Standardna Gibbsova energija reakcije

$G_r^{\theta}(T)$

Kombinacija standardne entropije i entalpije reakcije

$$\Delta_r G^{\theta} = \Delta_r H^{\theta} - T\Delta_r S^{\theta}$$

Standardna Gibbsova energija formiranja/stvaranja

$\Delta_f G^{\theta}$

Prema konvenciji:

$\Delta_f G^\theta$ elemenata u referentnom stanju jednake su nuli

$$\Delta_r G^\theta = \sum_{produkti} \nu \Delta_f G^\theta - \sum_{reaktanti} \nu \Delta_f G^\theta$$

$$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$$

$$\Delta_r G^{\theta}(298\,K) =$$

$$= \Delta_f G^{\theta}(CO_2, g) - \left[\Delta_f G^{\theta}(CO, g) + \frac{1}{2} \cdot \Delta_f G^{\theta}(O_2, g) \right] =$$

	$\Delta_f G^\theta\ (298) / kJmol^{-1}$
C, dijamant (s)	2,9
$CH_4(g)$	-50,7
$CO_2(g)$	-394,36
H_2O (l)	-237,1
$NH_3(g)$	-16,5
NaCl (s)	-384,1
CO(g)	-137,2
C_6H_6(l)	124,3

$$CO(g)+\frac{1}{2}O_2(g)\rightarrow CO_2(g)$$

$$\Delta_r G^{\theta}(298\,K)=$$

$$=\Delta_f G^{\theta}(CO_2,g)-\left[\Delta_f G^{\theta}(CO,g)+\frac{1}{2}\cdot\Delta_f G^{\theta}(O_2,g)\right]=$$

$$=-394{,}4\ -\left[-137{,}2+\frac{1}{2}\cdot 0\right]=$$

$$=-257\,,2kJmol^{-1}$$

$$\Delta_r G^\theta = \sum_{produkti} \nu \Delta_f G^\theta - \sum_{reaktanti} \nu \Delta_f G^\theta$$

Kad nismo kod standardnih uvjeta moramo znati

$$G = f(p,T)$$

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$$

Parcijalni diferencijalni kvocijenti

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$dU = \delta Q + \delta W$$

$$dS = \frac{\delta Q}{T} \qquad \delta Q = TdS$$

$$\delta W = -pdV$$

$$dU = TdS - pdV$$

$$dG = \cancel{TdS} - \cancel{pdV} + \cancel{pdV} + Vdp - \cancel{TdS} - SdT$$

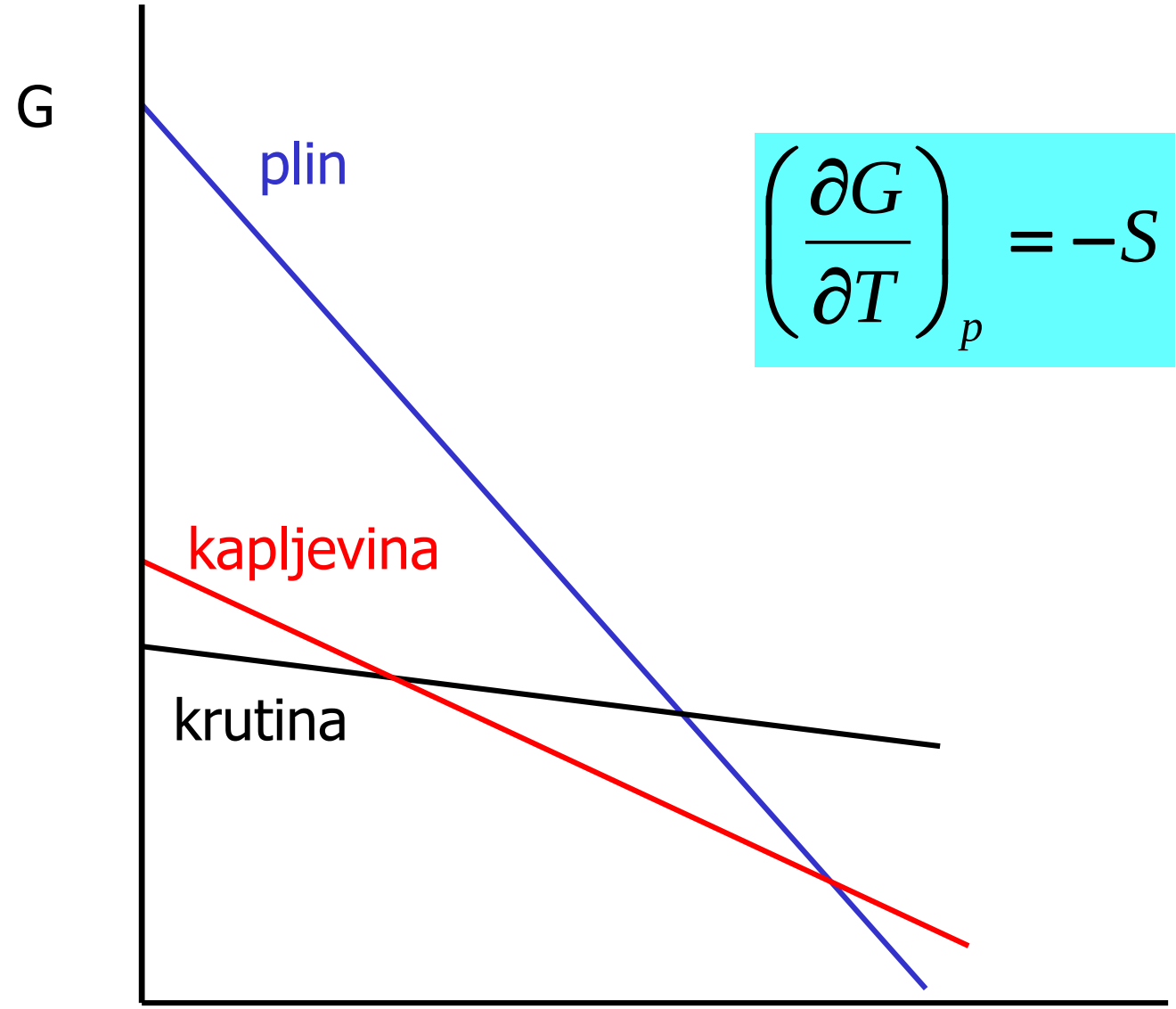
Zatvoreni sustav, koji ne vrši dodatni (neekspanzijski) rad

