Helmholtzova i Gibbsova energija

Helmholtzova energija: $A = U - TS \quad (T \text{ i } V = \text{konst.})$

Gibbsova energija: $G = H - TS \quad (T \text{ i } p = \text{konst.})$

$$dA = dU - TdS$$

$$dG = dH - TdS$$

Proces unutar sustava se odvija spontano ako je:

$$dA_{T,V} \leq 0$$

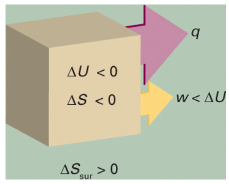
$$dG_{T,p} \leq 0$$

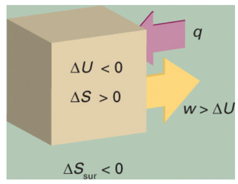
Helmholtzova energija

Promjena Helmholtzove funkcije (funkcije maksimalnog rada) za neki proces jednaka je najvećem iznosu rada koji se može dobiti u tom procesu pri konstantnoj temperaturi i volumenu.

$$dw_{max} = dA$$

$$w_{max} = \Delta A = \Delta U - T\Delta S$$





Gibbsova energija

Promjena Gibbsove funkcije (slobodne energije) jednaka je najvećem iznosu dodatnog (neekspanzijskog) rada koji se može dobiti u tom procesu pri konstantnom tlaku i temperaturi.

Kemijske reakcije se odvijaju spontano u onom smjeru u kojem se Gibbsova energija smanjuje.

$$dw_{max} = dG$$

$$w_{max} = \Delta G = \Delta H - T\Delta S$$

Std. reakcijska Gibbsova energija

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

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

$$\Delta_r G^{\ominus} = \sum_J \nu_J \Delta_f G^{\ominus}(J)$$

	$\Delta_f G^{\ominus}/(\text{kJ mol}^{-1})$
Diamond, C(s)	+2.9
Benzene, C_6H_6(l)	+124.3
Methane, CH_4(g)	−50.7
Carbon dioxide, CO_2(g)	−394.4
Water, H_2O(l)	−237.1
Ammonia, NH_3(g)	−16.5
Sodium chloride, NaCl(s)	−384.1

* More values are given in the *Data section*.

Temeljna (fundamentalna) jednadžba

Dolazi iz prvog i drugog zakona termodinamike i pokazuje da je unutarnja energija zatvorenog sustava funkcija reverzibilne ili ireverzibilne promjene volumena i entropije sustava.

$$dU = TdS - pdV$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Maxwellove jednadžbe:

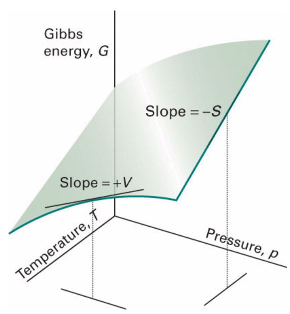
From *U*:	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
From *H*:	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
From *A*:	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
From *G*:	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

Svojstva Gibbsove energije

Temeljna jednadžba kemijske termodinamike:

$$dG = Vdp - SdT$$

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



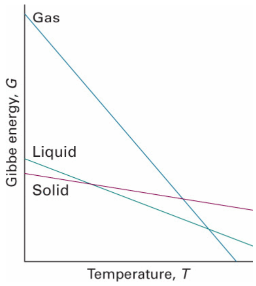
Ovisnost G o temperaturi

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

Gibbs-Helmholtzova jednadžba:

$$\left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$$

$$\left(\frac{\partial (\Delta G/T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$$



Ovisnost G o tlaku

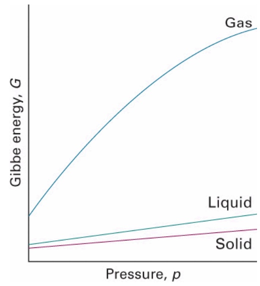
$$G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} V_m dp$$

Za tekućine i krutine:

$$G_m(p_f) = G_m(p_i) + (p_f - p_i)V_m$$

Za idealni plin:

$$G_m(p_f) = G_m(p_i) + RT\ln\frac{p_f}{p_i}$$



Fugacitet

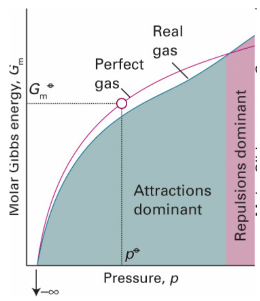
$$f = \phi p$$

Za idealni plin:

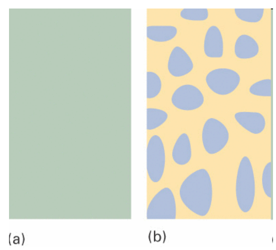
$$G_m(p) = G_m^{\ominus} + RT\ln\frac{p}{p^{\ominus}}$$

