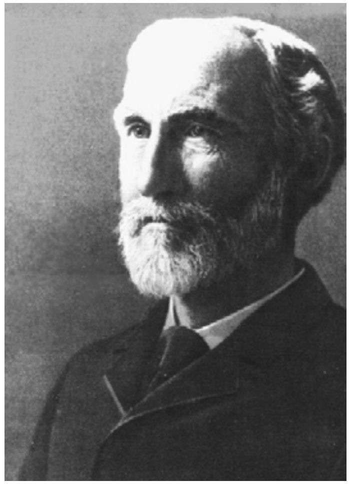
Overzicht

Hoofdwetten van de Thermodynamica

Samenvatting van ervaringsfeiten:

- 0^{de} hoofdwet: Thermisch evenwicht: thermometer
- 1^{ste} hoofdwet: Energiebehoud: thermochemie
- 2^{de} hoofdwet: Spontaniteit van processen: beschikbare arbeid
- 3^{de} hoofdwet: Absolute temperatuur

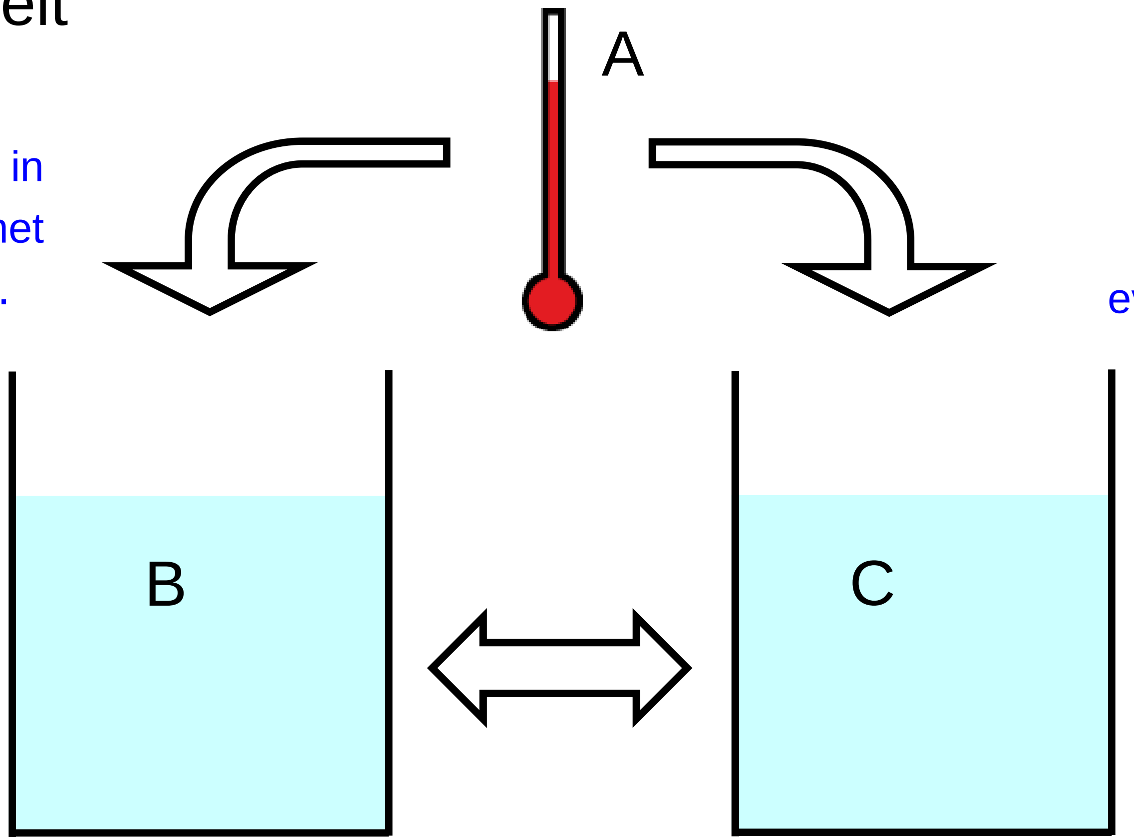


0de Hoofdwet: Thermisch evenwicht

Associativiteit

Als systeem A in evenwicht is met systeem B ...

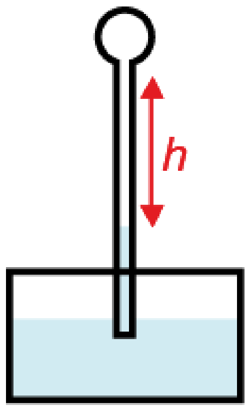
... en in evenwicht met systeem C



... dan is B in evenwicht met C.

0^{de} Hoofdwet: Thermometrie

Gasthermometer:



Gebaseerd op "ideale gaswet"

$$T \approx \frac{pV_m}{R}$$

10^5 Pa — molair volume $\frac{V}{n}$

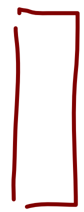
K — 8.314... $\frac{J}{K\,mol}$

$$V_m = \frac{RT}{P} = \frac{8.314 \times 300}{10^5}\ \frac{m^3}{mol} = 25\ \frac{L}{mol}$$

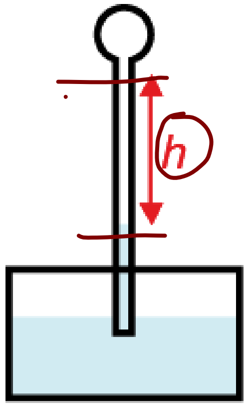
2500

methode — uitwerking

0^{de} Hoofdwet: Thermometrie



Gasthermometer:



$$h \propto \Delta T$$

$$p = \rho g h$$

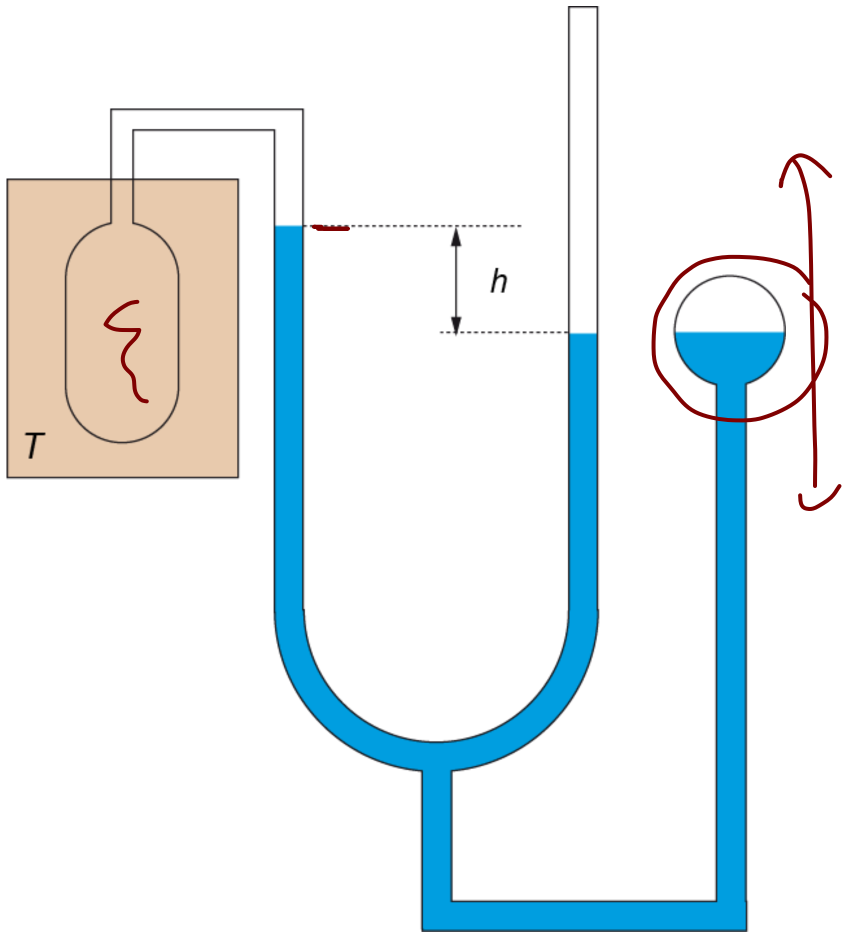
Voorbeeld:

0^{de} Hoofdwet: Thermometrie

Gasthermometer:

Verbeterde uitvoering: constant volume

$$\frac{T_1}{T_2} \approx \frac{p_1}{p_2} = \frac{h_1}{h_2}$$

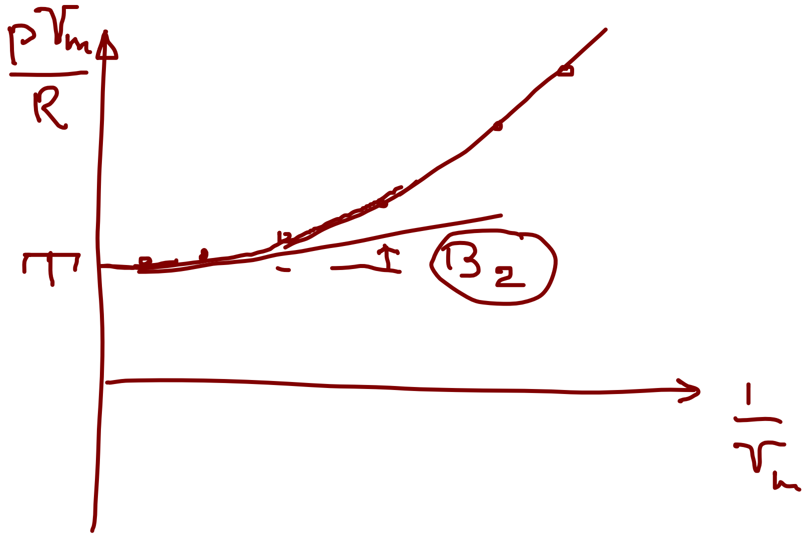


0^{de} Hoofdwet: Thermometrie

Voor realistische gassen:

Viriaalexpansie (H. Kamerlingh Onnes, 1853 – 1926)

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



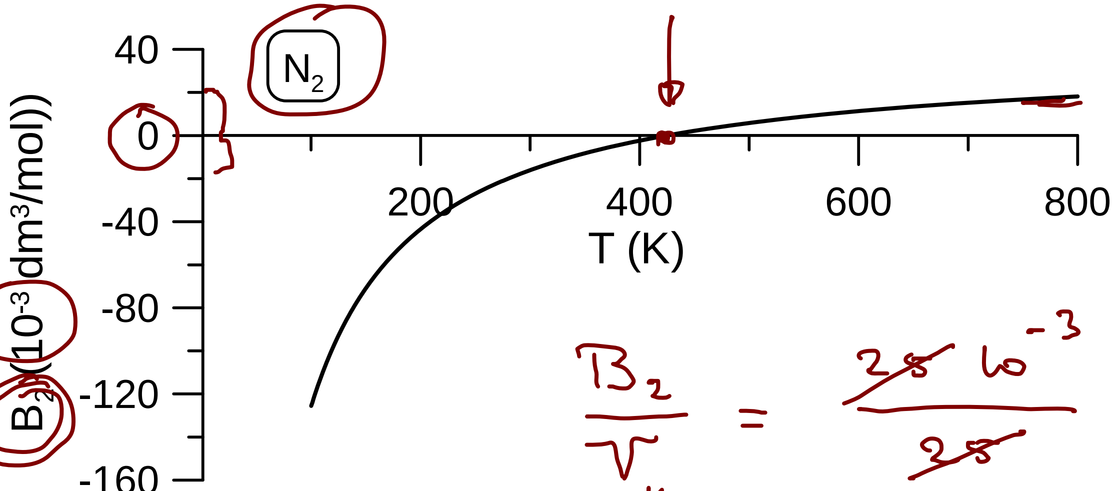
daarmee $$T = \lim_{V_m \to \infty} \frac{pV_m}{R}$$

Voorbeeld oneindige verdunningslimiet

0de Hoofdwet: Thermometrie

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

Viriaalcoëfficiënt:



1ste Hoofdwet: Energiebehoud

Energie is uitwisselbaar ...

