Obecná chemie 29.3.2022 (6. cvičení)

TERMODYNAMIKA I.

→ **modely plynů:**

- ideální plyn (IP) $pV = nRT$
  - R = molární plynová konstanta, $R = 8{,}314\ J\,K^{-1}mol^{-1}$
- van der Waalsův plyn (vdW) $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$
  - korekce tlak, korekce objem

a další modely (viriálový, ...)

→ **základní TD děje:**

- izotermický $T = konst.$
- izobarický $p = konst.$
- izochorický $V = konst.$
- adiabatický $Q = 0$

→ **1. TD věta**

$$\Delta U = W + Q$$
$$dU = dW + dQ$$

(1) $CaCO_3 \xrightarrow{t} CaO + CO_2$

$CaCO_3$ → 286 kg 6% nečistot ⇒ 268,84 kg čistého

$M_r(CaCO_3) = 40{,}08 + 12{,}01 + 3 \cdot 16{,}00 = 100{,}09$

$$V(CO_2) = \frac{nRT}{p} = \frac{RT}{p} \frac{m(CaCO_3)}{M(CaCO_3)} =$$

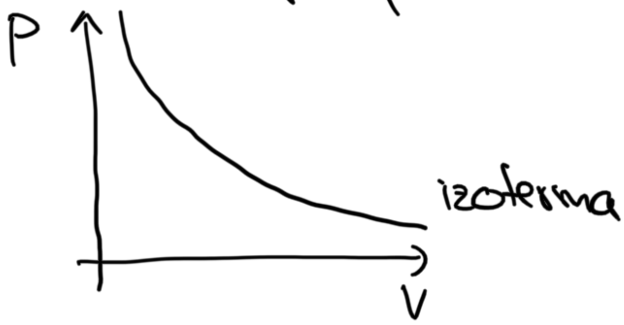
$$= \frac{8{,}314\ J\cdot K^{-1}\cdot mol^{-1}\cdot 298{,}15\ K\cdot 268\,840\ g}{100{,}1\ g\cdot mol^{-1}\cdot 101{,}325\ kPa} =$$

$$\doteq \underline{\underline{65{,}76\ dm^3}}$$

② izotermická expanze IP:

uvažujeme pouze objemovou práci $dW = -p_{ext}dV$

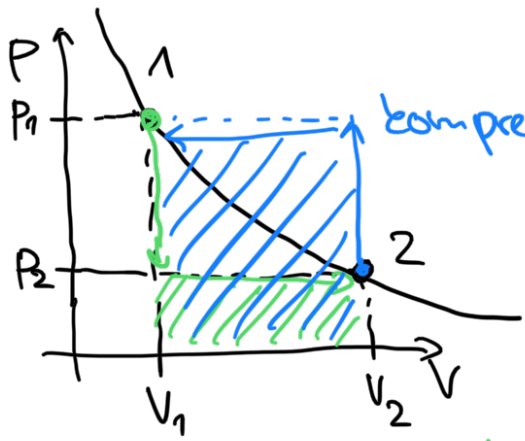
izotermická exp. $pV = nRT = konst.$



a) nevratně = prudce (okamžitě) změníme tlak na finální hodnotu

$$p_{ext} = konst. \equiv p_F$$

$$W = \int dW = \int_{V_I}^{V_F} (-p_{ext})\,dV = -p_F \int_{V_I}^{V_F} dV = -p_F(V_F - V_I)$$



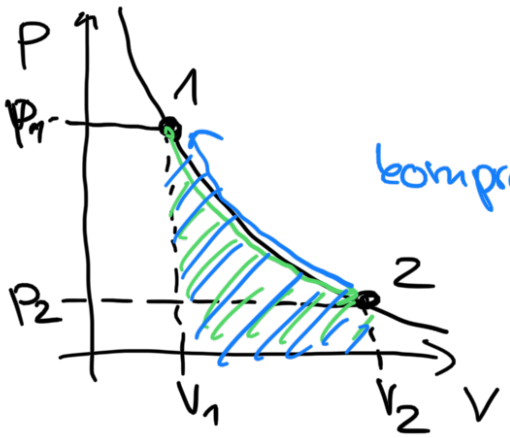
celkem $W_e + W_k = -(p_2 - p_1)(V_2 - V_1) \neq 0$

b) vratně = „po malých krůčcích"

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

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

$$W = -\int_{V_I}^{V_F} p_{ext}\, dV = -nRT \int_{V_I}^{V_F} \frac{1}{V} dV = -nRT \ln \frac{V_F}{V_I}$$



komprese $W_k = -nRT \ln \frac{V_1}{V_2}$

expanze $W_e = -nRT \ln \frac{V_2}{V_1}$

celkem $W_k + W_e = 0$

③ 1 mol IP $T = 293{,}15\,K$ $p = 101{,}3\,kPa$

$p_2 = \frac{1}{10} p_1$ $V_2 = 10 V_1$

izotermická expanze

$\Delta U = Q + W$ vnitřní energie IP $\Delta U = \frac{3}{2} R \Delta T = 0$ → pro izotermické děje $\Delta U = 0$

↓

pouze objemová $dW = -p dV$

irreverzibilně ⇒ $p = konst.$

$$\Rightarrow W = -p_2 \Delta V = -p_2 (V_2 - V_1) =$$
$$= -\frac{1}{10} p_1 (9 V_1) = -\frac{9}{10} p_1 V_1 =$$
$$= -\frac{9}{10} nRT =$$
$$= -\frac{9}{10} \cdot 1 \cdot 8{,}314 \cdot 293{,}15 \doteq \underline{\underline{2194\,J}}$$

$$\Rightarrow Q = \Delta U - W = \underline{\underline{-2194\,J}}$$

④ $V = 0{,}52\ m^3$ ...

