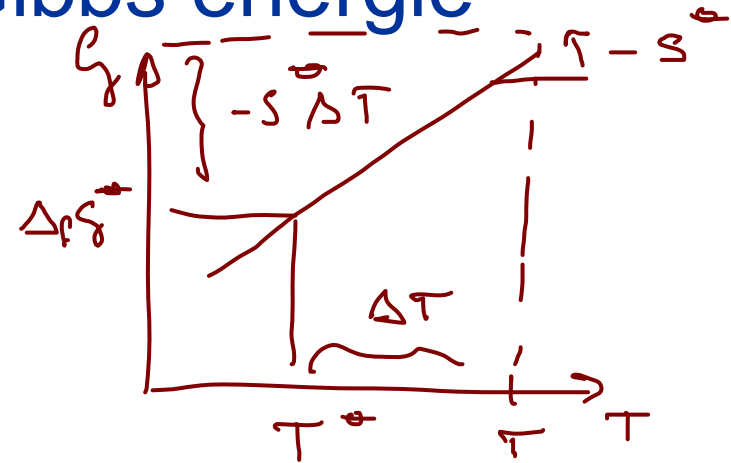
$$\Delta_r G = \sum_{j=1}^m \beta_j \Delta_f G^\ominus_{B_j} - \sum_{j=1}^n \alpha_j \Delta_f G^\ominus_{A_j}$$

$$\underbrace{\begin{pmatrix} -\alpha_1 \\ -\alpha_2 \\ \vdots \\ -\alpha_n \\ \beta_1 \\ \vdots \\ \beta_m \end{pmatrix}}_{\nu_j \cdot \Delta_f G^\ominus} \cdot \begin{pmatrix} \vdots \\ \Delta_f G \\ \vdots \end{pmatrix} = \Delta_r G$$

Temperatuurafhankelijkheid Gibbs energie

Kleine afwijkingen van standaardtemperatuur

$$\Delta_f G(T, p^\circ) \approx \Delta_f G^\circ(T^\circ, p^\circ) - (T - T^\circ)S^\circ$$