Mechanisch
- – Potentiële energie
- – Kinetische energie

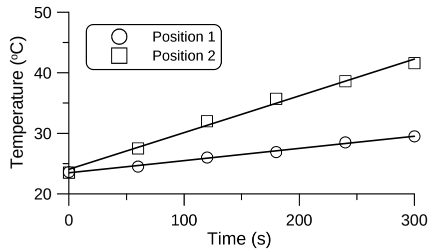
⇔ Elektrisch ← vrije electronen

⇔ Thermisch ← beweging molecule

⇔ Straling ← fotonen

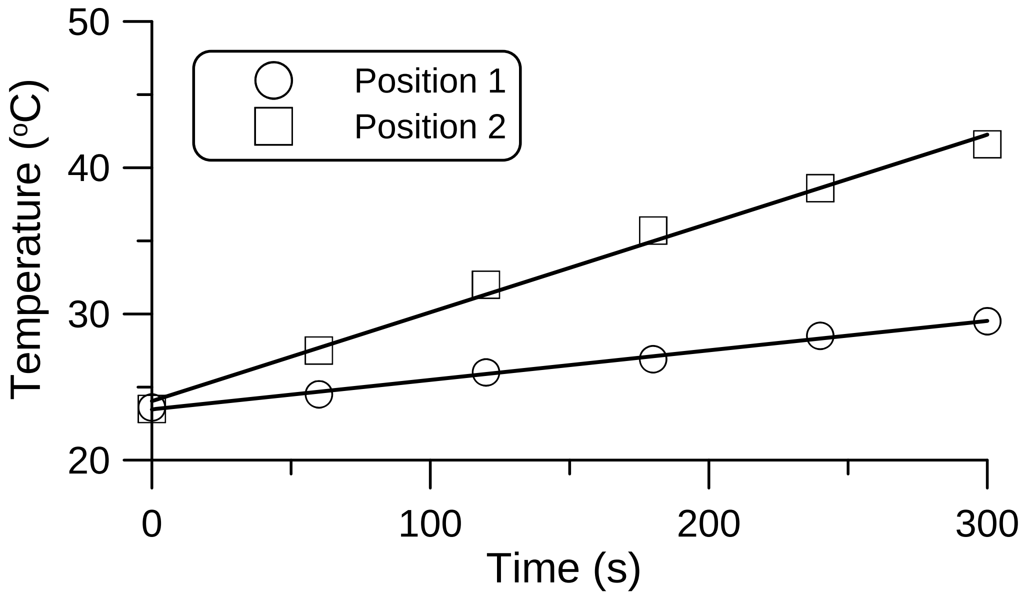
⇔ Nucleair ← binding elementaire deeltjes

⇔ Chemisch ← binding: electronen



1^{ste} Hoofdwet: Energiebehoud

Energie is uitwisselbaar ...



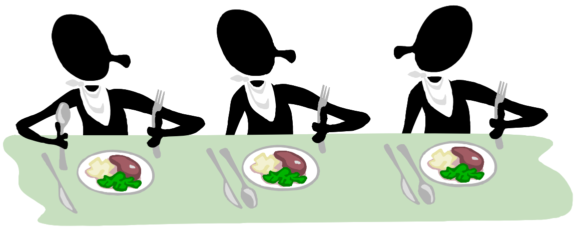
1^{ste} Hoofdwet: Energiebehoud

Energie is uitwisselbaar ...

... maar kan, net als massa, niet zomaar verdwijnen of ontstaan.