④ · $V = 0{,}530\ m^3$ $n = 1\ kmol$ $p = 5{,}07\ MPa$

IP: $pV = nRT \Rightarrow T = \frac{pV}{nR} \doteq \underline{\underline{323{,}2\ K}}$

vdW: $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$

$$\Rightarrow T = \frac{\left(p + \frac{an^2}{V^2}\right)(V - nb)}{nR} =$$

$$= \frac{(5{,}07 \cdot 10^6 + 1{,}3 \cdot 10^6)(0{,}530 - 4{,}28 \cdot 10^{-2})}{10^3 \cdot 8{,}314} \doteq$$

$$\doteq \underline{\underline{373{,}3\ K}}$$

$$\Rightarrow \underline{\underline{\Delta T = 50\ K}}$$

⑤ N_2 28 g $M_r = 28 \Rightarrow 1\ mol$

$p = 101{,}325\ kPa$ $T = 273{,}15\ K$

izotermické stlačení na $\frac{1}{10} V_1 - V_2$

vdW plyn $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$

→ vratně

$$W = \int_{V_1}^{V_2} dW = -\int_{V_1}^{V_2} p_{ext}\, dV = -\int_{V_1}^{V_2} \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right) dV =$$

$$= -nRT \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) - an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) =$$

$$V_1 = \frac{nRT}{p_1}$$

$$V_2 = \frac{nRT}{p_2} = \frac{1}{10} V_1 = \frac{nRT}{10 p_1}$$

$$= -nRT \ln\left(\frac{\frac{nRT}{10p_1} - nb}{\frac{nRT}{p_1} - nb}\right) - an^2\left(\frac{10p_1}{nRT} - \frac{p_1}{nRT}\right) =$$

$\frac{9p_1}{nRT}$

$$\cdot \quad \frac{\quad}{p_1} - nb \,) \qquad (\, V_1 RT \quad nRT \,)^{-}$$

$n = 1 \text{ mol}$

$R = 8{,}314 \ J \cdot K^{-1} \cdot mol^{-1}$

$T = 273{,}15 \ K$

$p_1 = 101{,}325 \ Pa$

$a = 0{,}137 \ Jm^3 mol^{-2}$

$b = 38{,}7 \cdot 10^{-6} m^3 mol^{-1}$

$$= 2271{,}0 \ \ln\left(\frac{-0{,}0364587 \cdot 10^{-3}}{-0{,}0162873 \cdot 10^{-3}}\right) - 55{,}01 \doteq \underline{\underline{1775 \ J}}$$

> <u>nevratně</u>

$$W = \int dW = -\int_{V_1}^{V_2} p_{ext} \, dV = -p_{ext} \Delta V$$

$$\Delta V = V_2 - V_1 = \frac{1}{10} V_1 - V_1 = -\frac{9}{10} V_1$$

$$p_{ext} = p_2 : \quad \left(p_2 + \frac{an^2}{V_2^2}\right)(V_2 - nb) = nRT$$

$$p_2 = \frac{nRT}{V_2 - nb} - \frac{an^2}{V_2^2}$$

$$p_2 = \frac{nRT}{+\frac{9}{10} V_1 - nb} - \frac{an^2}{\left(\frac{9}{10}\right)^2 V_1^2}$$

$$V_1 = \frac{nRT}{p_1}$$

$$p_2 = \frac{nRT}{+\frac{9}{10} \frac{nRT}{p_1} - nb} - \frac{a n^2}{\left(\frac{9}{10}\right)^2 \left(\frac{nRT}{p_1}\right)^2}$$

$$W = \left(\frac{RT}{+\frac{9}{10} \frac{RT}{p_1} - b} - \frac{a}{\left(\frac{9}{10}\right)^2 \left(\frac{RT}{p_1}\right)^2}\right) \cdot \underbrace{\frac{9}{10} \frac{nRT}{p_1}}_{= 0{,}02017}$$

$=$

⑥ $1\,kg\ Fe_2O_3$ ($M = 231{,}55\ g/mol$)

$c_p = 86{,}26 + 0{,}200892\,T$ ($J\,K^{-1}\,mol^{-1}$) tepelná kapacita

$Q = 400\ kJ$ $T_1 = 300\ K$ $T_2 = ?$

$1\,kg\ Fe_2O_3 \rightarrow \frac{1000\,g}{231{,}55\,g/mol} \doteq 4{,}3187\ mol$

$Q = 400\ kJ \rightarrow \frac{400\,kJ}{4{,}3187\,mol} = 92{,}62\ kJ/mol$

$$Q = \int_{T_1}^{T_2} c_p(T)\,dT = \int_{T_1}^{T_2} (86{,}26 + 0{,}200892\,T)\,dT$$

$$= 86{,}26(T_2 - T_1) + \frac{1}{2}\cdot 0{,}200892(T_2^2 - T_1^2)$$

$$86{,}26(T_2 - 300) + \frac{1}{2}\cdot 0{,}200892(T_2^2 - 300^2) = 92620$$

$$86{,}26\,T_2 - 25878 + 0{,}100446\,T_2^2 - 9040 = 92620$$

$$T_2 = 776\ K$$