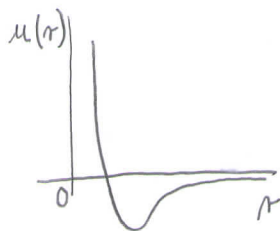


PONOVITEV FK

$$T, p, V, n$$

$$1) \quad pV = nRT$$

SPLOŠNA PLINSKA
ENACBA



$$p \cdot V_m = RT$$

velja za realne pline, ko velja:

$\lim_{p \rightarrow 0} (p \text{ gre proti vrednosti } 0)$

$\lim_{T \rightarrow \infty} (T \text{ je čim višja})$

2) VAN DER WAALSOVA ENACBA

$$\left(p + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

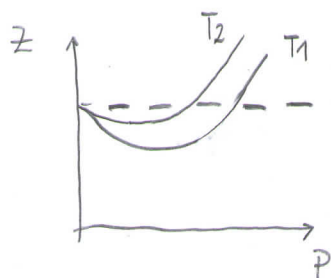
$$\left(p + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

velja za srednje tlake

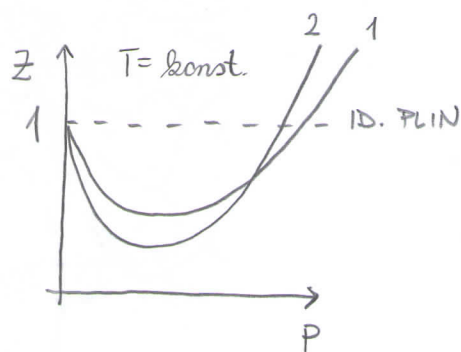
$a, b \dots$ Van der Waalsova parametra

$a \dots$ privlačne interakcije
 $b \dots$ odbojne interakcije

$$3) \quad \frac{p \cdot V_m}{RT} = Z \quad (\text{za idealni plin je } 1)$$



$$T_2 > T_1$$

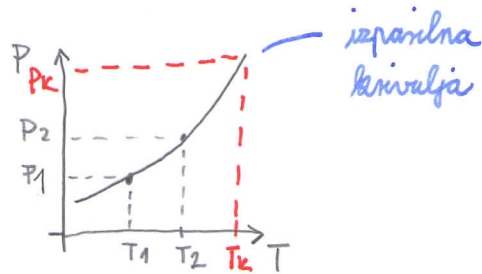
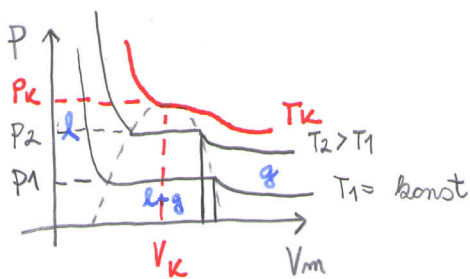


$Z > 1 \dots$ težja stisljivost

$Z < 1 \dots$ lažja stisljivost

kot pri
id. plinu

4)



$P_k, T_k, V_k \dots$ kritične konst.

primer: He, CO₂

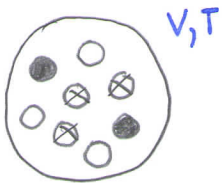
$$T_k(\text{He}) = 5 \text{ K}$$

$$T_k(\text{CO}_2) = 310 \text{ K}$$

$$\left\{ \begin{array}{l} \frac{T_{\text{He}}}{T_k(\text{He})} = \frac{T_{\text{CO}_2}}{T_k(\text{CO}_2)} = T_r \end{array} \right.$$

Plini so v **KORESPONDENTNEM** stanju, ko imata taki temperaturi, da se oba obnašata enako; T_r je enak za oba. V teh razmerah je enak Z .