$$dG = Vdp - SdT$$

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$$

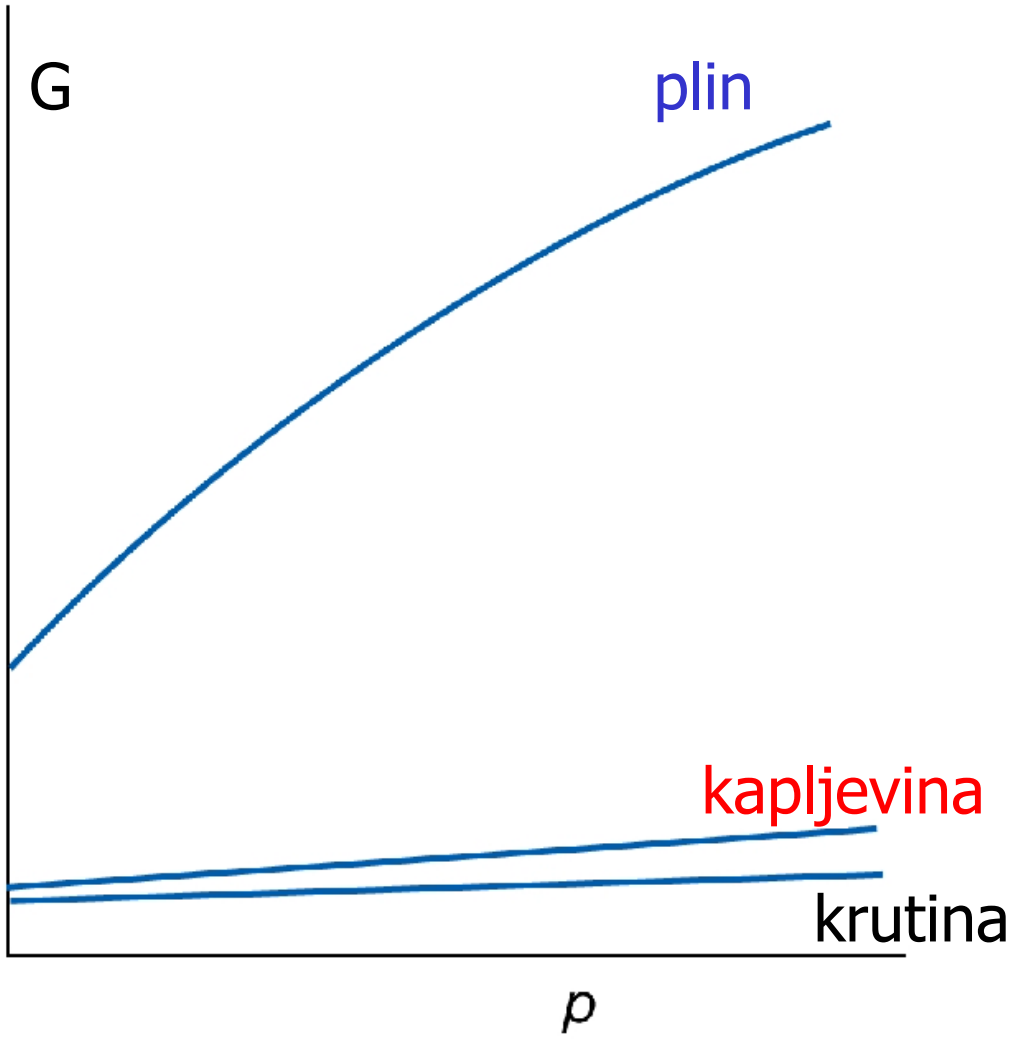
$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$



