TOPNOST, HITROST RAZTAPLJANJA

Definicija: Topnost (oz. nasičena raztopina) predstavlja stanje, ko je topljenec (trdni, tekoči, plinast) v ravnotežju z raztopino (topljencem, raztopljenim v topilu).

- kvantitativni izraz
- pri določeni T
- homogena molekularna disperzija

Pojma: nasičena raztopina, prenasičena (supersaturated) raztopina

Fazno pravilo – topnost (primeri: mešanje dveh tekočin, fenol, voda; evtektik – timol, salol)

Načini izražanja topnosti: US farmakopeja (tudi Ph. Jug. IV)

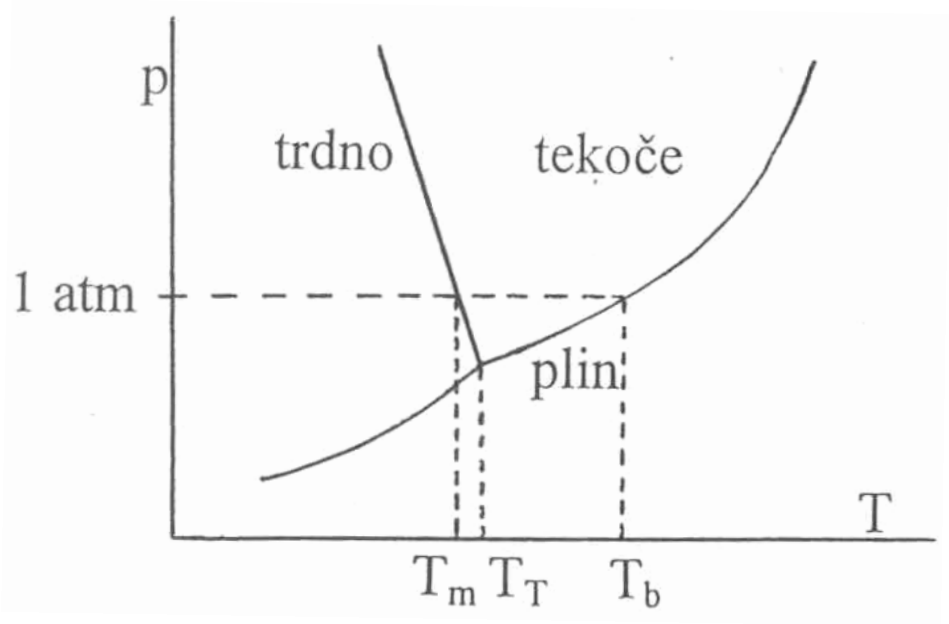
št. ml topila, v katerih se raztopi 1 g topljenca (npr. 1 g borne kisline se raztopi v 18 mL vode).

Molalnost, molarnost, procenti

Interakcije topilo – topljenec: **“Podobno se topi v podobnem”; polarnost (dipolni moment) – ni vedno dovolj. Vodikova vez, kisl. – bazične lastnosti (Lewis) → interakcije; razmerje polarne : nepolarne skupine; razvejanje (n – butil alkohol – 8 g/100 mL H_2O, terciarni butanol v vseh razmerjih topen s H_2O). Dielektrična konstanta: 80 – H_2O, 5 – CH_3Cl, 2 – benzen.**

Acido – bazna ravnotežja: **šibke kisl. (organske narave) niso popolnoma topne v H_2O; npr. fenoli in karboksilne kisline – dobro topne v raztopinah močnih baz.**