5)



$$\begin{aligned} p_1 V &= n_1 R T \\ p_2 V &= n_2 R T \\ &\vdots \end{aligned}$$

$$p = p_1 + p_2 + \dots = \frac{RT}{V} (n_1 + n_2 + \dots) = \frac{RT}{V} \sum n_i$$

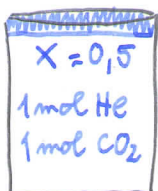
$$p_i = \frac{RT}{V} \cdot n_i$$

$$\frac{p_i}{p} = \frac{n_i}{\sum n_i} = X_i$$

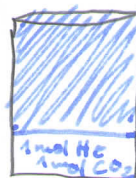
$$p_i = X_i \cdot p$$

molski delež

primer: He, CO₂



$$p = 0,0001 \text{ bar}$$



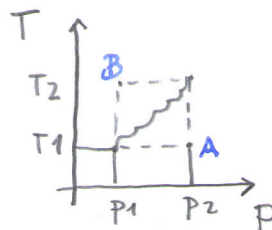
$$p = 100 \text{ bar} \Rightarrow$$

$$p_i \neq 0,5 \cdot p$$

6) $z = z(x, y)$

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

(M) (N)



pot A:
 $P_1 \rightarrow P_2$
 $T_1 \rightarrow T_2$

pot B:
 $T_1 \rightarrow T_2$
 $P_1 \rightarrow P_2$

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} \quad \left\{ \begin{array}{l} \text{TOTALNI DIFERENCIAL, ki označuje} \\ \text{FUNKCIJO STANJA} \end{array} \right.$$

primer:

$$P \cdot (V_m - b) = RT$$

$$P = \frac{RT}{V_m - b} \Rightarrow$$

$$P = P(T, V_m) \Rightarrow$$

$$dP = \left(\frac{\partial P}{\partial T} \right)_{V_m} dT + \left(\frac{\partial P}{\partial V_m} \right)_T dV_m$$

$$dP = \frac{R}{V_m - b} dT + \left(-\frac{RT}{(V_m - b)^2} \right) dV_m$$

$$\frac{\partial}{\partial V_m} \rightarrow \frac{-R}{(V_m - b)^2} \quad \frac{\partial}{\partial T} \rightarrow \frac{R}{(V_m - b)^2}$$

Plak je FUNKCIJA STANJA,
 saj imamo EKSTAKTNI DIFERENCIAL

$$E_{k,m} = \frac{3}{2} RT$$

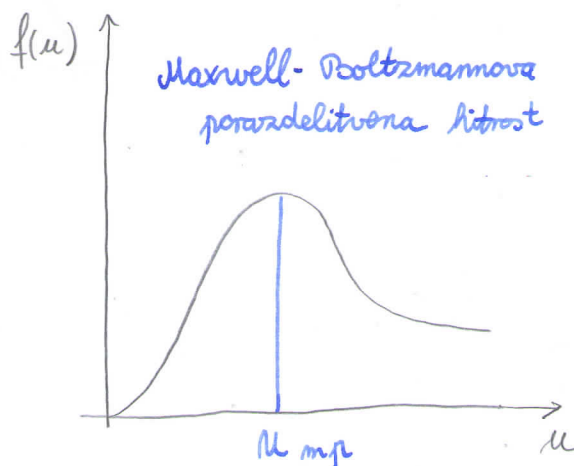
velja za enoatomarne
 pline, saj gledamo
 le translacijo

$$C_{P,m} - C_{V,m} = R$$

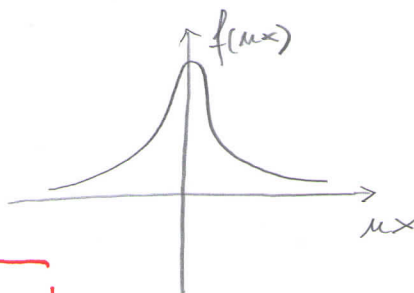
$$C_{P,m} = \frac{5}{2} R \quad \text{— enoatomarni plin}$$

$$C_{V,m} = \left(\frac{\partial q_v}{\partial T} \right)_v = \left(\frac{\partial E_m}{\partial T} \right)_v = \frac{3}{2} R$$

$$\frac{1}{N} \cdot \frac{dN_u}{du} = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2kT}}$$



$$\frac{1}{N} \frac{dN_{ux}}{d\mu_x} = \left(\frac{m}{2\pi RT} \right)^{\frac{1}{2}} \cdot e^{-\frac{m\mu_x^2}{2kT}}$$



$$u_{rms} = \sqrt{\bar{u}^2}$$

$$u_{mp}$$

$$\bar{u}$$

$$u_{mp} = \sqrt{\frac{2RT}{M}}$$

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}}$$

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$Z_1 = \sqrt{2} \rho \cdot \delta \cdot \bar{u}$$