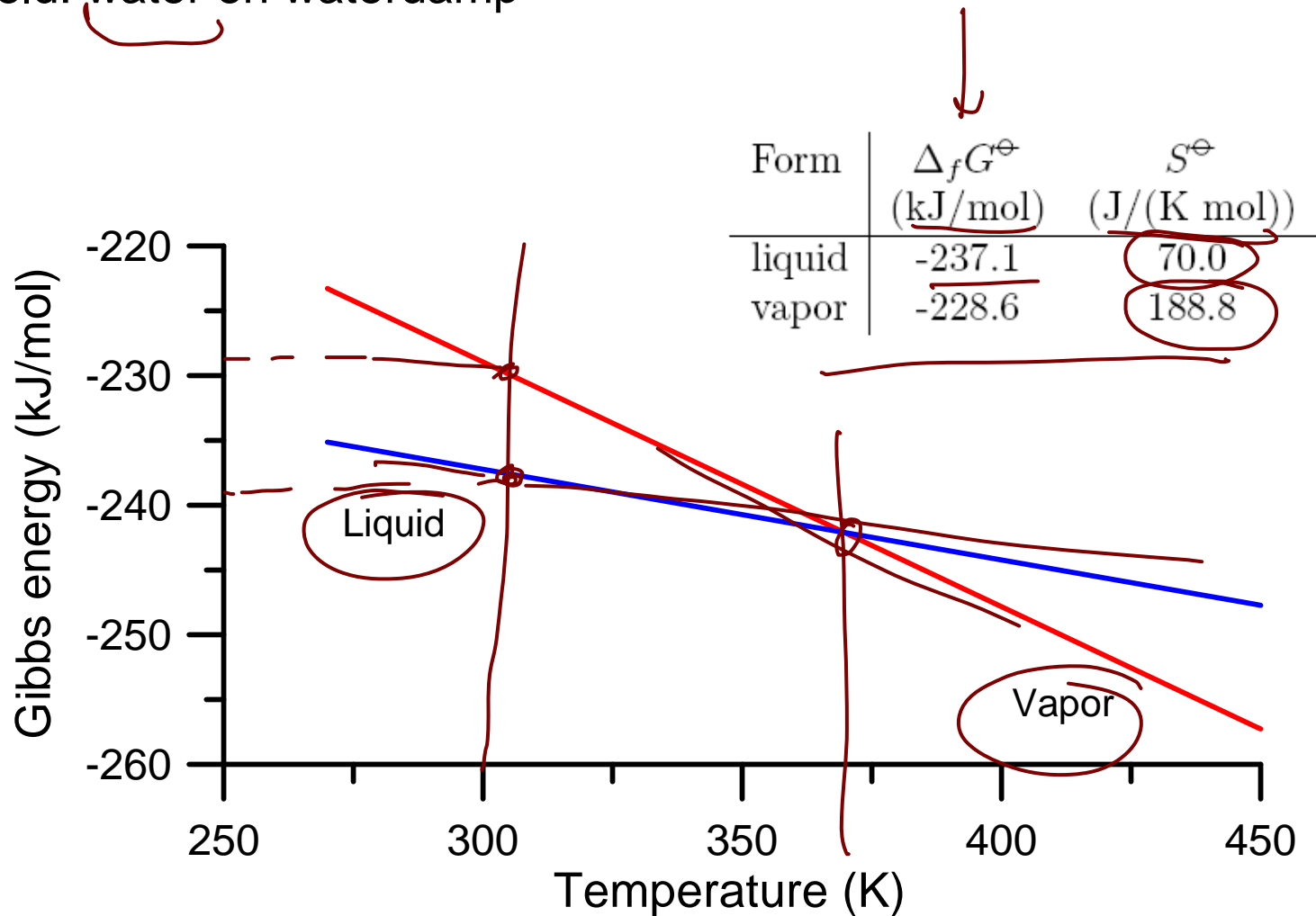


absolute entropie

Molecular formula	Name	Crystal				Liquid				Gas			
		$\Delta_f H^\circ$ kJ/mol	$\Delta_f G^\circ$ kJ/mol	S° J/mol K	C_p J/mol K	$\Delta_f H^\circ$ kJ/mol	$\Delta_f G^\circ$ kJ/mol	S° J/mol K	C_p J/mol K	$\Delta_f H^\circ$ kJ/mol	$\Delta_f G^\circ$ kJ/mol	S° J/mol K	C_p J/mol K
BF ₃ H ₃ P	Trihydro(phosphorus trifluoride)boron									-854.0			
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BH ₃	Borane(3)									89.2	93.3	188.2	36.0
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BH ₄ Na	Sodium borohydride	-188.6	-123.9	101.3	86.8								
BI ₃	Boron triiodide									71.1	20.7	349.2	70.8

Temperatuurafhankelijkheid Gibbs energie

Voorbeeld: water en waterdamp



Drukafhankelijkheid Gibbs energie

Afwijkingen van standaarddruk

$$\Delta_f G(p, T^\circ) \approx \Delta_f G^\circ(p^\circ, T^\circ) + (p - p^\circ)V_m$$

voor vloeistoffen en vaste stoffen

$$V_m = M / \rho$$

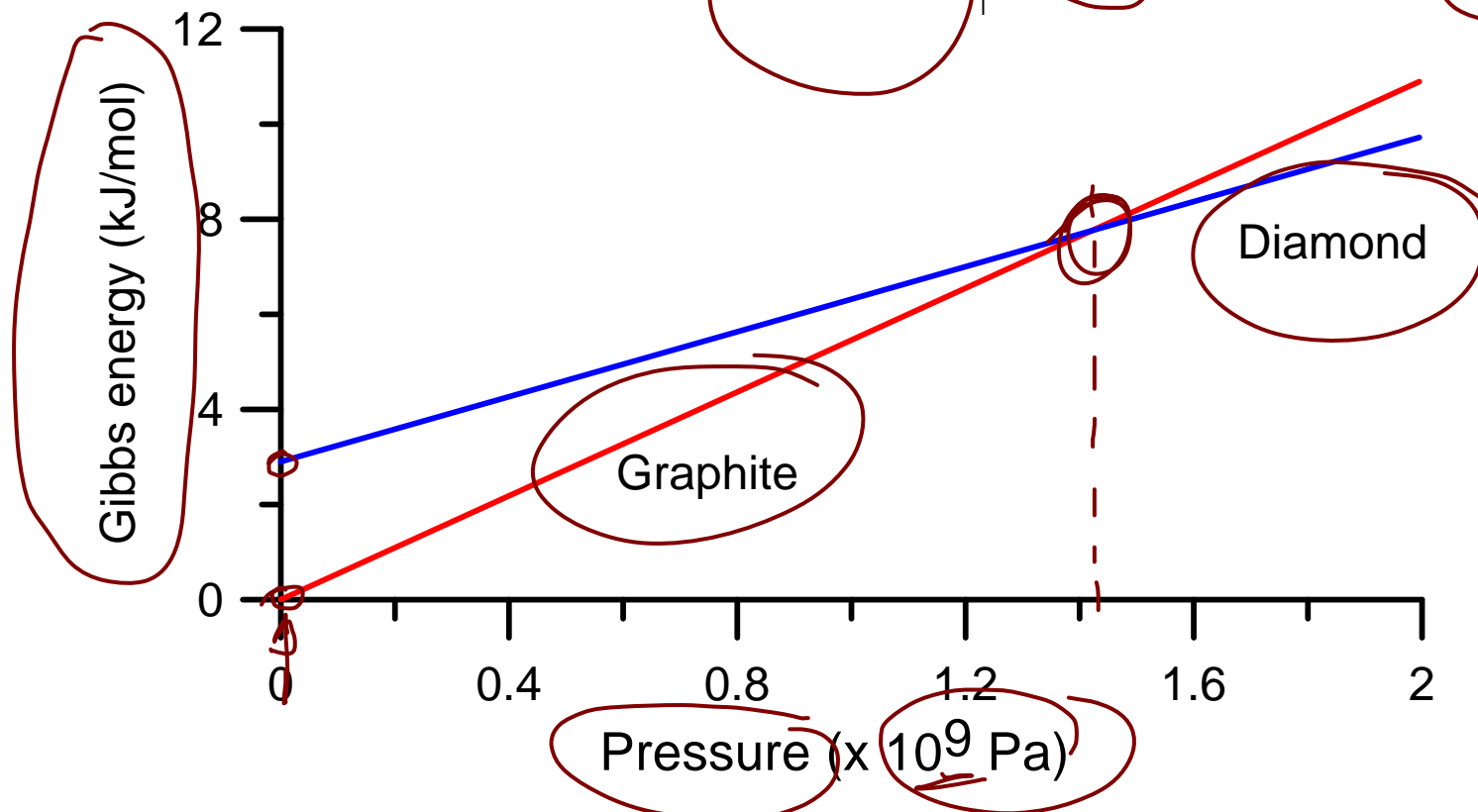
$$= \frac{100.0 \cdot 10^{-3} \text{ kg/mol}}{2.5 \cdot 10^3 \text{ kg/m}^3} = 40 \cdot 10^{-6} \text{ m}^3/\text{mol}$$