Solvatacija – dipolne interakcije, npr. H – vez → ↑ topnost



T_m, T_T

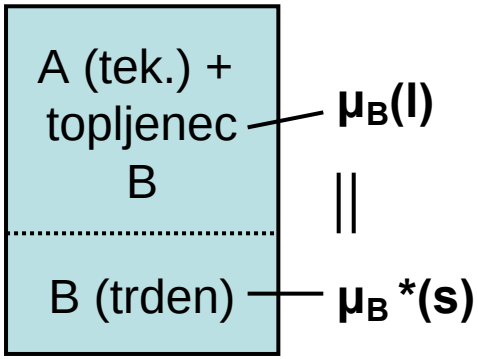
IDEALNA TOPNOST

V ravnotežju:

$$\mu_B(l) = \mu_B^*(s)$$

$$\mu_B(l) = \mu_B^*(l) + RT\ln x_B$$

$$\mu_B^*(s) = \mu_B^*(l) + RT\ln x_B$$



$$\ln x_B = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT} = -\frac{\Delta G_{fus}}{RT} = -\frac{\Delta H_{fus}}{RT} + \frac{\Delta S_{fus}}{R}$$

ΔS_{fus} in ΔH_{fus} = konst. v širšem T območju

Pri T* (temperatura tališča) je $\Delta G_{fus} = 0$ →

$$0 = -\frac{\Delta H_{fus}}{RT^*} + \frac{\Delta S_{fus}}{R}$$

in pri T: $$\ln x_B = \frac{-\Delta H_{fus}}{RT} + \frac{\Delta S_{fus}}{R}$$

$$\ln x_B = \frac{-\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

IDEALNA TOPNOST

$$\left.\begin{aligned}\mu_B(l) &= \mu_B^*(s)\\ \mu_B(l) &= \mu_B^*(l) + RT\ln x_B\end{aligned}\right\} \quad \mu_B^*(s) = \mu_B^*(l) + RT\ln x_B$$

$$\ln x_B = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT} = -\frac{\Delta G_{fus}}{RT} = -\frac{\Delta H_{fus}}{RT} + \frac{\Delta S_{fus}}{R}$$

$$\left.\begin{aligned}T = T_{tal}(T^*) &= 0 = -\frac{\Delta H_{fus}}{RT^*} + \frac{\Delta S_{fus}}{R}\\ T = \text{neka}T &= \ln x_B = -\frac{\Delta H_{fus}}{RT} + \frac{\Delta S_{fus}}{R}\end{aligned}\right\} \Longrightarrow$$

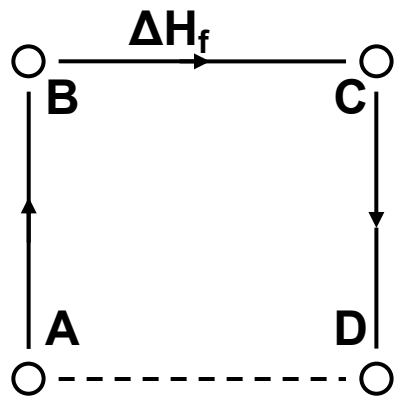
$$\ln x_B = -\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

trojna točka topljenca

temp. T_t

$$\Delta H_{A-B} = \int_{T}^{T_t} c_{p,s} dT$$

$$\Delta S_{A-B} = \int_{T}^{T_t} (c_{p,s}/T) dT$$



$$\Delta H_{C-D} = \int_{T_t}^{T} c_{p,l} dT$$

$$\Delta S_{C-D} = \int_{T_t}^{T} (c_{p,l}/T) dT$$

trdni topljenec 1 mol

tekočina 1 mol

temperatura določanja topnosti topljenca (T)

$\Delta G_{A\text{-}D} = \mu_l - \mu_s = RT\ln(f_l/f_s)$

$f_l = f_0$ = fugativnost standardnega stanja

$a = f/f_0\ (P/P_0) = x\gamma$

$\Delta G = \mu_l - \mu_s = RT\ln(f_l/f_s)$

Ker velja: $\mu_i = \mu_i^0 + RT\ln\left(f_i/f_i^0\right)$

fazi α, β:

$$\mu_i^\alpha = \mu_i^{0\alpha} + RT\ln\left(f_i^\alpha/f_i^{0\alpha}\right)$$

$$\mu_i^\beta = \mu_i^{0\beta} + RT\ln\left(f_i^\beta/f_i^{0\beta}\right)$$

fazi α, β v ravnotežju: $\mu_i^\alpha = \mu_i^\beta$

$$\mu_i^{0\alpha} + RT\ln\left(f_i^\alpha/f_i^{0\alpha}\right) = \mu_i^{0\beta} + RT\ln\left(f_i^\beta/f_i^{0\beta}\right) \qquad \text{(X)}$$