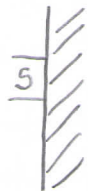
$$\frac{N}{V} \quad \pi d^2$$

frekvencia trkov ene mol. z ostalimi molekulami
[št. trkov/s]

$$Z_{11} = \frac{\sqrt{2}}{2} \rho^2 \delta \bar{u}$$

frekvencia trkov vseh mol. z ostalimi molekulami
[št. trkov/s m³]

$$\lambda = \frac{\bar{u}}{Z_1}$$



trki na
steno posode

$$\frac{1}{s} \frac{dZ_s}{dt} = \frac{1}{4} \cdot \rho \cdot \bar{u}$$

$$\nu = \frac{1}{4} \rho \bar{u} = \frac{1}{4} \cdot \rho \cdot \sqrt{\frac{8RT}{\pi M}} =$$

$$\nu = k \cdot \rho \cdot \sqrt{\frac{1}{M}}$$

Izhajanje iz posode:

2 plina

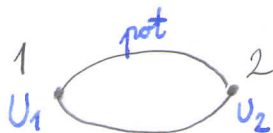
$$\nu_1 = k \cdot \rho_1 \cdot M_1^{-\frac{1}{2}}$$

$$\nu_2 = k \cdot \rho_2 \cdot M_2^{-\frac{1}{2}}$$

$$\frac{\nu_1}{\nu_2} = \frac{\rho_1}{\rho_2} \cdot \frac{M_2^{\frac{1}{2}}}{M_1^{\frac{1}{2}}}$$

Če sta gostoti enaki, na hitrost
vplivata le molski masi plinov.

$$\int_{U_1}^{U_2} dU = \int_{pot} dg + \int_{pot} dnr$$



$$\Delta U = q + w$$

$$dU = dg + dnr ; \begin{cases} w_{nv} = 0 \\ w_v = 0 \end{cases} \left\{ \begin{array}{l} V \text{ je enaka } 0 \\ \text{konst.} \end{array} \right.$$

$$dU = dg_v$$

$$q_v = \Delta U$$

$$dg_p = dH$$

$$H = U + pV$$

$$q_p = \Delta H$$

$$c_p > c_v$$

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T$$

$$c_p - c_v = \left(\frac{\partial V}{\partial T} \right)_p [p + \pi_T]$$

Termodinamska definicija IDEALNEGA PLINA je, da je notranji tlak $\pi_T = 0$.

$$c_p - c_v = \frac{T \cdot V \cdot \alpha^2}{\beta_T}$$

$$\text{pri baterem je: } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

Maxwellova enačba:

$$dA = -pdV - SdT$$

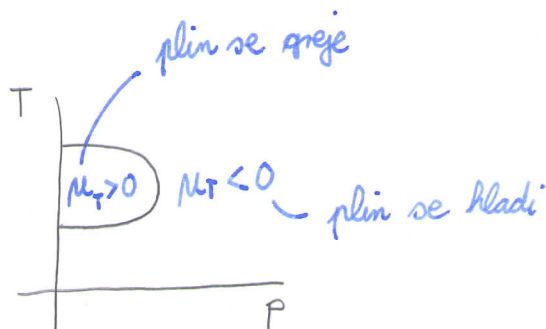
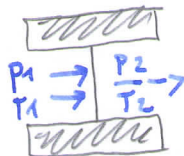
$$\left(\frac{dp}{dT} \right)_v = \left(\frac{dS}{dV} \right)_T$$

Tplotna kapaciteta narasča v smeri:

He < O₂ < NH₃
 najmanjša največja
 mol. mol.