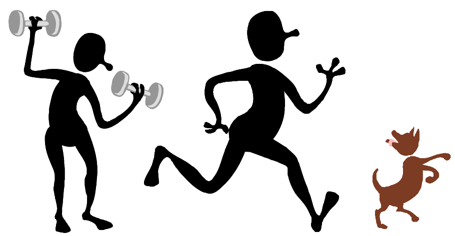
Wel is er een reserve: de enthalpie

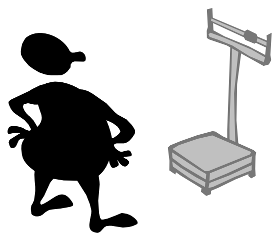
ΔH_{in}



$$\Delta H = \Delta H_{in} - \Delta H_{uit}$$

ΔH_{uit}



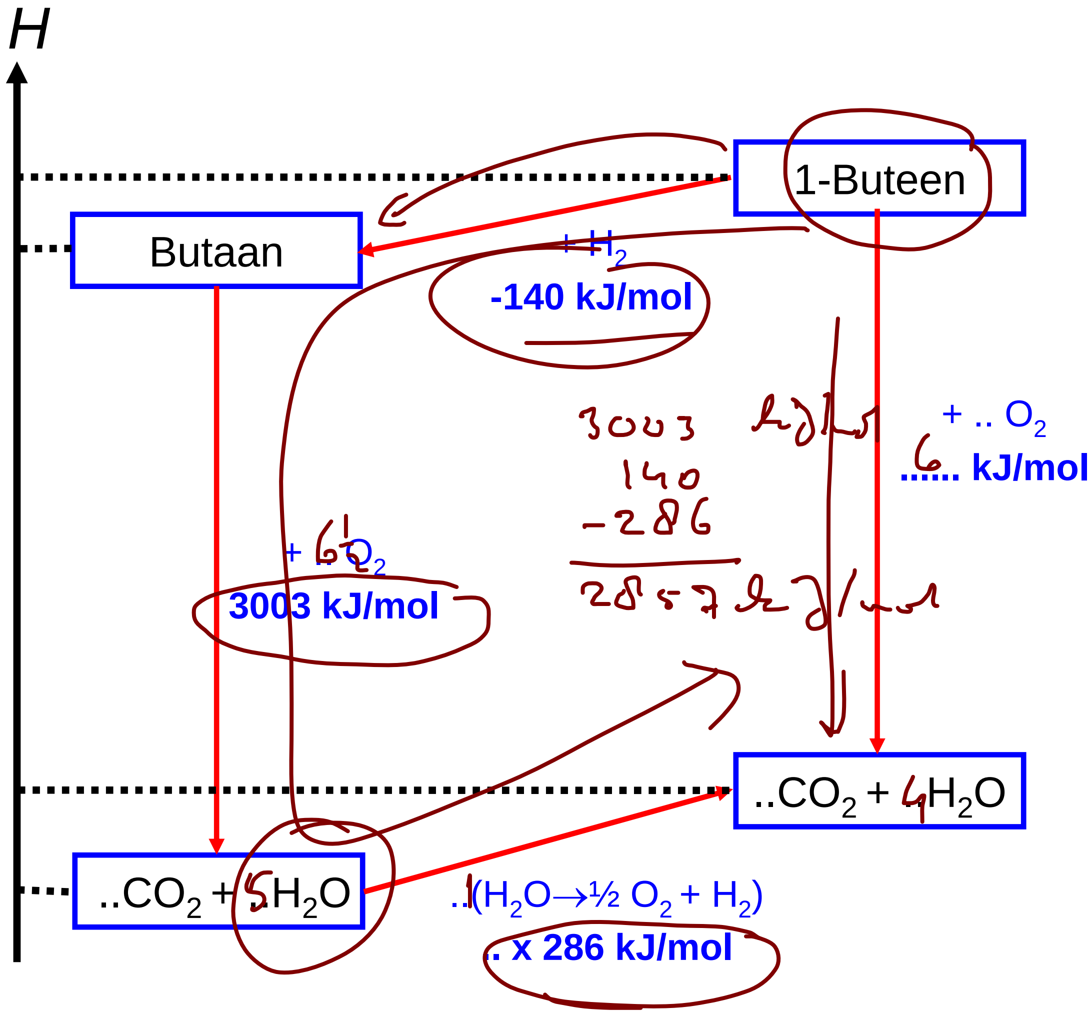


1ste Hoofdwet: Thermochemie

Wet van Hess

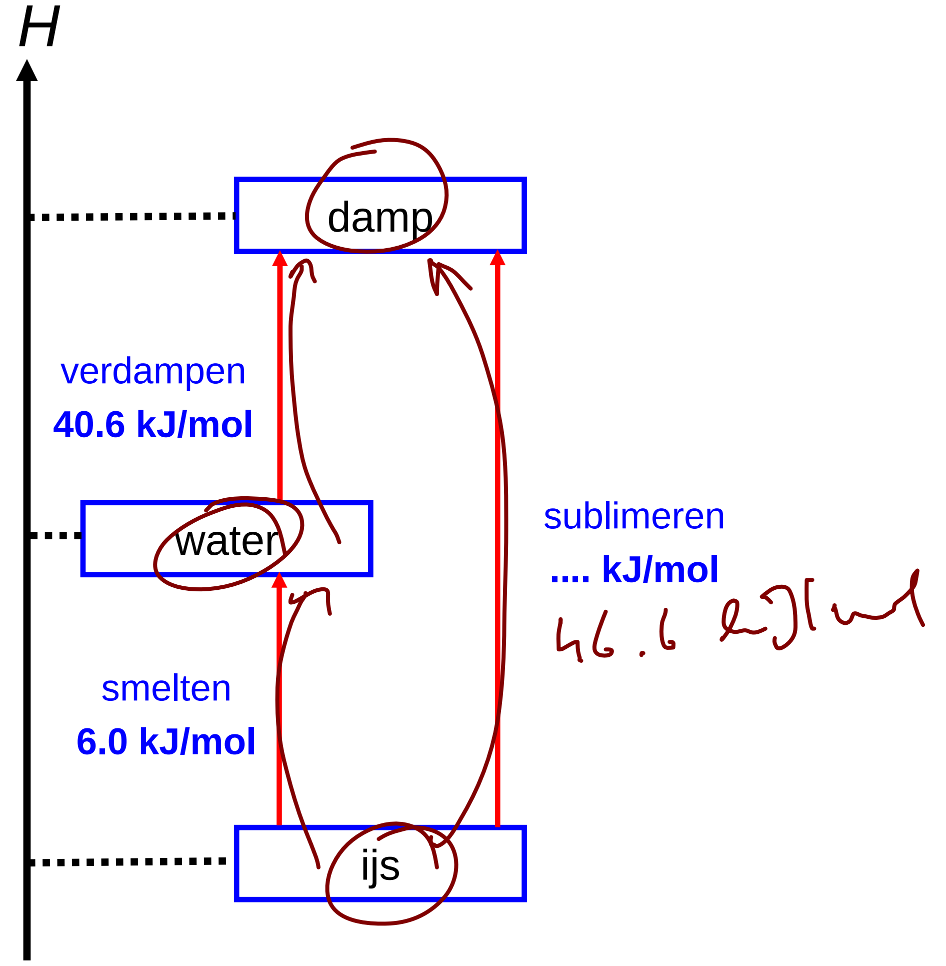
$C_4H_{10} + 6\frac{1}{2} O_2 \rightarrow 4 CO_2 + 5 H_2O$