No.	Name	Formula	CAS Reg No.	Mol. weight	Physical form	mp/°C	bp/°C	Density g cm ⁻³	Solubility g/100 g H ₂ O	Qualitative solubility
626	Calcium silicide (CaSi ₂)	CaSi ₂	12013-56-8	96.249	gray hex cry	1040		2.50		i cold H ₂ O; reac hot H ₂ O; s acid
627	Calcium stannate trihydrate	CaSnO ₃ · 3H ₂ O	12013-46-6*	260.832	wh cry pow	dec ≈350				i H ₂ O
628	Calcium stearate	Ca(C ₁₈ H ₃₅ O ₂) ₂	1592-23-0	607.017	granular powder	180				i H ₂ O, EtOH
629	Calcium succinate trihydrate	CaC ₄ H ₄ O ₄ · 3H ₂ O	140-99-8	210.196	needles					sl H ₂ O; s dil acid; i EtOH
630	Calcium sulfate	CaSO ₄	7778-18-9	136.141	orth cry	1460		2.96	0.205 ²⁵	
631	Calcium sulfate hemihydrate	CaSO ₄ · 0.5H ₂ O	10034-76-1	145.149	wh powder				0.205 ²⁵	
632	Calcium sulfate dihydrate	CaSO ₄ · 2H ₂ O	10101-41-4	172.171	monocl cry or powder	150 dec		2.32	0.205 ²⁰	i os
633	Calcium sulfide	CaS	20548-54-3	72.143	wh-yel cub cry; hyg	2524		2.59		sl H ₂ O; i EtOH
634	Calcium sulfite dihydrate	CaSO ₃ · 2H ₂ O	10257-55-3	156.172	wh powder				0.0070 ²⁵	sl EtOH; s acid
635	Calcium tartrate tetrahydrate	CaC ₄ H ₄ O ₆ · 4H ₂ O	3164-34-9*	260.210	wh pow				0.04 ¹⁰	s dil acid; sl EtOH
636	Calcium telluride	CaTe	12013-57-9	167.68	wh cub cry	1600 dec		4.87		
637	Calcium tetrahydroaluminate	Ca(AlH ₄) ₂	16941-10-9	102.105	gray powder; flam					reac H ₂ O; s thf; i eth, bz
638	Calcium thiocyanate tetrahydrate	Ca(SCN) ₂ · 4H ₂ O	2092-16-2	228.304	hyg cry	160 dec				vs H ₂ O; s EtOH, ace
639	Calcium thiosulfate hexahydrate	CaS ₂ O ₃ · 6H ₂ O	10124-41-1	260.298	tricl cry	45 dec		1.87		s H ₂ O; i EtOH
640	Calcium titanate	CaTiO ₃	12049-50-2	135.943	cub cry	1980		3.98		
641	Calcium tungstate	CaWO ₄	7790-75-2	287.92	wh tetr cry	1620		6.06	0.2 ¹⁸	s hot acid
642	Calcium zirconate	CaZrO ₃	12013-47-7	179.300	powder	2550				
643	Californium	Cf	7440-71-3	251	hex or cub metal	900		15.1		
644	Carbon (diamond)	C	7782-40-3	12.011	col cub cry	4440 (12.4 GPa)		3.513		i H ₂ O
645	Carbon (graphite)	C	7782-42-5	12.011	soft blk hex cry	4489 tp (10.3 MPa)	3825 sp	2.2		i H ₂ O
646	Carbon black	C	1333-86-4	12.011	fine blk pow					i H ₂ O