$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$S > 0 \rightarrow G \downarrow \; kad \;\; T \uparrow \qquad (p = konst.)$$



$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$V > 0 \rightarrow G \uparrow \; kad \quad p \uparrow \qquad (T = konst.)$$

Ovisnost Gibbsove energije o temperaturi

T ≠ konst, p=konst

$$G = H - TS$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_p$$

GIBBS-HELMHOLTZOVA JEDNADŽBA

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_p \quad / T$$

IV semestar:

$$\frac{G}{T} = \frac{H}{T} + \left(\frac{\partial G}{\partial T}\right)_p$$

Konstanta ravnoteže reakcije ovisi o G/T

$\Delta_r G^\theta/T = -R\ln K$

$$\left[\frac{d\left(\frac{G}{T}\right)}{dT}\right]_p = \left[\frac{d(GT^{-1})}{dT}\right]_p = \left(\frac{dG}{dT}\right)_p \cdot \frac{1}{T} - \frac{G}{T^2}$$

$$\left(\frac{dG}{dT}\right)_p \cdot \frac{1}{T} - \frac{G}{T^2} = \frac{T\left(\frac{dG}{dT}\right)_p - G}{T^2} = \frac{\cancel{G} - H - \cancel{G}}{T^2}$$

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_p$$

$$\left[\frac{d\left(\frac{G}{T}\right)}{dT}\right]_p = \frac{-H}{T^2}$$

$$\left[\frac{d\left(\frac{G}{T}\right)}{dT}\right]_p = \left[\frac{d\left(\frac{G}{T}\right)}{d\left(\frac{1}{T}\right)}\right]_p \cdot \frac{d\left(\frac{1}{T}\right)}{dT} = \left[\frac{d\left(\frac{G}{T}\right)}{d\left(\frac{1}{T}\right)}\right] \cdot \left(-\frac{1}{T^2}\right) = \frac{-H}{T^2}$$

$$\left[\frac{d\left(\frac{G}{T}\right)}{d(1/T)}\right]_p = H$$

Za promjene fizikalnih stanja ili kemijsko reakciju

$$\left[\frac{d\left(\frac{\Delta G}{T}\right)}{dT}\right]_p = \frac{-\Delta H}{T^2}$$

$$d\left(\frac{\Delta G}{T}\right) = \frac{-\Delta H}{T^2}\cdot dT \qquad / \int$$

$$\frac{\Delta G}{T} = \int \frac{-\Delta H}{T^2} \cdot dT + I_2$$

$$\Delta H(T) = \Delta a \cdot T + \frac{\Delta b}{2} \cdot T^2 - \Delta c \cdot T^{-1} + I_1$$

$$\frac{\Delta G}{T} = \int - \frac{(\Delta a \cdot T + \frac{\Delta b}{2} \cdot T^2 - \Delta c \cdot T^{-1} + I_1)}{T^2} \cdot dT + I_2$$

I_1 Kirchhoff-ov zakon ($\Delta H(298)$)