$C_4H_8 + 6 O_2 \rightarrow 4 CO_2 + 4 H_2O$



1ste Hoofdwet: Thermochemie

Wet van Hess



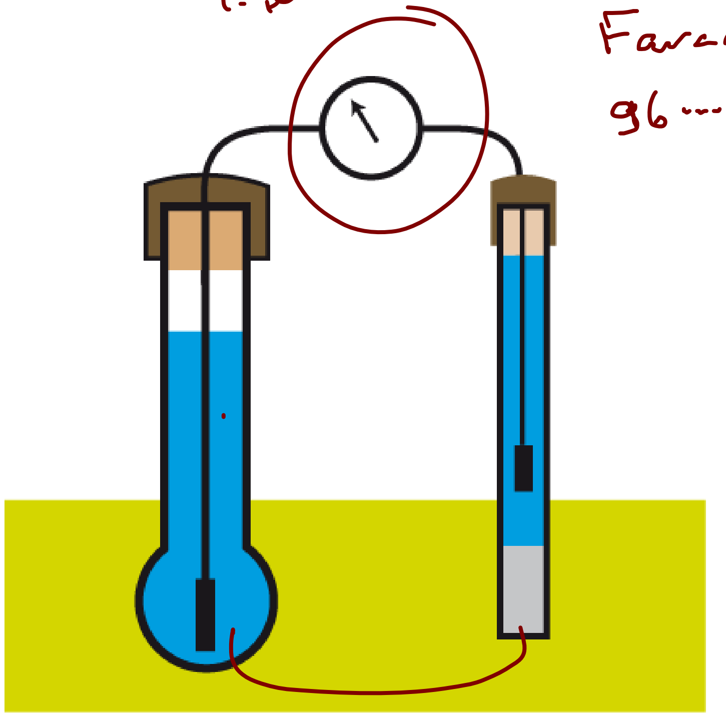
2^{de} Hoofdwet: Gibbs energie

... Meetbaar

$V = \frac{\Delta G}{\nu_e F}$

1.8 V ↗

Faraday cst 96... C/mol



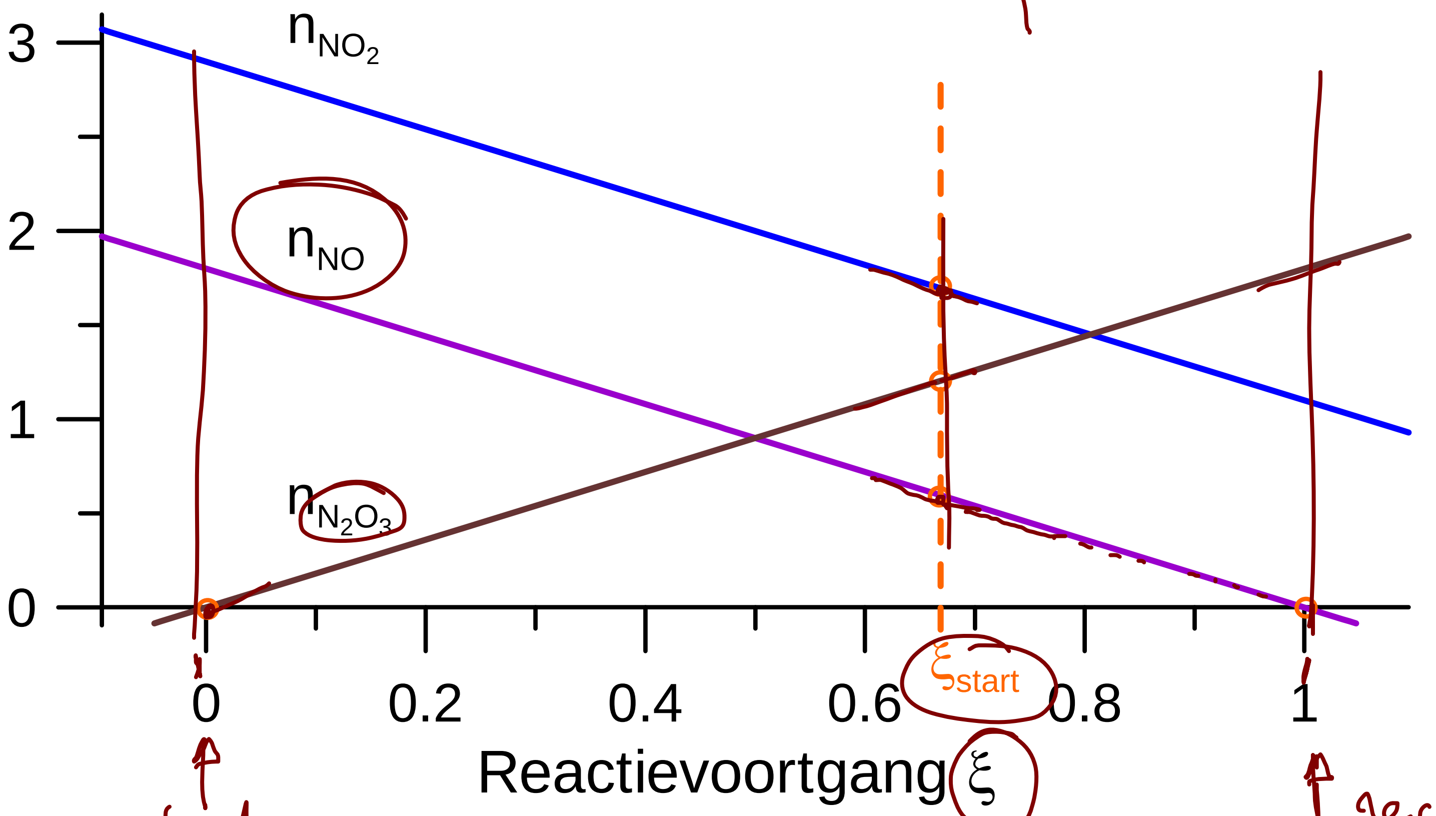
... en getabelleerd

$T^{\circ} = 298\ K \quad p^{\circ} = 1\ bar$

Molecular formula	Name	Crystal $\Delta_f H^\circ$ kJ/mol	Crystal $\Delta_f G^\circ$ kJ/mol	Crystal S° J/mol K	Crystal C_p J/mol K	Liquid $\Delta_f H^\circ$ kJ/mol	Liquid $\Delta_f G^\circ$ kJ/mol	Liquid S° J/mol K	Liquid C_p J/mol K	Gas $\Delta_f H^\circ$ kJ/mol	Gas $\Delta_f G^\circ$ kJ/mol	Gas S° J/mol K	Gas C_p J/mol K
Cl_3V	Vanadium(III) chloride	-580.7	-511.2	131.0	93.2								
Cl_3Y	Yttrium chloride	-1000.0								-750.2			75.0
Cl_3Yb	Ytterbium(III) chloride	-959.8											
Cl_4Ge	Germanium(IV) chloride					-531.8	-462.7	245.6		-495.8	-457.3	347.7	96.1
Cl_4Hf	Hafnium(IV) chloride	-990.4	-901.3	190.8	120.5					-884.5			
Cl_4Pa	Protactinium(IV) chloride	-1043.0	-953.0	192.0									
Cl_4Pb	Lead(IV) chloride					-329.3							
Cl_4Pt	Platinum(IV) chloride	-231.8											
Cl_4Si	Tetrachlorosilane					-687.0	-619.8	239.7	145.3	-657.0	-617.0	330.7	90.3
Cl_4Sn	Tin(IV) chloride					-511.3	-440.1	258.6	165.3	-471.5	-432.2	365.8	98.3
Cl_4Te	Tellurium tetrachloride	-326.4			138.5								
Cl_4Th	Thorium(IV) chloride	-1186.2	-1094.1	190.4	120.3					-964.4	-932.0	390.7	107.5
Cl_4Ti	Titanium(IV) chloride					-804.2	-737.2	252.3	145.2	-763.2	-726.3	353.2	95.4
Cl_4U	Uranium(IV) chloride	-1019.2	-930.0	197.1	122.0					-809.6	-786.6	419.0	
Cl_4V	Vanadium(IV) chloride					-569.4	-503.7	255.0		-525.5	-492.0	362.4	96.2
Cl_4Zr	Zirconium(IV) chloride	-980.5	-889.9	181.6	119.8								
Cl_5Nb	Niobium(V) chloride	-797.5	-683.2	210.5	148.1					-703.7	-646.0	400.6	120.8
Cl_5P	Phosphorus(V) chloride	-443.5								-374.9	-305.0	364.6	112.8
Cl_5Pa	Protactinium(V) chloride	-1145.0	-1034.0	238.0									
Cl_5Ta	Tantalum(V) chloride	-859.0											
Cl_6U	Uranium(VI) chloride	-1092.0	-962.0	285.8	175.7					-1013.0	-928.0	431.0	
Cl_6W	Tungsten(VI) chloride	-602.5								-513.8			
Cm	Curium	0.0											
Co	Cobalt	0.0		30.0	24.8					424.7	380.3	179.5	23.0
CoF_2	Cobalt(II) fluoride	-692.0	-647.2	82.0	68.8								
CoH_2O_2	Cobalt(II) hydroxide	-539.7	-454.3	79.0									
CoI_2	Cobalt(II) iodide	-88.7											
CoN_2O_6	Cobalt(II) nitrate	-420.5											
CoO	Cobalt(II) oxide	-237.9	-214.2	53.0	55.2								
CoO_4S	Cobalt(II) sulfate	-888.3	-782.3	118.0									
CoS	Cobalt(II) sulfide	-82.8											
Co_2S_3	Cobalt(III) sulfide	-147.3											
Co_3O_4	Cobalt(II,III) oxide	-891.0	-774.0	102.5	123.4								
Cr	Chromium	0.0		23.8	23.4					396.6	351.8	174.5	20.8
CrF_2	Chromium(II) fluoride	-778.0											
CrF_3	Chromium(III) fluoride	-1159.0	-1088.0	93.9	78.7								