Drukafhankelijkheid Gibbs energie

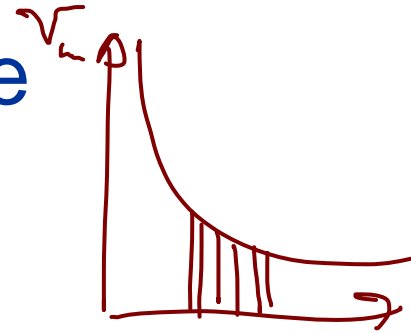
Voorbeeld: diamant en grafiet

Form	$\Delta_f G^\circ$ (kJ/mol)	M (g/mol)	ρ (kg/dm ³)
graphite	0	12.011	2.200
diamond	2.9	12.011	3.513



Drukafhankelijkheid Gibbs energie

Kleine afwijkingen van standaarddruk



$$\Delta_f G(p, T^\circ) \approx \Delta_f G^\circ(p^\circ, T^\circ) + \underbrace{(p - p^\circ) V_m}$$

voor gassen

$$V_m \approx \frac{RT}{p}$$

$$\int_{p^\circ}^p \frac{RT}{p'} dp' = RT \ln \frac{p}{p^\circ}$$

waarmee

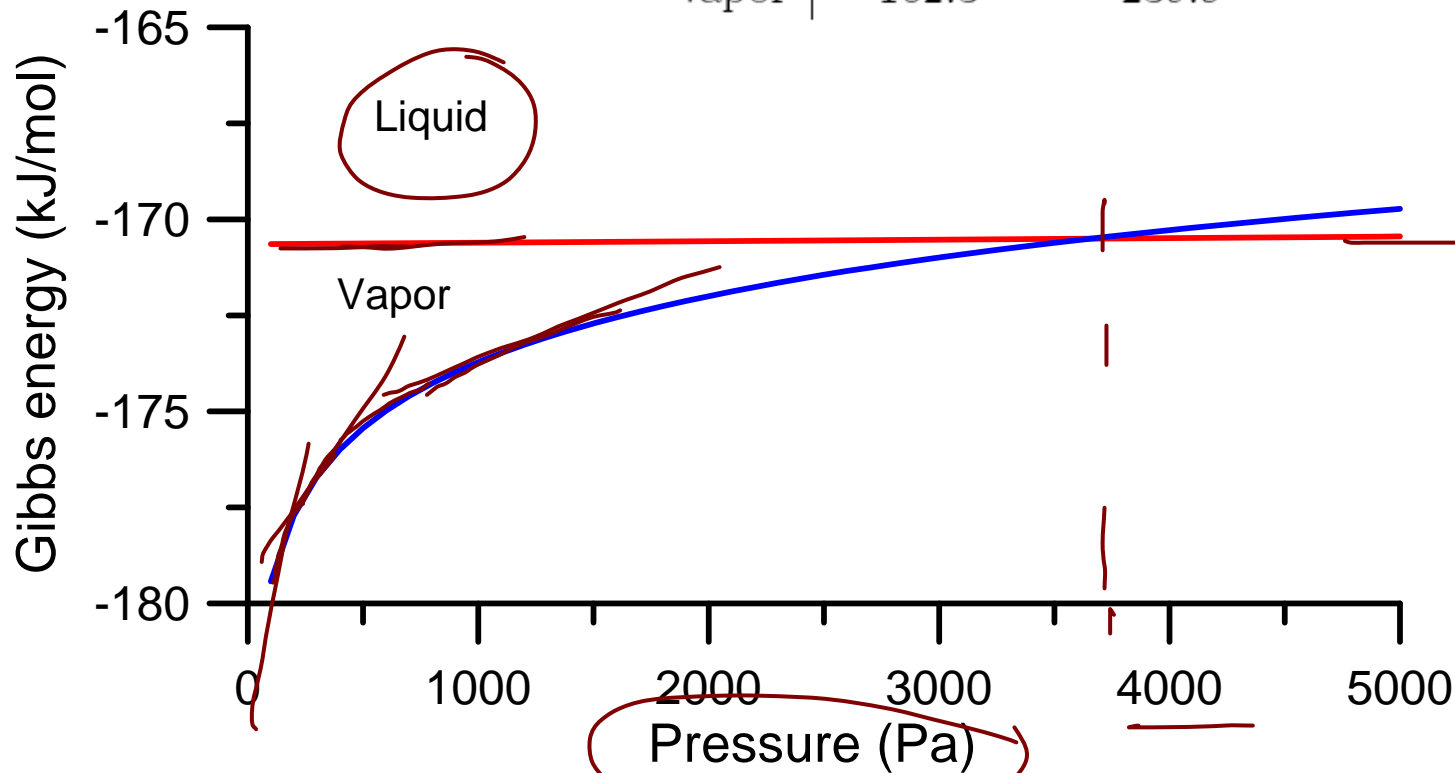
$$\Delta_f G_{\text{gas}}(p, T^\circ) \approx \Delta_f G^\circ_{\text{gas}}(p^\circ, T^\circ) + RT^\circ \ln \left(\frac{p}{p^\circ} \right)$$