Uz poznavanje $\Delta G(298)$- izračunavanje I_2

Za određeni temperaturni interval:

$$\int_{T_1}^{T_2} d\left(\frac{\Delta G}{T}\right) = \left(\frac{\Delta G_2}{T_2}\right) - \left(\frac{\Delta G_1}{T_1}\right) =$$

$$= -\int_{T_1}^{T_2} \frac{(\Delta a \cdot T + \frac{\Delta b}{2} \cdot T^2 - \Delta c \cdot T^{-1})}{T^2} \cdot dT$$

$$\left[\frac{d\left(\frac{G}{T}\right)}{d(1/T)}\right]_p = H$$

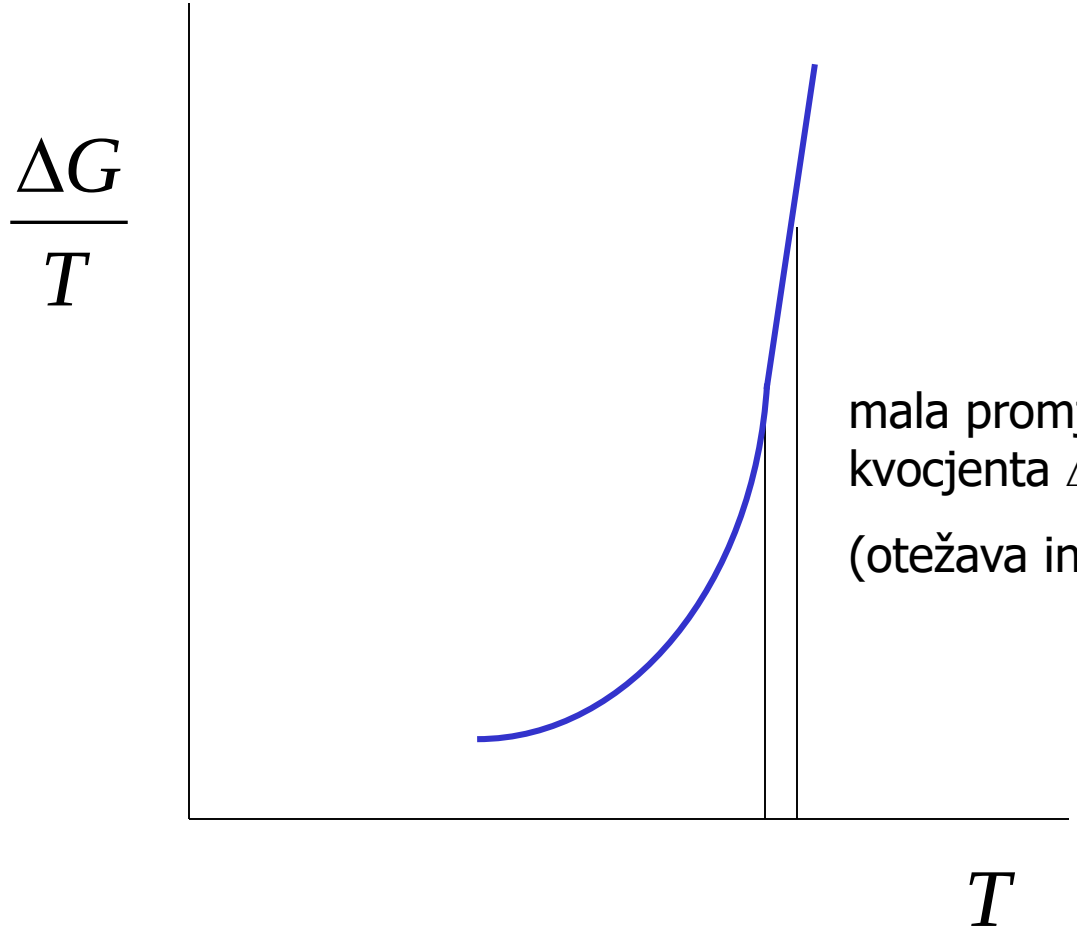
Za "uski" temperaturni interval (ΔT<50 K)

$$\left(\frac{\Delta G_2}{T_2}\right) - \left(\frac{\Delta G_1}{T_1}\right) = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{\Delta G}{T} \quad vs. \quad T$$

-tablice

-grafički prikazi



mala promjena T$\rightarrow$ velika promjena kvocjenta ΔG/T

(otežava interpolaciju/ekstrapolaciju)

GIAUQUE FUNKCIJA, Φ

$$\Phi = \frac{G^{\theta}(T) - H^{\theta}(298)}{T}$$

$$\frac{G^{\theta}(T)}{T} = \Phi + \frac{H^{\theta}(298)}{T}$$

$$\frac{\Delta G_r{}^{\theta}(T)}{T} = \Delta_r \Phi + \frac{\Delta H_r{}^{\theta}(298)}{T}$$

$\Delta_r \Phi$ → tablice

$\frac{\Delta H_r{}^{\theta}(298)}{T}$ → iz standardnih entalpija formiranja spoja

Ovisnost $\Delta\Phi$ o T nije više tako strma u usporedbi s krivuljom $\Delta G/T$ vs. T → lakša, preciznija interpolacija/ekstrapolacija.