2^{de} Hoofdwet: Spontaniteit van Processen

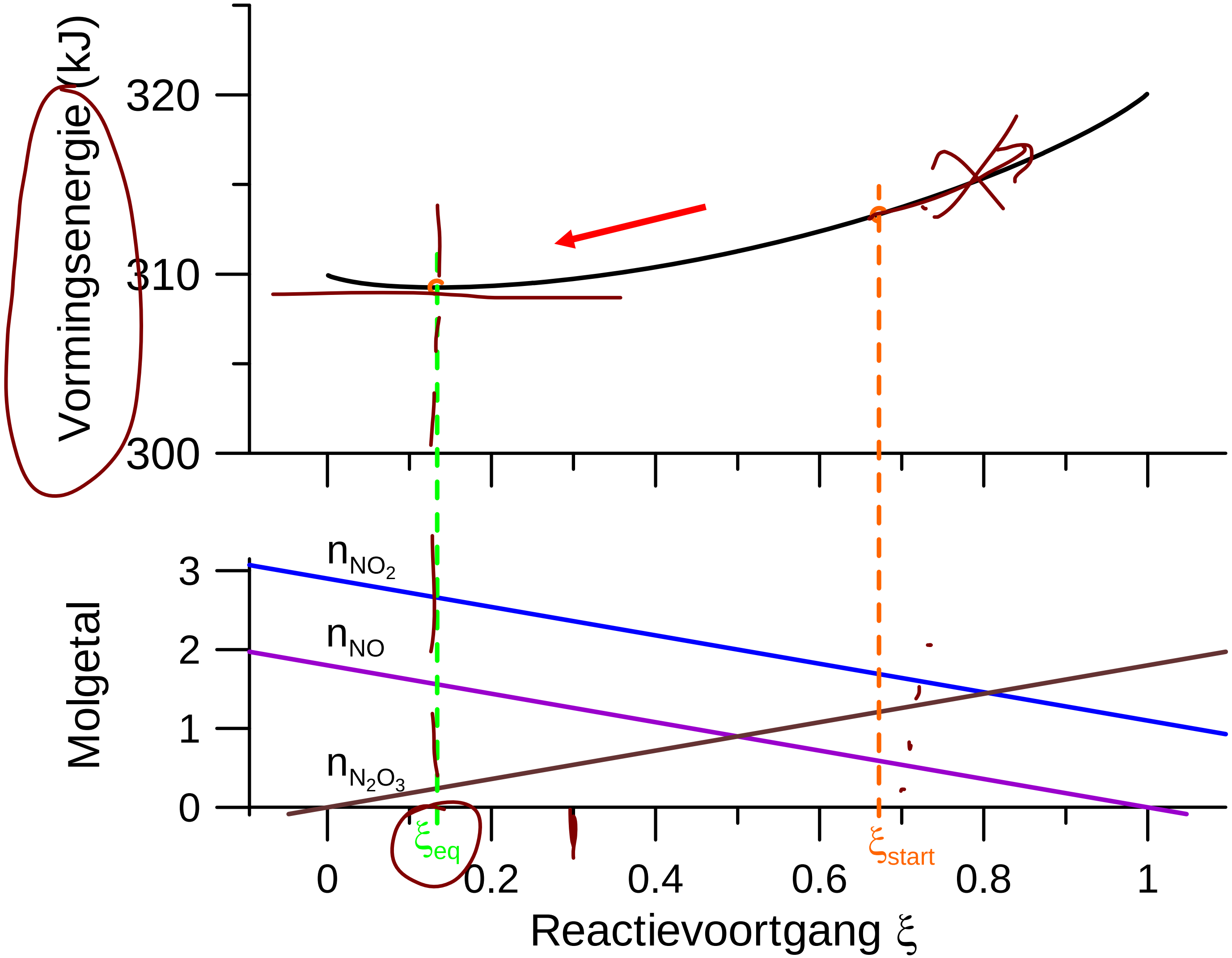
Reactie $NO + NO_2 \Leftrightarrow N_2O_3$, voortgang $\Delta\xi = \Delta n_k / \nu_k$



Welke kant gaat dit op?

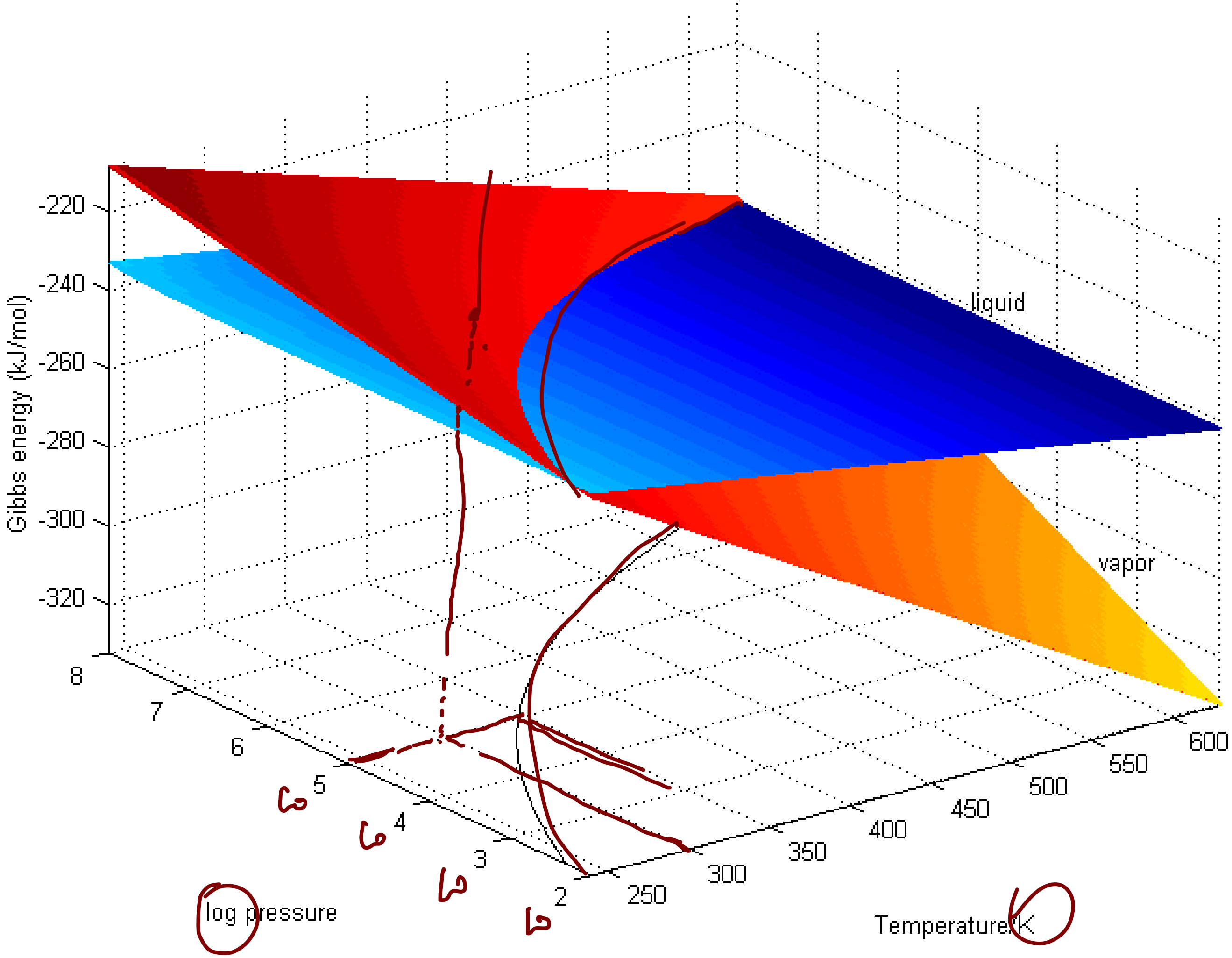
2^{de} Hoofdwet: Spontaniteit van Processen