Drukafhankelijkheid Gibbs energie

Voorbeeld: methanol

Form	$\Delta_f G^\ominus$ (kJ/mol)	S^\ominus (J/(K mol))	V_m (cm ³ /mol)
liquid	-166.6	126.8	40.5
vapor	-162.3	239.9	—



Gibbs energie van "ideale" mengsels

Bruikbaar voor

- verdunde gassen
- sterk verdunde oplossingen

Voor B verdund ($x \ll 1$) opgelost in A:

$$\Delta_f G_B(p, T, x) \approx \Delta_f G_B(p, T) + RT \ln x$$

Handwritten annotations: A red arrow points to the 'x' in the denominator of the fraction $\frac{n_B}{n_A + n_B}$ above the equation. A red bracket underlines the entire equation.

en voor de oplossing

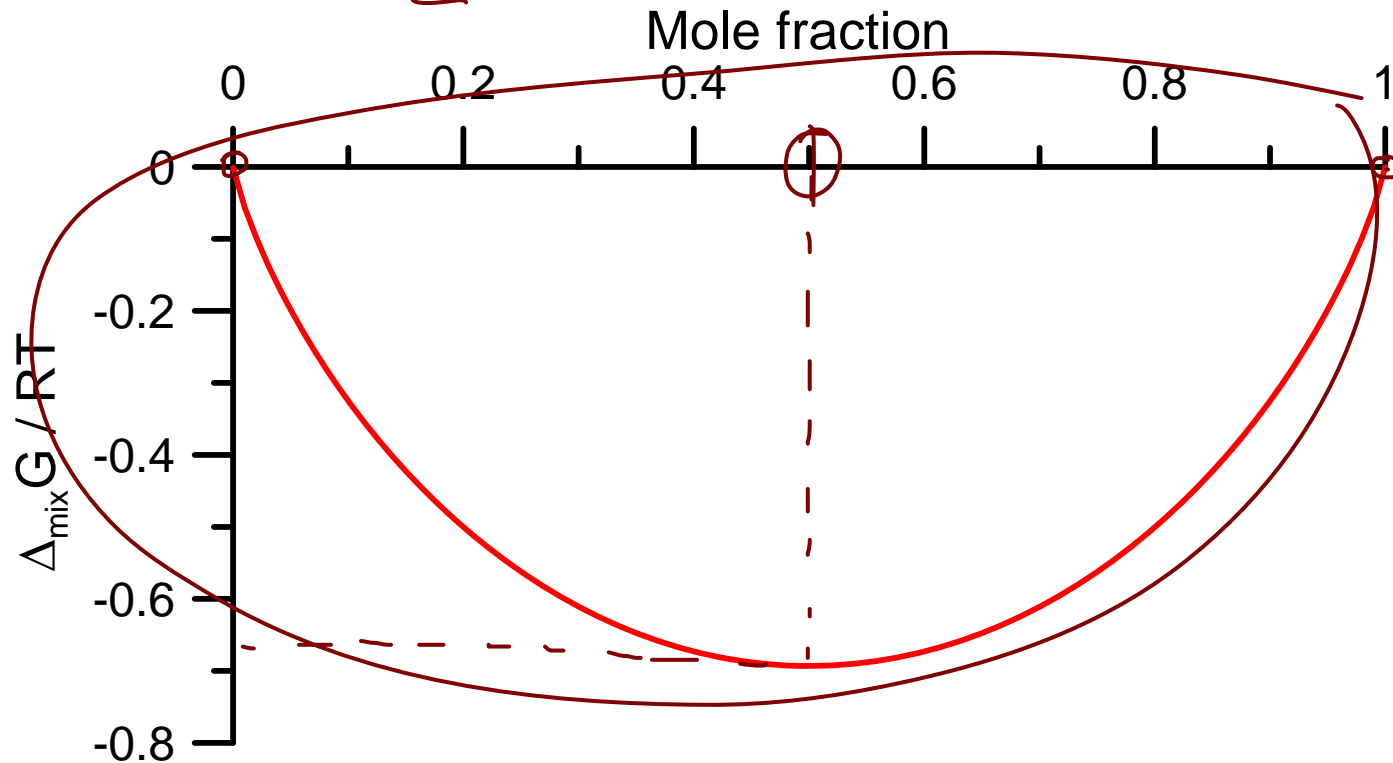
$$\Delta_f G_{B \subset A} \approx (1-x)\Delta_f G_A + x\Delta_f G_B + RT \{(1-x)\ln(1-x) + x\ln x\}$$