1. Če sta standardni stanji komponente i v obeh fazah enaki:

$$\mu_i^{0\alpha} = \mu_i^{0\beta} \Rightarrow f_i^{0\alpha} = f_i^{0\beta} \Rightarrow f_i^\alpha = f_i^\beta$$

2. Standardno stanje komponente i je v obeh fazah pri enaki temperaturi, vendar pa sta p in sestava obeh faz različna:

$$\mu_i^{0\alpha} = \mu_i^{0\beta} + RT\ln\left(f_i^{0\alpha}/f_i^{0\beta}\right)$$

Če ta izraz vstavimo v enačbo X, spet dobimo:

$$f_i^{\alpha} = f_i^{\beta}$$

Ravnotežje, izraženo s kemijskimi potenciali, lahko nadomestimo z izrazom, da morajo biti fugativnosti pri dani T za katerokoli i komponento enake v vseh fazah.

Idealna topnost: γ = 1

$$\Delta G_{A-D} = -RT \cdot \ln a = \underline{\underline{-RT \cdot \ln x}}$$

$$\Delta G_{A-D} = \Delta H_{A-D} - T\Delta S_{A-D}$$

$$\Delta H_{A-D} = \Delta H_{A-B} + \Delta H_{B-C} + \Delta H_{C-D}$$

$$\Delta H_{A-D} = \int_{T}^{T_t} c_{p,s}\, dT + \Delta H_f + \int_{T_t}^{T} c_{p,l}\, dT = \Delta H_f + c_{p,s}\left(T_t - T\right) + c_{p,l}\left(T - T_t\right) =$$

$$= \Delta H_f + \left(c_{p,s} - c_{p,l}\right)\left(T_t - T\right)$$

Če je: $\Delta c_p = \Delta c_{p,l} - \Delta c_{p,s} \rightarrow$

$$\Delta H_{A-D} = \Delta H_f + \Delta c_p (T - T_t) = \Delta H_f + \int_{T_t}^{T} \Delta c_p \, dT$$

molska toplotna kapaciteta: pri p = konst.: $c_p = (\delta H / \delta T)_p$

pri V = konst.: $c_v = (\delta U / \delta T)_v$

$c_p > c_v$ (pri p = konst. se T dvigne manj – zaradi dela, ki ga sistem opravlja, kot pri V = konst.)

Idealni plin: $c_p - c_v = \left(\frac{\delta H}{\delta T}\right)_p - \left(\frac{\delta U}{\delta T}\right)_p$ (pri p = konst.)

$H = U + pV = U + nRT \rightarrow$

$$c_p - c_v = \left(\frac{\delta U}{\delta T}\right)_p + nR - \left(\frac{\delta U}{\delta T}\right)_p = \underline{\underline{nR}}$$

$$\Delta S_{A-D} = \Delta S_f + \int_{T_t}^{T} \left(\Delta c_p / T\right) dT$$

pri T_t: $\Delta S_f = \Delta H_f / T_t$

Kombinacija gornjih enačb (za ΔG_{A-D}, ΔH_{A-D}, ΔS_{A-D},):

$\Delta G_{A-D} = \Delta H_{A-D} - T\Delta S_{A-D}$

$$\Delta G_{A-D} = \Delta H_f + \int_{T_t}^{T} \Delta c_p \, dT - T\left(\frac{\Delta H_f}{T_t} + \Delta c_p \ln \frac{T}{T_t}\right)$$