Temperature ne preide TRANSLACIJSKA E.

$$C_{p,m} - C_{v,m} = R$$



$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

$\partial P < 0$ - prehod cez steno / bat
 Joule-Thomsonov efekt

IDEALNI PLIN:

1) $C_{p,m} - C_{v,m} = R$

2) $\mu_{JT} = 0$

3) $w = - \int_{V_1}^{V_2} p_{\text{zun}} dV$

$C_{v,m} \neq f(T) \Rightarrow$

$n \cdot C_{v,m} \Delta T = - p_{\text{zun}} \Delta V$

$$\Delta T = - \frac{p_{\text{zun}} \Delta V}{n \cdot C_{v,m}}$$

irverzibilno delo:

IR $w \Rightarrow w_{IR} = - p_{\text{zun}} \Delta V$

• $T = \text{konst.} \Rightarrow$ IZOTERNI PROCES

$\Delta U = q + w = 0 \Rightarrow \underline{q = -w}$

• $q = 0 \Rightarrow$ ADIABATNI PROCES

$\Delta U = w \Rightarrow \int_{T_1}^{T_2} n C_{v,m} dT = - p_{\text{zun}} \Delta V$

irverzibilno delo:

IR $w \Rightarrow w_{IR} = - nR \int_{V_1}^{V_2} \frac{T}{V} dV$

• $T = \text{konst.} \Rightarrow$

$w = - nRT \ln \frac{V_2}{V_1}$

$\Delta U = 0$

$\underline{q = -w}$

• $q = 0 \Rightarrow$

$T \cdot V^{\gamma-1} = \text{konst.}$
 $p \cdot V^{\gamma} = \text{konst.}$
 $\gamma = \frac{C_p}{C_v}$

$$W_{REV} = \frac{P_1 V_1}{\gamma - 1} \left[\left(\frac{V_1}{V_2} \right)^{\gamma - 1} - 1 \right]$$

$$\Delta U = w + \overset{0}{q}$$

$$\underline{\underline{n \cdot \int_{T_1}^{T_2} C_{v,m} dT = \Delta U = w}}$$

$$p = 1 \text{ bar} \Rightarrow \Delta_r H^\ominus$$

$$\Delta_{tv} H^\ominus$$



$$\Delta_r H^\ominus = \sum \nu \Delta_{tv} H^\ominus(P) - \sum \nu \Delta_{tv} H^\ominus(R)$$



$$\Delta_r H^\ominus = \frac{1}{2} \Delta_{tv} H^\ominus(C) - [\Delta_{tv} H^\ominus(A) + 2 \cdot \Delta_{tv} H^\ominus(B)]$$

- podatki za $\Delta_{tv} H^\ominus$ so podani pri 25°C

Iščemo pri 100°C:

$$\Delta_r H^\ominus(100^\circ\text{C}) = \Delta_r H^\ominus(25^\circ\text{C}) +$$

$$\int_{T_1=25^\circ\text{C}}^{T_2=100^\circ\text{C}} \Delta C_p \cdot dT$$

$$\Delta C_p = \frac{1}{2} \cdot C_{p,m}(C) - [C_{p,m}(A) + 2 C_{p,m}(B)]$$



g... grafit
d... diamant



$$C_g - C_d = 0$$



$$\Delta H = \Delta H_1 - \Delta H_2$$

to lahko naredimo, saj so
ENTALPIJE funkcije stanj

$$\Delta S_{V,U} \geq 0$$

IR
REV
IZOLIRAN
SISTEM

$$\Delta S_{TOT} \geq 0$$

$$\Delta S + \Delta S_{OK} \geq 0$$

$$\Delta S \geq \frac{q}{T}$$

$$\Delta S = nR \ln \frac{V_2}{V_1} + n \int_{T_1}^{T_2} \frac{C_{V,m} dT}{T}$$

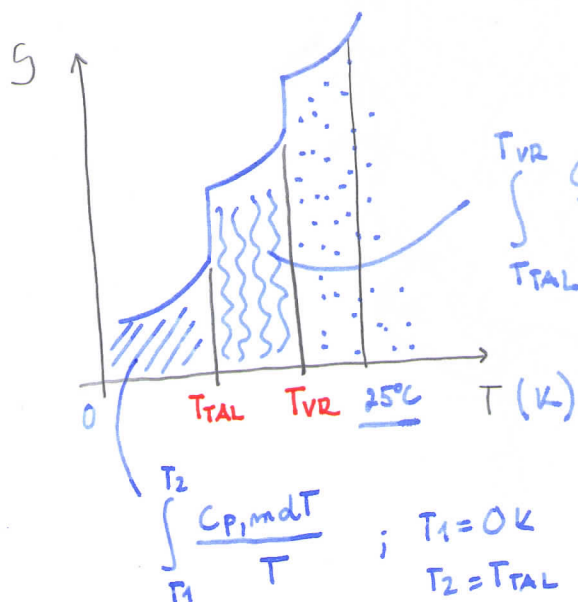
$$\Delta S = nR \ln \frac{V_2}{V_1} + n \cdot C_{V,m} \ln \frac{T_2}{T_1}$$

Ukvarži in razloži; kolikšen je ΔS sistema, če imamo irverzibilno adiabatsko ekspanzijo!