Handwritten annotations: A red box encloses the entire equation. Red arrows point to the terms $(1-x)\Delta_f G_A$, $x\Delta_f G_B$, and the logarithmic term. A red circle highlights the $x\Delta_f G_B$ term, and another red circle highlights the logarithmic term with a downward arrow pointing to it.

Gibbs energie van "ideale" mengsels

Gibbs energie voor ideale menging

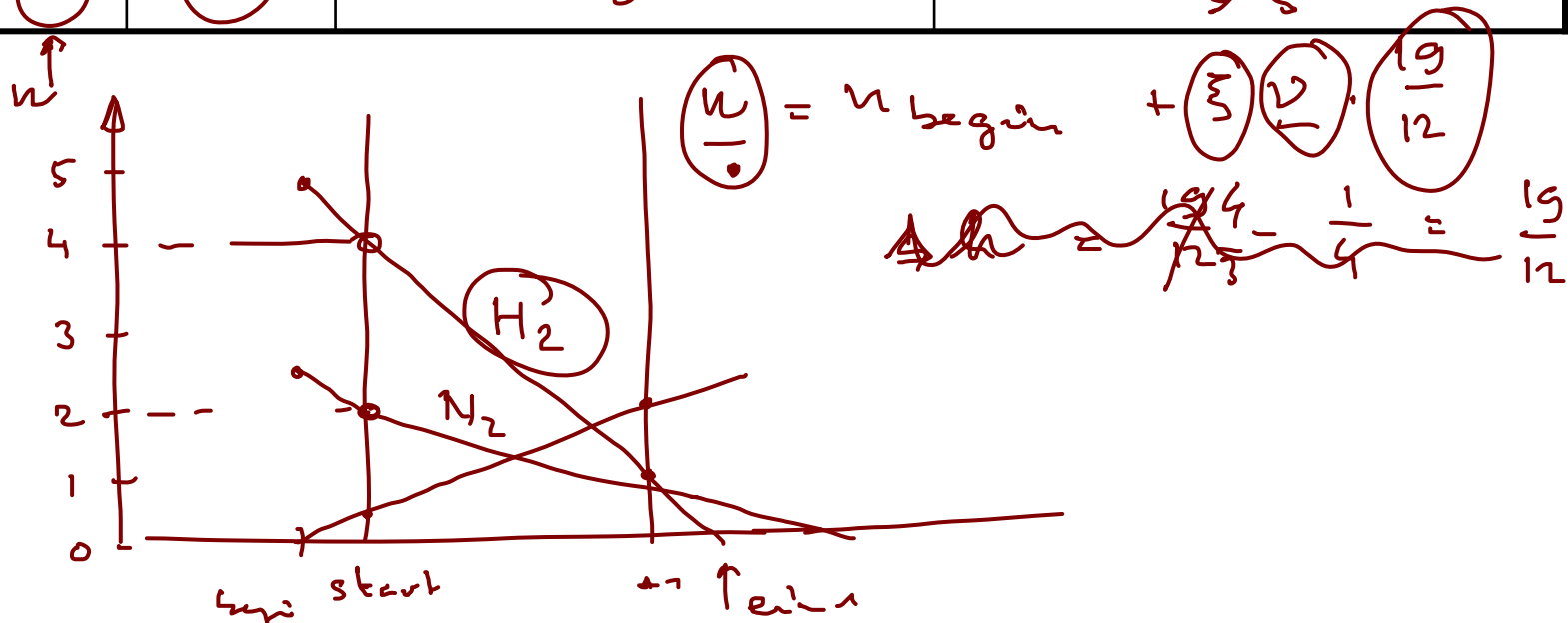
$$\Delta_{\text{mix}} G = RT \{ \overline{(1-x)} \ln(1-x) + \overline{x} \ln x \} \leq 0 \quad -\ln 2 \approx -0.7$$