Ovisnost Gibbsove energije o tlaku

T=konst, p≠konst

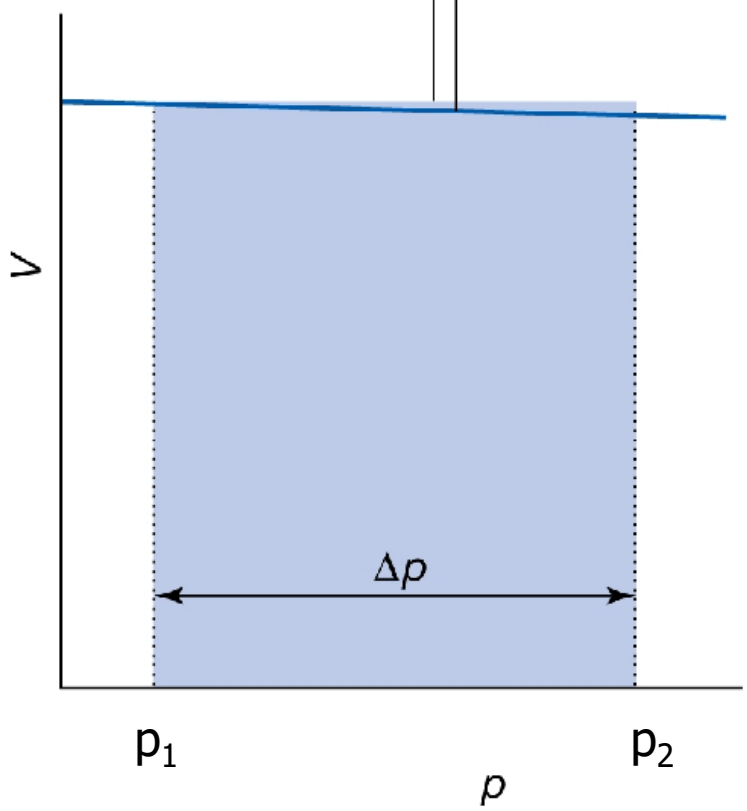
$$dG = Vdp - SdT$$

$$dG = Vdp$$

1.Kondenzirane faze (krutine i kapljevine)

Pretpostavljeni konstantni volumen

Stvarni volumen



$$dG = Vdp$$

1. Kondenzirane faze (krutine i kapljevine)

$$\int dG = V \int dp$$

$$\int_{G_{m,1}}^{G_{m,2}} dG_m = V_m \int_{p_1}^{p_2} dp$$

$$G_{m,2} - G_{m,1} = \Delta G_m = V_m (p_2 - p_1) = V_m \Delta p$$

?ΔG_m ($H_2O(l)$)

pri porastu tlaka od 1,0 na 2,0 bara, pri 298 K

$$V_m = 18{,}0\, cm^3 mol^{-1}$$

$$G_{m,2} - G_{m,1} = \Delta G_m = V_m \Delta p$$

$$\Delta G_m = 18{,}0 \cdot 10^{-6}\, m^3 mol^{-1} \cdot 1 \cdot 10^5\, Pa =$$

$$= \boxed{+1{,}8\, J mol^{-1}}$$

?ΔG_m leda pri -10°C, gustoće 0,917gcm^{-3}, pri porastu tlaka od 1,0 na 2,0 bara

$$V_m = \frac{M}{\rho}$$

$$G_{m,2} - G_{m,1} = \Delta G_m = V_m \Delta p$$

$$\Delta G_m = \frac{18{,}0 \cdot g mol^{-1}}{0{,}917 g \cdot 10^6 m^{-3}} \cdot 1 \cdot 10^5 Pa =$$