$\Delta G_{A-D} = - RT \cdot \ln x$

$$\ln x = -\frac{\Delta H_f}{RT} - \frac{\Delta c_p}{RT}\left(T - T_t\right) + \frac{T\Delta H_f}{RT \cdot T_t} + \frac{T\Delta c_p}{RT} \cdot \ln \frac{T}{T_t} =$$

$$= -\frac{\Delta H_f}{RT_t}\left(\frac{T_t - T}{T}\right) + \frac{\Delta c_p\left(T_t - T\right)}{RT} - \frac{\Delta c_p}{R} \cdot \ln \frac{T_t}{T}$$

Ker je $T_t \approx T_m$ (temperatura tališča)

Δc_p = majhna vrednost in

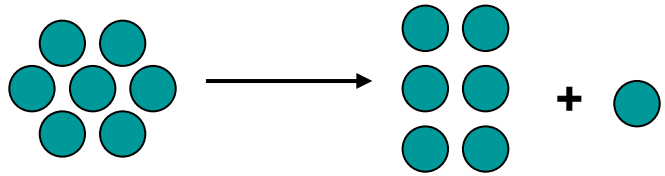
$$\frac{T_m - T}{T} \approx \ln \frac{T_m}{T}$$ (Taylorjeva vrsta)

$$\left(\begin{aligned} &\ln \frac{T_m}{T} = \frac{T + \Delta T}{T} = \ln 1 + x \left(x = \Delta T / T \right) \\ &\frac{T_m - T}{T} = \frac{T + \Delta T - T}{T} = \frac{\Delta T}{T} \left(= x \right) \end{aligned} \right)$$

$$\ln x = -\frac{\Delta H_f}{R T_m} \left(\frac{T_m - T}{T} \right) = \underline{\underline{-\frac{\Delta S_f}{R} \left(\frac{T_m - T}{T} \right)}}$$

$$\ln x = -\frac{\Delta S_f}{R} \left(\frac{T_m - T}{T} \right) - \ln \gamma$$

DOLOČITEV AKTIVNOSTNEGA KOEFICIENTA (γ_2) V ENAČBI ZA TOPNOST

1) 

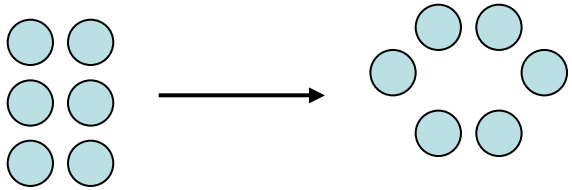
topljenec **molekula topljenca se loči od faze topljenca in preide v parno fazo**

Cepitev vezi med 2 sosednjima molekulama, delo: 2 w_{22}

22 – indeks, nanaša se na interakcije med molekulami topljenca

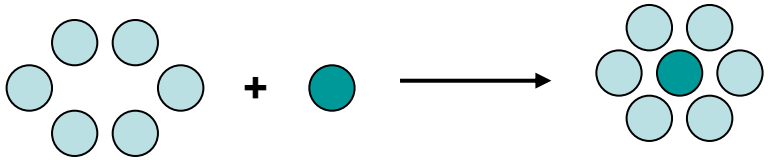
Prostor, ki nastane, molekule topljenca zaprejo: E = – w_{22} (se sprosti).

Σdelo: w_{22}

2) 

topilo **tvorba prostora v topilu**

Delo za ta korak: w_{11} (indeks 11 – interakcije med molekulami topila)

3) 

molekula topljenca preide iz parne faze v nastali prostor

Pridobljeno delo (znižanje potencialne energije): – w_{12}

Ko se zasedeni prostor zapre: potencialna energija se dodatno zniža za:

– w_{12} · Σdelo (energ.) = – $2w_{12}$

Celotno delo (energija) za ta proces: $w_{22} + w_{11} - 2w_{12}$

$$\ln \gamma_2 = (w_{22} + w_{11} - 2w_{12}) \frac{V_2 \Phi_1^2}{RT}$$

V_2 – molarni volumen (podhlajene) taline topljenca

Φ_1 – volumski delež topila ($x_1V_1 / (x_1V_1 + x_2V_2)$)