Haber Bosch synthese ammonia



	ν	n_{start}	n_{begin}	n_{eind}
N_2	-1	2	$2 - (-1) \cdot \frac{1}{4} = 2 \frac{1}{4}$	$2 \frac{1}{4} - 1 \cdot \frac{19}{12} = \frac{2}{3}$
H_2	-3	4	$4 - (-3) \cdot \frac{1}{4} = 4 \frac{3}{4}$	$4 \frac{3}{4} - 3 \cdot \frac{19}{12} = 0$
NH_3	2	0.5	$0.5 - 2 \cdot \frac{1}{4} = 0$	$0 + 2 \cdot \frac{19}{12} = \frac{19}{6} = 3 \frac{1}{6}$
H_2O	0	5	5	5

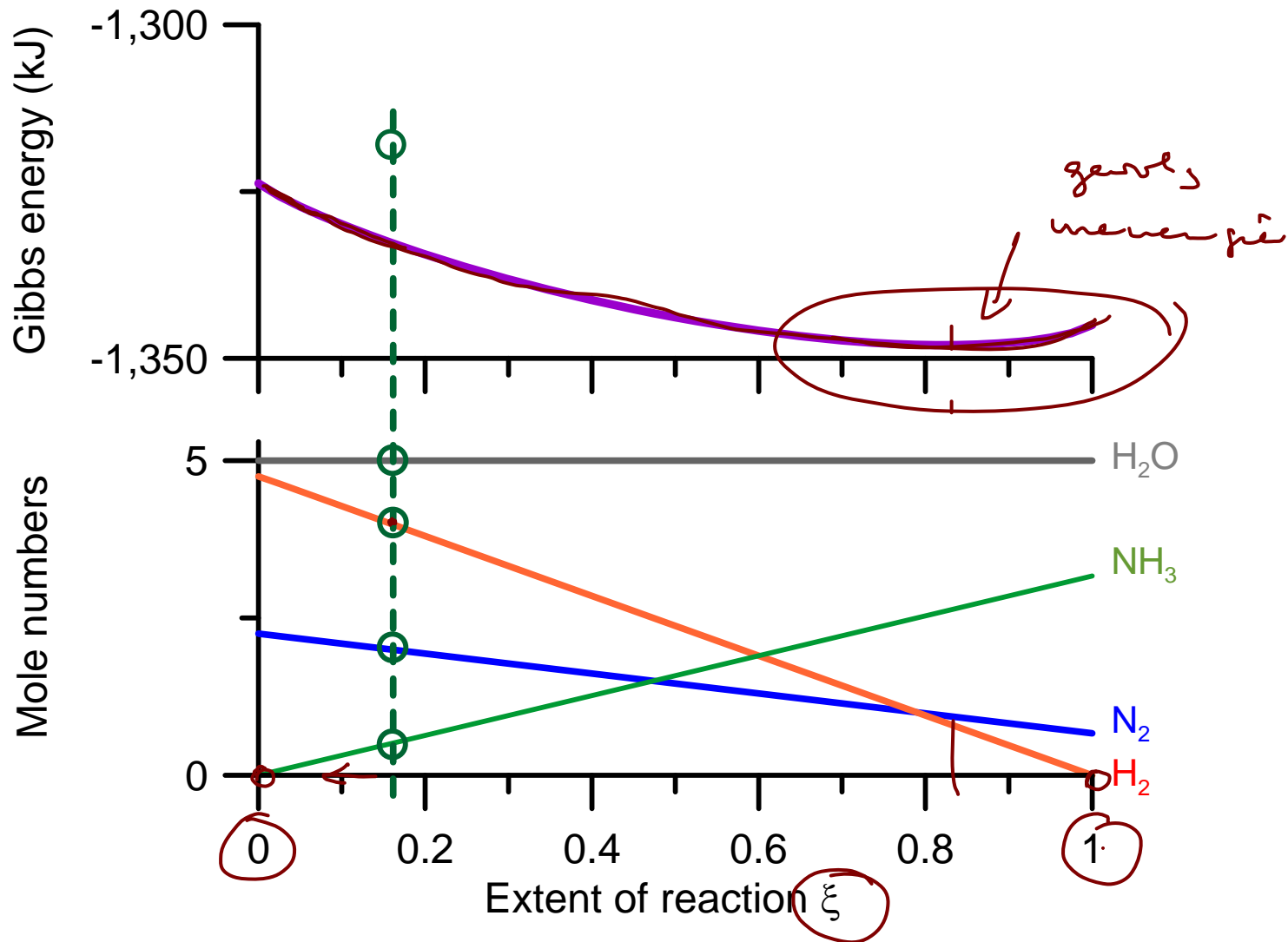


Haber Bosch synthese ammonia

	ν	$\Delta_f G^\circ$ (kJ/mol)	S° (J/(Kmol))	$\Delta_f G$ (kJ/mol)
N_2	-1	0	191.6	
H_2	-3	0	130.7	
NH_3	2	-16.4	192.8	
H_2O	0	-228.6	188.8	

$$\Delta_r G = \frac{n}{\nu} \cdot \left\{ \Delta_f G^\circ - S^\circ (T - T^\circ) + RT \ln \left(\frac{p_{H_2}}{p^\circ} \right)^{\nu_{H_2}} \right\}$$