$$= \boxed{+1{,}96 Jmol^{-1}}$$

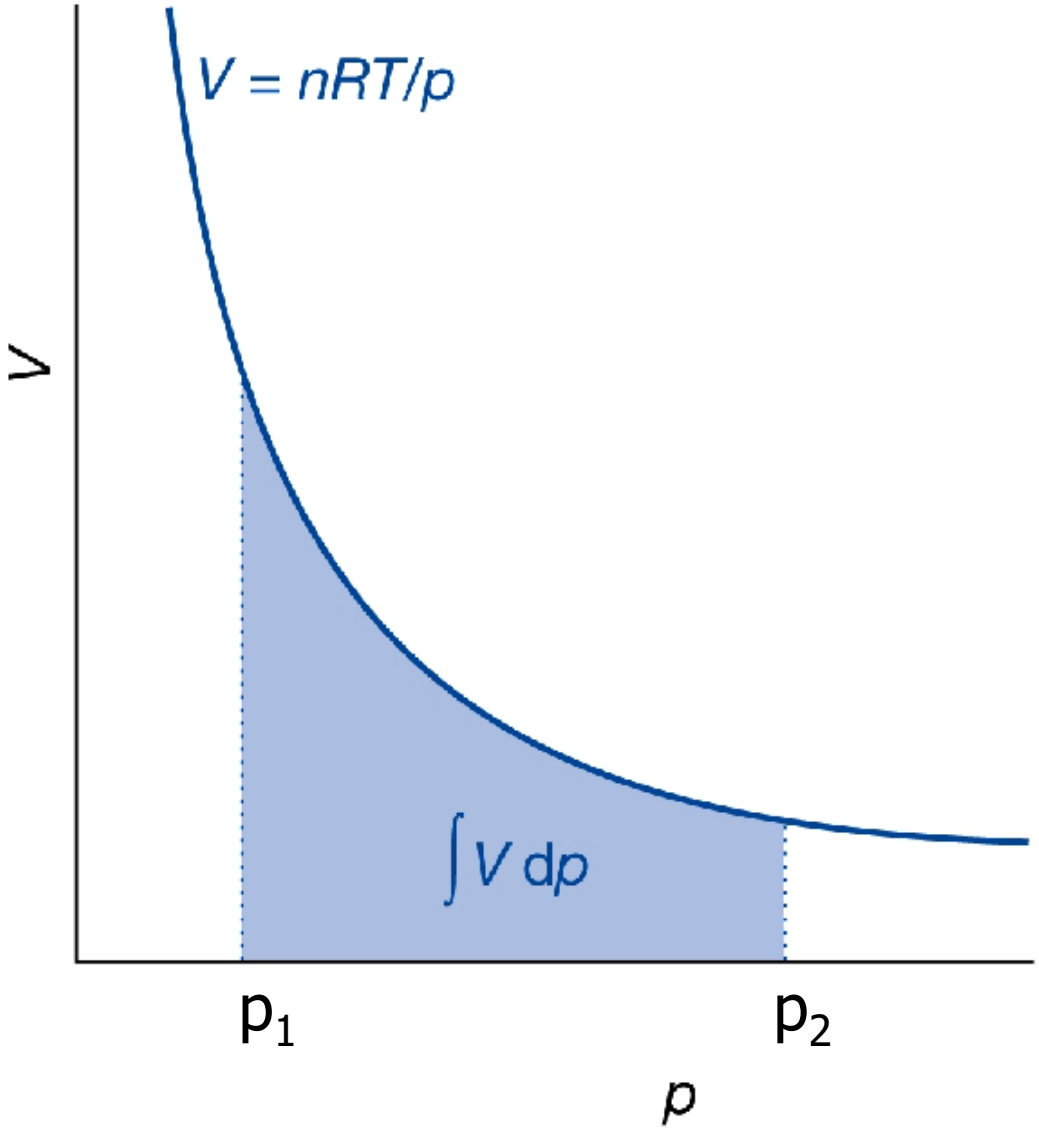
2.Plinovi

Volumen značajno ovisi o tlaku !

$$\int_{G_1}^{G_2} dG = G_2 - G_1 = \Delta G = \int_{p_1}^{p_2} V dp$$

2 a. Idealni plinovi

$$V = \frac{nRT}{p}$$


V = nRT/p
V
∫V dp
p1
p2
p

$$V = \frac{nRT}{p}$$

$$\int_{G_1}^{G_2} dG = G_2 - G_1 = \Delta G = nRT \int_{p_1}^{p_2} \frac{dp}{p} = nRT \ln \frac{p_2}{p_1}$$

$$\Delta G_m = RT \ln \frac{p_2}{p_1}$$

$p_2 = 10\ p_1$

T=298 K

$$\Delta G_m = 8{,}314\ Jmol^{-1}K^{-1} \cdot 298\ K \cdot 2{,}303 = 5704{,}82\ Jmol^{-1}$$