- a) $\Delta S > 0$
- b) $\Delta S = 0$
- c) $\Delta S < 0$

$$\Delta S_{TOT} = \Delta S + \Delta S_{OK} = 0$$

• pri reverzibilni ad. eksp: b) $\Delta S = 0$, saj je $\Delta S_{TOT} = 0 \wedge \Delta S_{OK} = 0$



$$S(T) = S(0) + n \int_0^T \frac{C_{P,m} dT}{T} + \dots$$

$$[\text{trajne } S \text{ elementar } \neq 0]$$

entropije so TABELIRANE po absolutnih vrednostih

$$(\Delta U)_{S,V} \leq 0$$

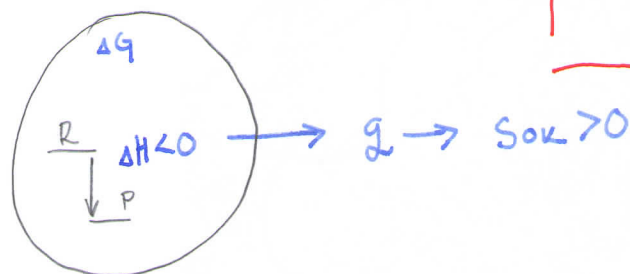
$$A = U - TS ; (\Delta A)_{V,T} \leq 0 \quad \text{PROSTA ENERGIJA}$$

$$G = H - TS ; (\Delta G)_{P,T} \leq 0 \quad \text{v laboratoriji PROSTA ENTALPIJA}$$

$$(\Delta A)_T = W_{\text{MAX}} \text{ in } (\Delta G)_T = W_{\text{MAX, NEVOLUMSKI}}$$

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S < 0$$



Za spontanost procesa je najbolj ugodno:

- znižanje entalpije (ENERGIJSKI PRISPEVEK)
- zvišanje entropije (ENTROPIJSKI PRISPEVEK)

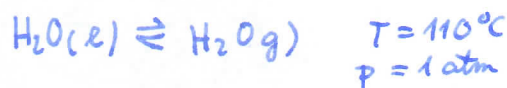
Primer:

$$T = 100^\circ\text{C}$$

$$P = 1 \text{ atm}$$



$$\left. \begin{array}{l} \Delta S > 0 \\ \Delta H > 0 \end{array} \right\} \Delta G = 0$$



$$\left. \begin{array}{l} \Delta S > 0 \\ \Delta H > 0 \end{array} \right\} \Delta G < 0, \text{ saj je prispevek entropije } \underline{\text{večji}}$$

Primer:

$$P = 1 \text{ atm}$$

$$T = 5^\circ\text{C}$$

Za H_2O ima tistaj $\text{H}_2\text{O}(s)$ večji hem. potencial μ_s kot μ_l .

$$\mu_s > \mu_l$$

$$l \rightarrow s \quad \Delta G > 0$$

Primer: $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$ $T = -10^\circ\text{C}$, $p = 1 \text{ atm}$

Izračunaj ΔG , hoče 1 mol ledu stali pri $T = -10^\circ\text{C}$ in tlaku 1 atm!

$$\Delta G_{263} = \Delta H_{263} - 263 \text{ K} \cdot \Delta S_{263} =$$

$$= \left[\Delta H_{273} + \int_{273}^{263} \Delta C_p dT \right] - 263 \text{ K} \cdot \left(\Delta S_{273} + \int_{273}^{263} \frac{\Delta C_p dT}{T} \right)$$

$$\underline{m \cdot \Delta_{\text{TAL}} H_m}$$

$$\underline{\frac{m \cdot \Delta_{\text{TAL}} H_m}{273}}$$

$$\boxed{\Delta C_p = C_p(l) - C_p(s)}$$