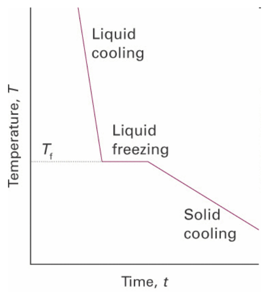
Za realni plin:

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



Fizićke transformacije čistih tvari

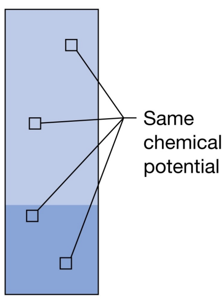




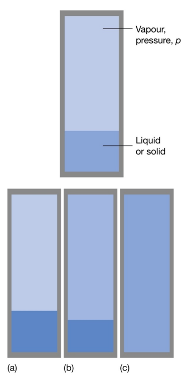
Faze u ravnoteži

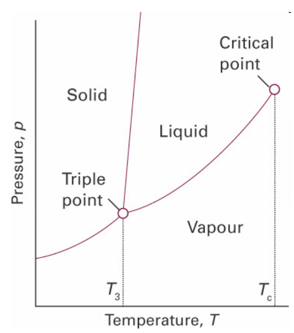
U faznoj ravnoteži, kemijski potencijal čiste tvari je isti u svim djelovima uzorka, bez obzira na broj prisutnih faza.

Kemijski potencijal: $\mu = G_m$

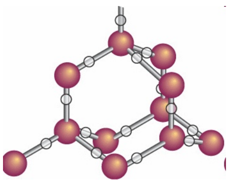


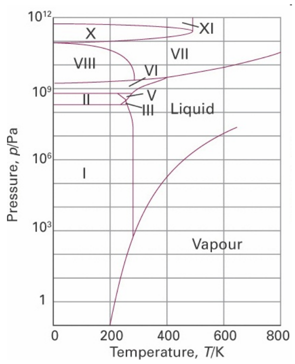
Fazni diagram





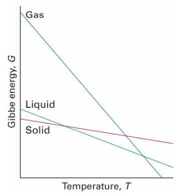
Fazni diagram vode

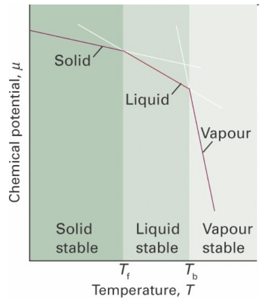




Temperaturna ovisnost μ

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

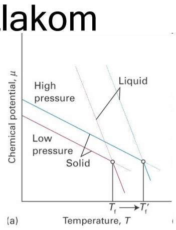




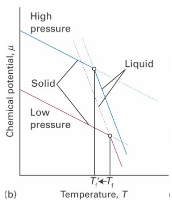
Promjena μ s tlakom

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$

$$V_m(s) < V_m(l)$$

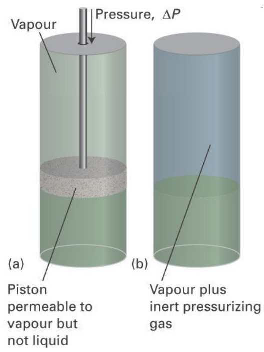


$$V_m(s) > V_m(l)$$



Tekuća faza pod tlakom

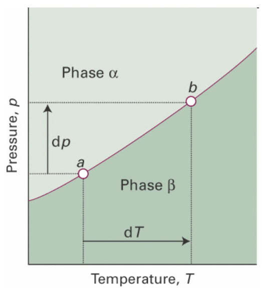
$$p = p^* e^{\frac{V_m(l)\Delta p}{RT}}$$



Fazni prijelazi

Clapeyronova jednadžba:

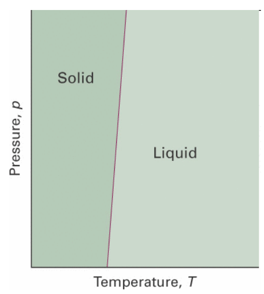
$$\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}$$



Fazni prijelazi između s i l

$$\frac{dp}{dT} = \frac{\Delta_{fus} H}{T \Delta_{fus} V}$$

$$p = p^* + \frac{\Delta_{fus} H}{T^* \Delta_{fus} V}(T - T^*)$$



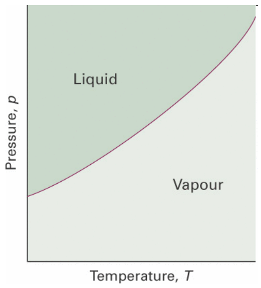
Fazni prijelazi između l i g

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$

Clausius-Clapeyronova jednadžba:

$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$$

$$p = p^* e^{\frac{-\Delta_{vap}H}{R}(\frac{1}{T}-\frac{1}{T^*})}$$



Fazni prijelazi između s i g

$$\frac{dp}{dT} = \frac{\Delta_{sub}H}{T\Delta_{sub}V}$$

$$p = p^* e^{\frac{-\Delta_{sub}H}{R}(\frac{1}{T}-\frac{1}{T^*})}$$