?ΔG_m vodene pare (uz pretpostavku da se ponaša kao idealni plin)

pri porastu tlaka od 1,0 na 2,0 bara, pri 298 K

$$\Delta G_m = RT \ln \frac{p_2}{p_1}$$

$$\Delta G_m = 8{,}314\, J mol^{-1} K^{-1} \cdot 298\, K \cdot \ln 2 =$$

$$= +1717\ J mol^{-1}$$

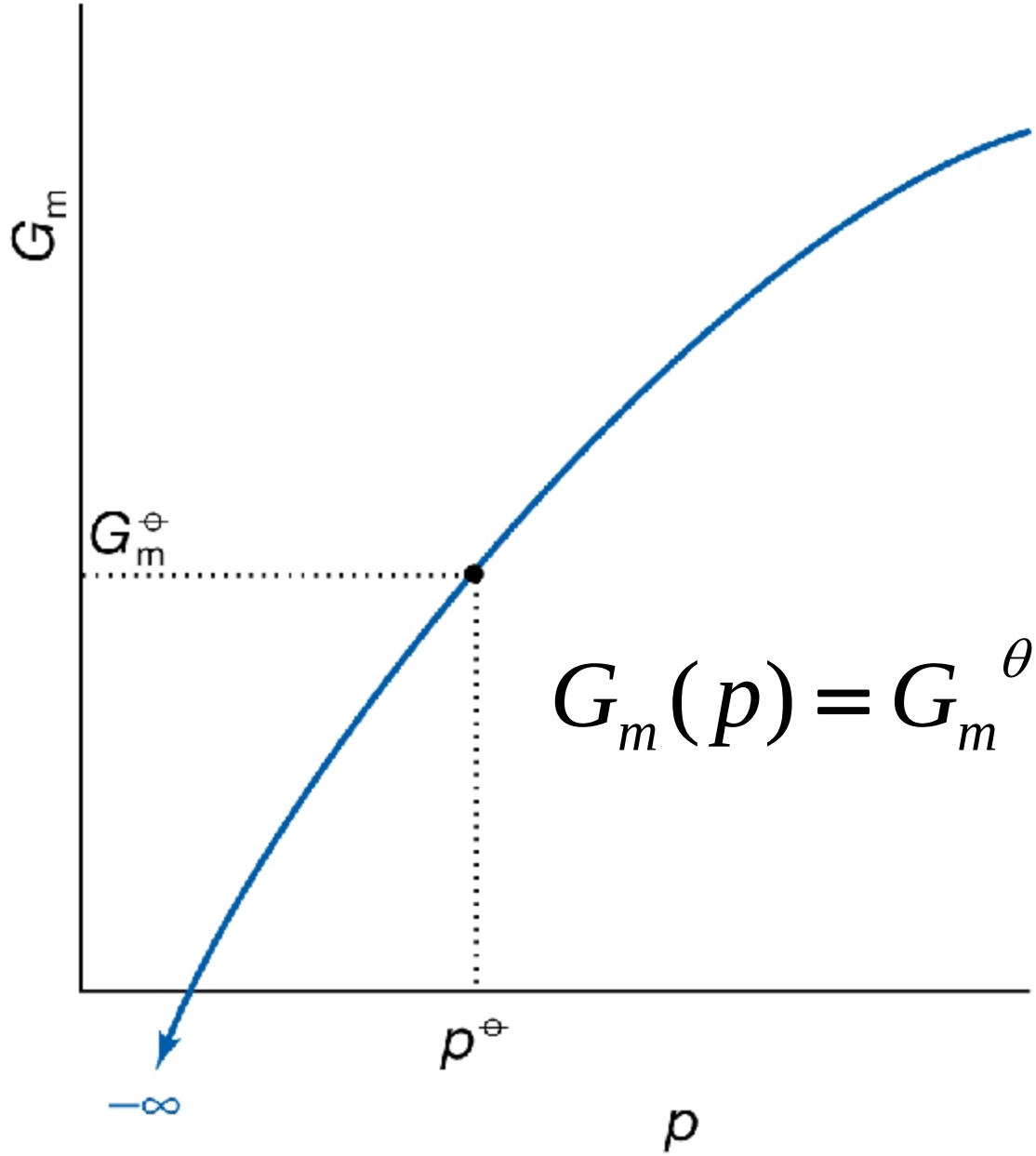
$$\Delta G_m = RT \ln \frac{p_2}{p_1}$$

$$p_1 = p^\theta$$

Standardni tlak:
10^5 Pa (1 bar)

$$G_1 = G^\theta$$

$$G_m(p) = G_m{}^\theta + RT \ln \frac{p}{p^\theta}$$



$$G_m(p) = G_m{}^{\theta} + RT \ln \frac{p}{p^{\theta}}$$

2b. Realni plinovi

G. N. Lewis-predlaže uvođenje”efektivnog” ili “korigiranog” tlaka

fugacitet

Fugacitivnost-(lat)-”tendencija da se pobjegne”

$$f = \gamma_f \cdot p$$

Koeficijent fugacitivnosti , tablice!