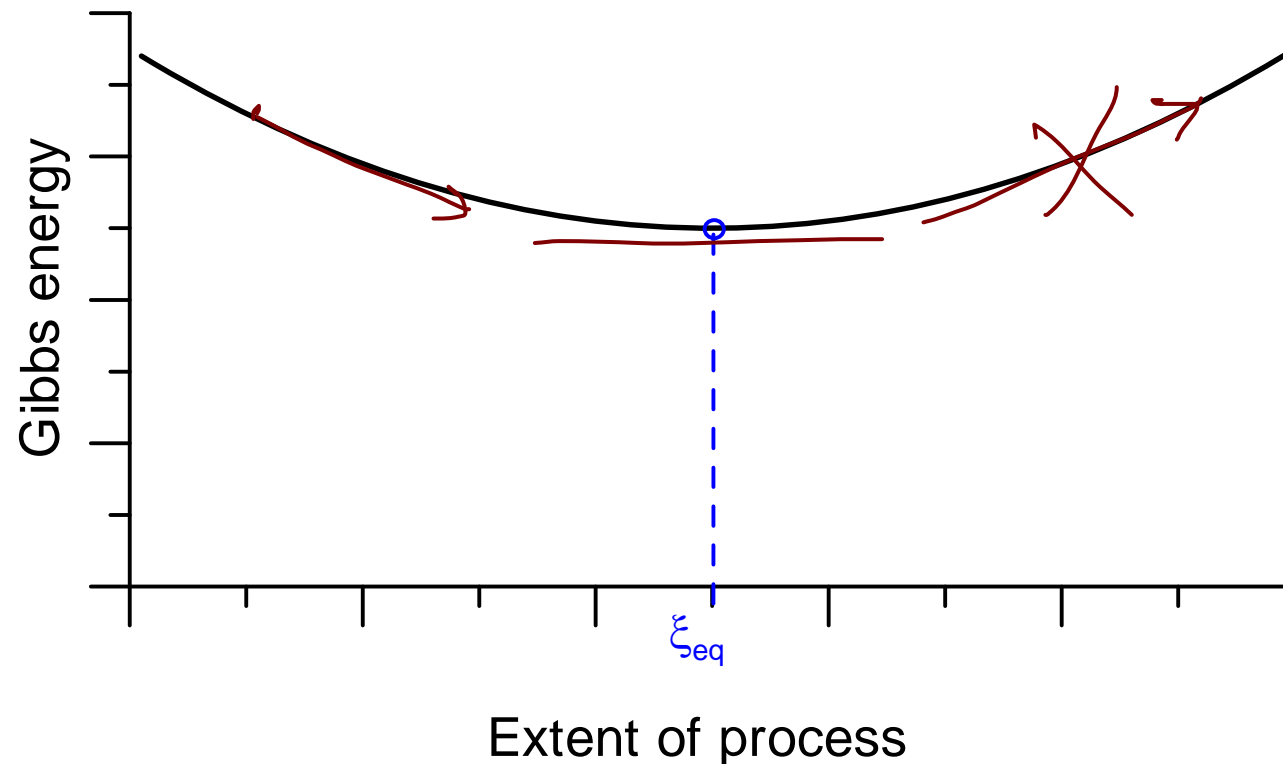
Haber Bosch synthese ammonia



Gibbs energie als voorspeller

2^{de} hoofdwet: processen met

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



Gibbs energie

Toestandsfunctie

Eenheid Joule

$$G(T, p, \{n_j\})$$

$$\frac{\partial G}{\partial T} = -S$$

$$\frac{\partial G}{\partial p} = V$$

$$\frac{\partial G}{\partial n_j} = \mu_j$$

chemische
potentiaal

$$\Delta_f G^\ominus + RT \ln a_j$$

Gibbs energie

Veranderingen

$$dG = -SdT + Vdp + \sum_j \mu_j dn_j$$

$$\int_T^{T+\Delta T} SdT \approx S_{\Delta T} \int_p^{p+\Delta p} T dp$$

$$G = \sum_j n_j \Delta_f G_j$$