Dat hangt van de “affiniteit” af*!*



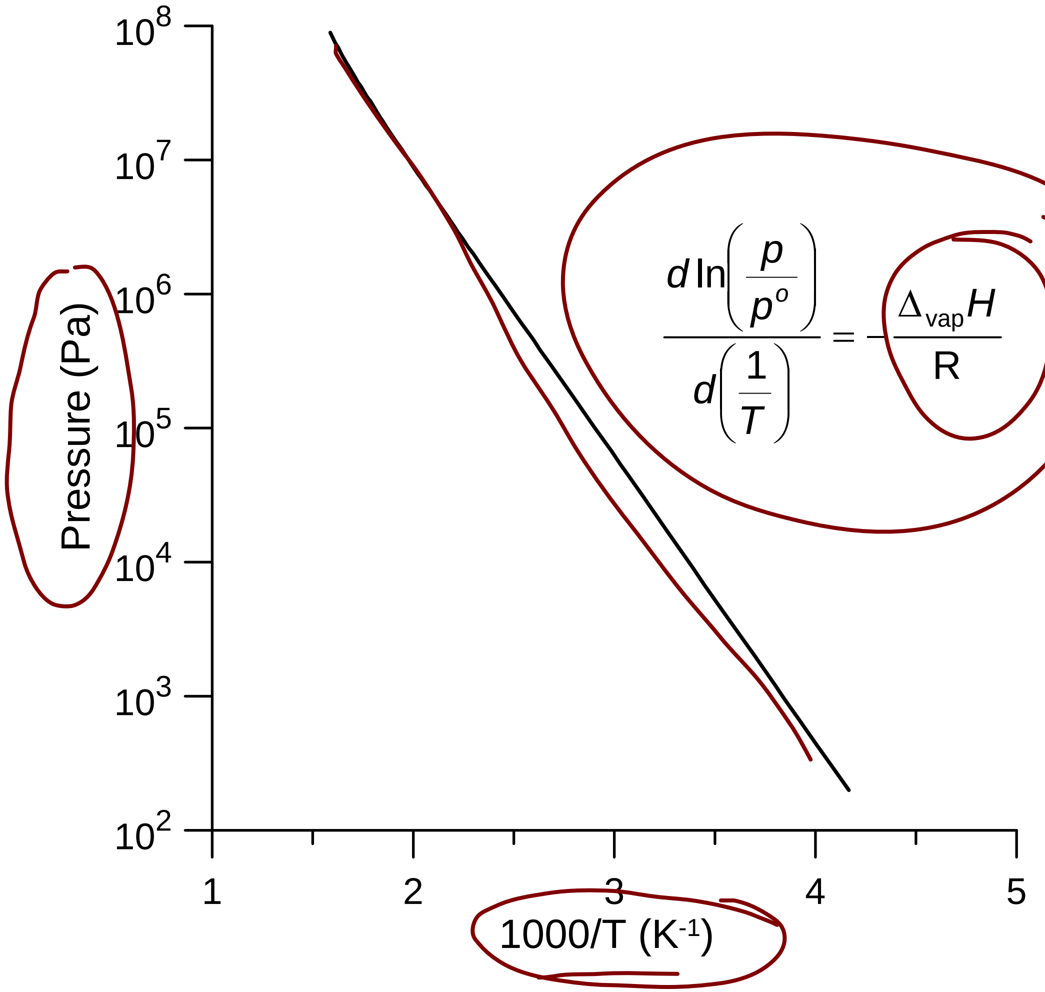
2de Hoofdwet: Fasenevenwichten

Vloeistof – damp evenwicht



2^{de} Hoofdwet: Fasenevenwichten

Fasenlijn voldoet aan Clausius – Clapeyron vergelijking



$$\frac{d\ln\left(\frac{p}{p^o}\right)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta_{vap}H}{R}$$

2de Hoofdwet: Fasenevenwichten

$$\frac{d\ln\left(\frac{p}{p^o}\right)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta_{vap}H}{R}$$

Voorbeeld Clausius – Clapeyron vergelijking

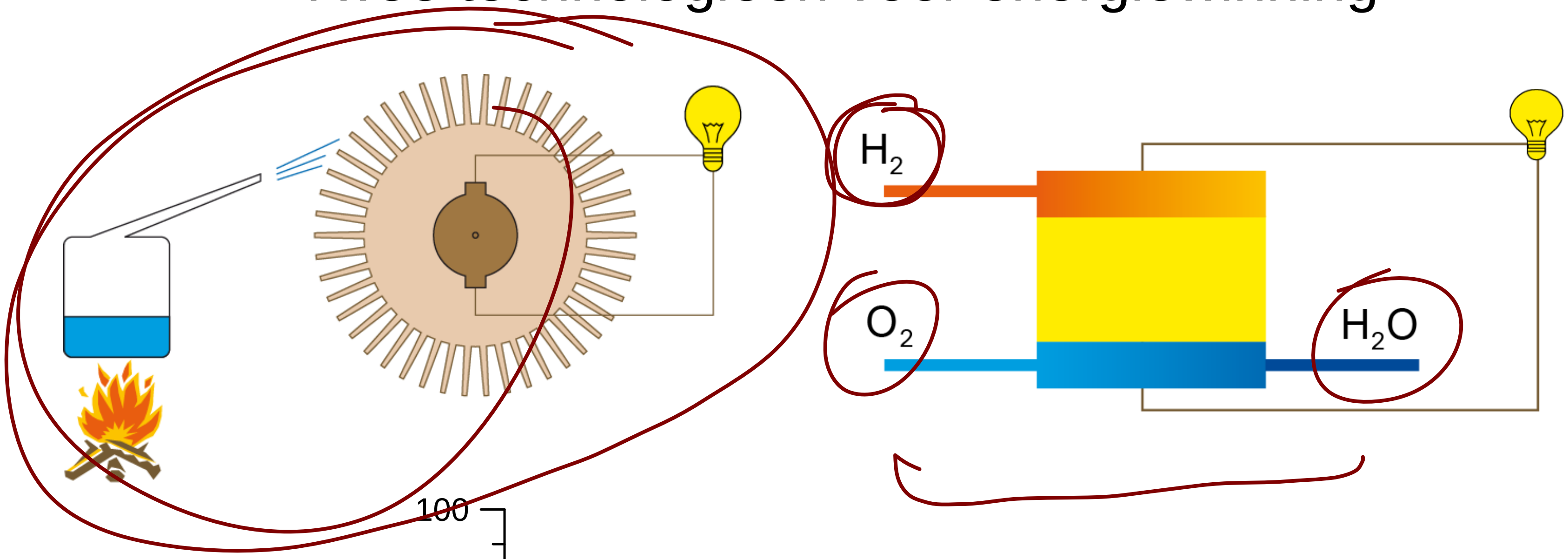
$$d\ln\left(\frac{p}{p^o}\right) = -\frac{\Delta_{vap}H}{R}\, d\frac{1}{T}$$