$$\gamma_f = \frac{f}{p} \neq 1$$

Realni plin

$$\lim_{p \to 0} \frac{f}{p} = 1$$

$$\ln \gamma_f = \int_0^p \frac{z-1}{p} dp$$

$$dG_m = RTd \ln f$$

$$G_{2,m} - G_{1,m} = \Delta G_m = RT \ln \frac{f_2}{f_1}$$

Dogovorno:

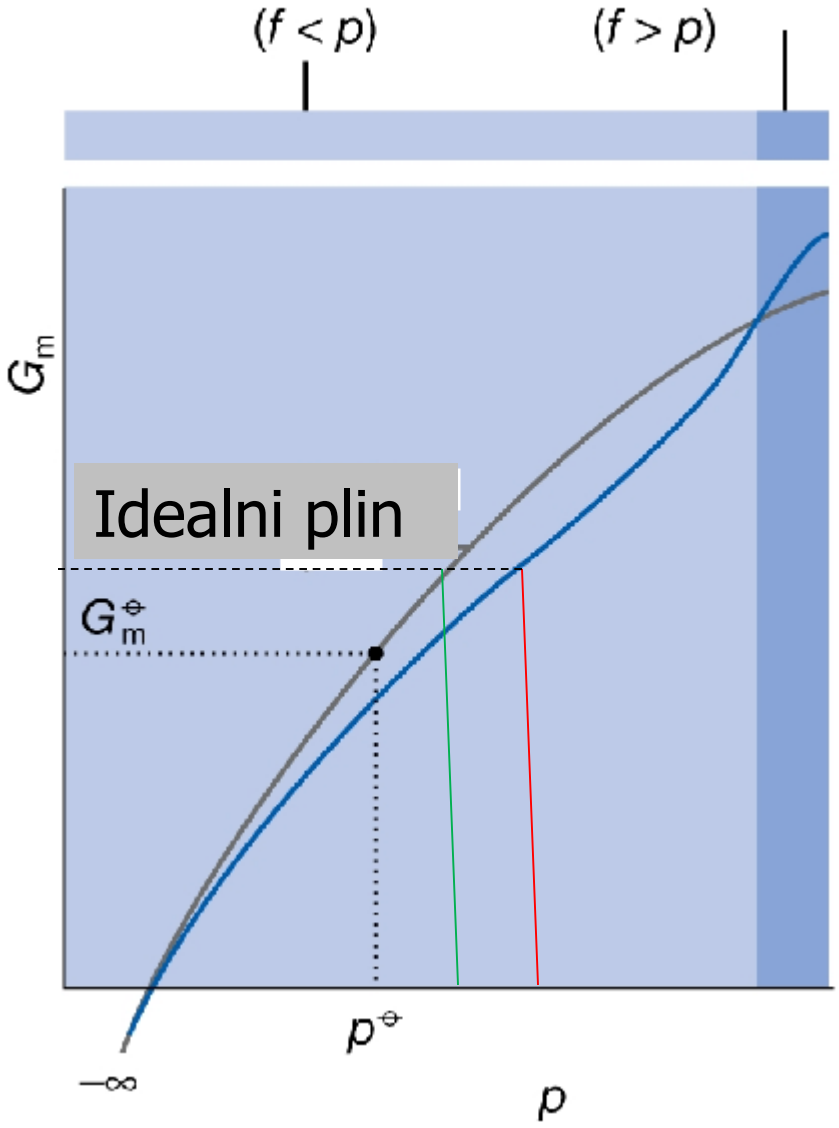
Početno (standardno)stanje -(referentni fugacitet)

STANJE IDEALNOG PLINA

$$G_m = G^{\theta}{}_m + RT \ln \frac{f}{p^{\theta}}$$

Dominiraju privlačne sile

Dominiraju odbojne sile



N_2, 273 K

p/atm	f/atm
1	0,99955
10	9,956
100	97,03
1000	1839



- Vrste sustava
- Definicijske jednadžbe (U,H,S,G)
- Zakoni termodinamike (1.;2.;3.)
- Standardno stanje tvari/ referentno stanje tvari
- Termokemijski zakoni
- Egzotermni i endotermni procesi
- Toplinski kapaciteti, povezanost Cp i Cv, kinetičko-molekularno objašnjenje
- Reverzibilnost/ireverzibilnost
- Adijabatski procesi
- Carnotov kružni proces
- Spontani i nespontani procesi
- G=f(P,T)
- fugacitet