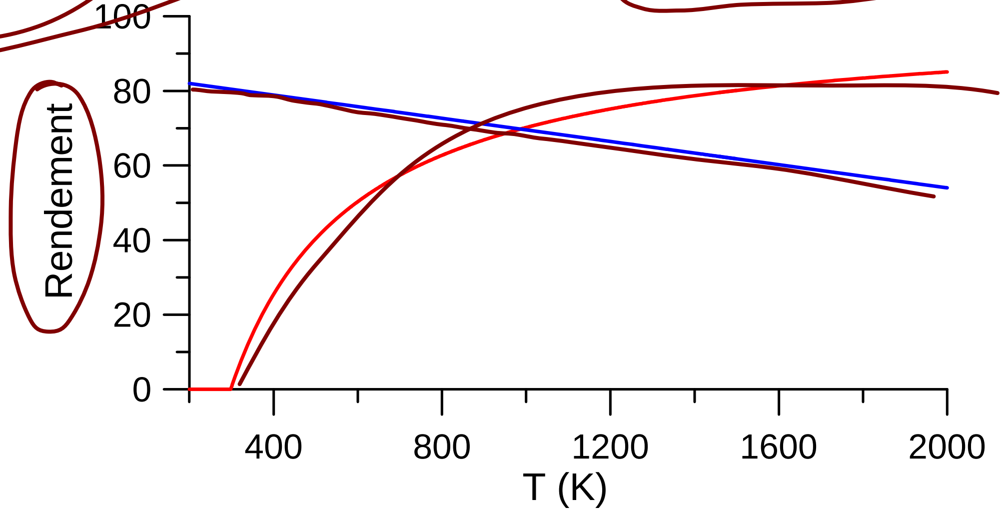
$$\int_{p_1}^{p_2}$$

$$\ln\frac{p_2}{p_1} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

2^{de} Hoofdwet: Beschikbare Arbeid

Twee technologieën voor energiewinning





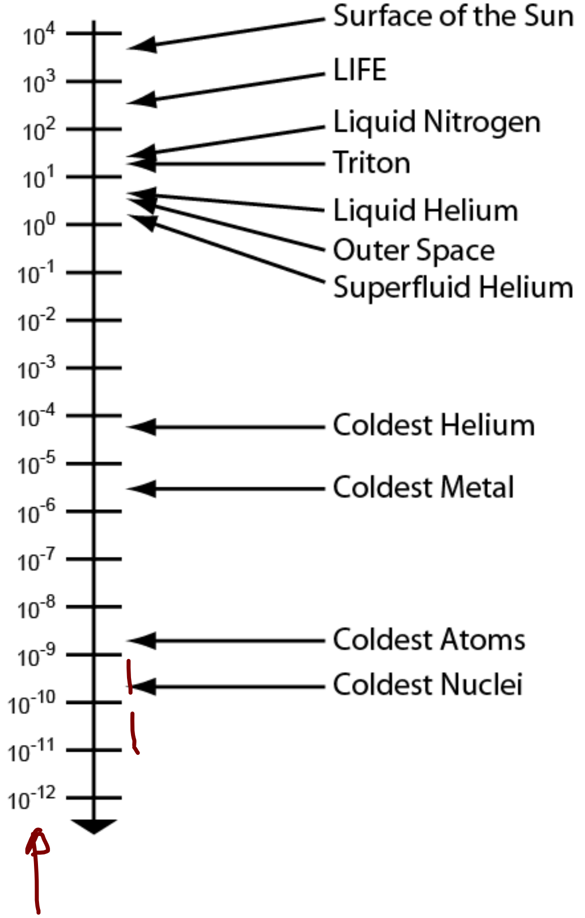
2^{de} Hoofdwet: Beschikbare Arbeid

Voorbeeld brandstofcel

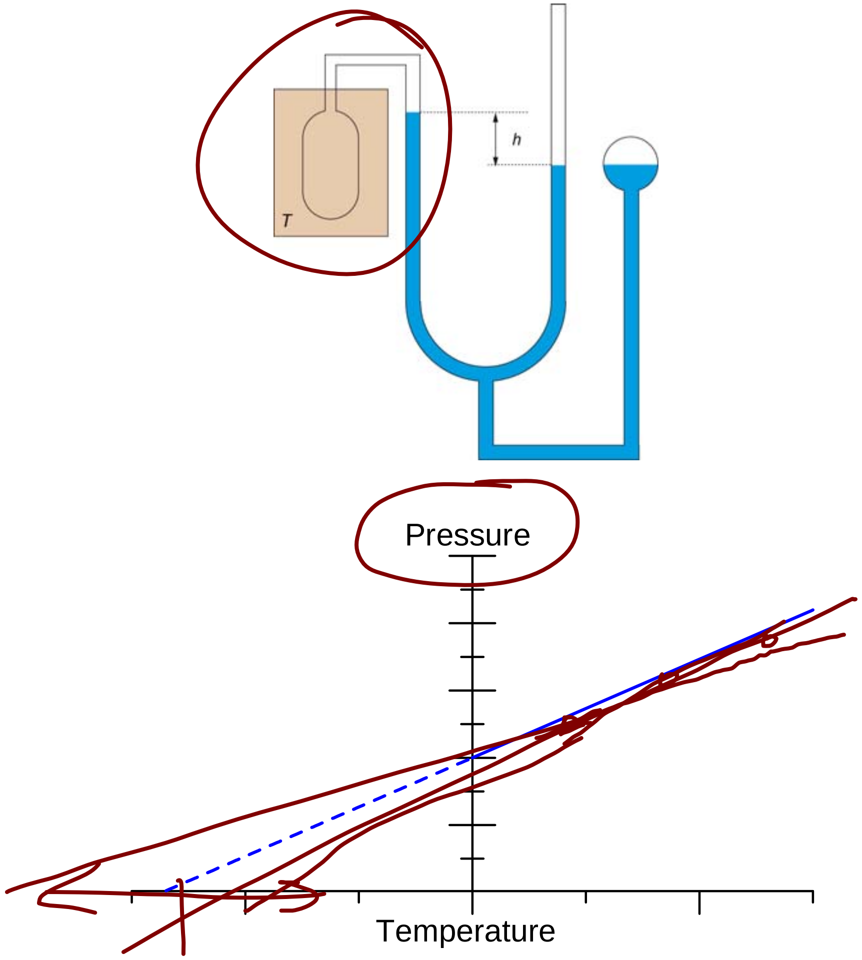
opgave

3^{de} Hoofdwet: Absolute Nulpunt

Is nooit haalbaar ...



... behalve door extrapolatie



3de Hoofdwet: Absolute Nulpunt

Voorbeeld: