① Izpelji enačbo za izotermno reverzibilno delo Van der Waalsovega plina!

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$n = 2\ mol$
$T = 300K$
$a = 0,23026\ mPa\ mol^{-2}$
$b = 4,3067 \cdot 10^{-5}\ m^3 mol^{-1}$
$V_1 = 2,00\ dm^3$
$V_2 = 10,00\ dm^3$

$$W = -\int_{V_1}^{V_2} p_z \cdot dV = -\int_{V_1}^{V_2} p\,dV$$

za idealni plin:

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

$V_m \to \infty$
$\frac{1}{V_m} \to 0$

$pV = nRT$ splošna

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

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$V = n \cdot V_m$
$dV = n \cdot dV_m$

$$= n \int_{V_{m1}}^{V_{m2}} \left(\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right) dV_m =$$

$$= -n \left( RT \ln(V_m - b)\Big|_{V_{m1}}^{V_{m2}} - a\left(-\frac{1}{V_m}\Big|_{V_{m1}}^{V_{m2}}\right)\right) = -n\left(RT \ln \frac{V_{m2} - b}{V_{m1} - b} + a\left(\frac{1}{V_{m2}} - \frac{1}{V_{m1}}\right)\right) =$$

izpeljava enačbe

$$V_{m1} = \frac{V_1}{n} = \frac{2,00\ dm^3}{2\ mol} = 1\ dm^3/mol$$
$$V_{m2} = \frac{V_2}{n} = \frac{10,00\ dm^3}{2\ mol} = 5\ dm^3/mol$$

$$= -2\ mol \left(8,314\ J\ mol^{-1}K^{-1} \cdot 300K \cdot \ln \frac{5 \cdot 10^{-3}\ m^3 - 4,3067 \cdot 10^{-5}\ m^3 mol^{-1}}{10^{-3}\ m^3 - 4,3067 \cdot 10^{-5}\ m^3 mol^{-1}} + \right.$$

$$\left. + 0,23026\ mPa\ mol^{-2}\left(\frac{1\ m^3}{5 \cdot 10^{-3}} - \frac{1\ m^3}{10^{-3}}\right)\right) =$$

$$W = -7837\ J = -7,84\ kJ$$

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

$$= -2\ mol \cdot 8,314\ J\ mol^{-1}K^{-1} \cdot 300K \cdot \ln \frac{5}{1} = \left\{ \text{idealni plin} \right.$$

$$= -8028\ J = -8,03\ kJ$$

② Imamo 1 mol enoatomnega idealnega plina.

$n = 1\ mol$
$T_1 = 25°C$
$V_1 = 10\ L$
$V_2 = 50\ L$ ) ekspanzija

a) IZOTERMNA EKSPANZIJA — $w = ?$, $p_2 = ?$

b) ADIABATNA EKSPANZIJA — $w = ?$, $p_2 = ?$, $T_2 = ?$

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

$w = -1\ mol \cdot 8{,}314 \frac{J}{mol\,K} \cdot 298\ K \ln \frac{50\ L}{10\ L} =$

$= \underline{-3{,}99\ kJ}$ !

$p_2 = \frac{nRT_2}{V_2} = \frac{nRT}{V_2} = \frac{1\ mol \cdot 8{,}314\ J\,(mol\,K)^{-1} \cdot 298\ K}{50 \cdot 10^{-3}\ m^3} =$

$= 49576\ Pa = \underline{49{,}58\ kPa}$

b) $\boxed{q = 0}$ $\quad \Delta u = q + w$ $\quad \Delta u = w$

$u = u(T, V) \Rightarrow$

$du = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T \cdot dV$

$\underline{du = C_V dT + \Pi_T dV}$ $\quad \boxed{\Pi_T = 0}$ idealni plin

$du = C_V dT$ $\quad C_V = n \cdot C_{Vm}$

$\Delta u = \int_{T_1}^{T_2} C_V dT = n \int_{T_1}^{T_2} C_{Vm} \cdot dT$ $\quad \boxed{C_{Vm} = \frac{3}{2}R}$

$w = \frac{p_1 V_1}{\varkappa - 1}\left[\left(\frac{V_1}{V_2}\right)^{\varkappa - 1} - 1\right] =$ $\quad \left(\frac{p_1 V_1}{\varkappa - 1} = \frac{nRT_1}{V_1}\right)$

$= \frac{nRT_1}{\varkappa - 1}\left[\left(\frac{V_1}{V_2}\right)^{\varkappa - 1} - 1\right]$

$\varkappa = \frac{C_p}{C_V} = \frac{C_{pm}}{C_{Vm}} = \frac{C_{Vm} + R}{C_{Vm}} = \frac{\frac{3}{2}R + R}{\frac{3}{2}R} =$ $\quad C_{pm} - C_{Vm} = R$

$= \frac{5}{3}$

$= \frac{1\ mol \cdot 8{,}314\ J\,mol^{-1}K^{-1} \cdot 298\ K}{\frac{5}{3}R - 1}\left[\left(\frac{10\ L}{50\ L}\right)^{\frac{5}{3}-1} - 1\right] =$

$= -2447\ J = \underline{-2{,}45\ kJ}$ ! Adialatno delo je manjše kot izotermno.

dve enačbi:

$T_2$ / $T_2 = \frac{p_2 \cdot V_2}{nR}$

$T_1 \cdot V_1^{\varkappa - 1} = T_2 \cdot V_2^{\varkappa - 1}$

$p_1 \cdot V_1^{\varkappa} = p_2 \cdot V_2^{\varkappa}$

$p_2 = \frac{p_1 \cdot V_1^{\varkappa}}{V_2^{\varkappa}} = \frac{nRT \cdot V_1^{\varkappa}}{V_1 \cdot V_2^{\varkappa}} = \frac{1\ mol \cdot 8{,}314\ J\,(mol\,K)^{-1} \cdot 298\ K}{10\ L} \cdot \left(\frac{1}{5}\right)^{\frac{5}{3}}$

$T_2 = \frac{16955\ Pa \cdot 50 \cdot 10^{-3}\ m^3}{1\ mol \cdot 8{,}314\ J\,(mol\,K)^{-1}} = \underline{101{,}97\ K}$

$p_2 = 16955\ Pa = \underline{16{,}96\ kPa}$

nadaljevanje:

$$w = \Delta u = n\int_{T_1}^{T_2} C_{vm}\,dT = nC_{vm}(T_2 - T_1) =$$

$$= 1\,mol \cdot \frac{3}{2}R(101{,}97\,K - 298\,K) =$$

$$= \underline{\underline{-2{,}45\,kJ}}$$

} 2. enačba za izračun dela

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③ $n = 1\,mol$

$c_{pm} = 20{,}8\ J(mol\,K)^{-1}$

$p_1 = 3{,}25\,atm$

$T_1 = 310\,K$

→ reverzibilna adiabatna ekspanzija

$p_2 = 2{,}50\,atm$

$T_2 = ?$

$V_2 = ?$

$w = ?$

$$p_1 \cdot V_1^{\varkappa} = p_2 \cdot V_2^{\varkappa}$$

$$p_1^{\frac{1}{\varkappa}} \cdot V_1 = p_2^{\frac{1}{\varkappa}} \cdot V_2$$

$$V_2 = \frac{p_1^{\frac{1}{\varkappa}} \cdot V_1}{p_2^{\frac{1}{\varkappa}}} = \left(\frac{p_1}{p_2}\right)^{\frac{1}{\varkappa}} \cdot V_1 = \left(\frac{p_1}{p_2}\right)^{\frac{1}{\varkappa}} \frac{nRT_1}{p_1}$$

$$\varkappa = \frac{c_{pm}}{c_{vm}} = \frac{c_{pm}}{c_{pm} - R} = \frac{20{,}8\ J(mol\,K)^{-1}}{12{,}486\ J(mol\,K)^{-1}} = \underline{\underline{1{,}666}}$$

$$\left(\frac{3{,}25\,atm}{2{,}5\,atm}\right)^{1{,}666^{-1}} \cdot \frac{1\,mol \cdot 8{,}314\,J/mol\,K \cdot 310\,K}{3{,}25 \cdot 1{,}013 \cdot 10^5\,Pa} =$$

$$= 9{,}16 \cdot 10^{-3}\,m^3 = \underline{\underline{9{,}16\,L}}$$

$$T_2 = \frac{p_2 V_2}{nR} = \frac{2{,}50 \cdot 1{,}013 \cdot 10^5\,Pa \cdot 9{,}16 \cdot 10^{-3}\,m^3}{1\,mol \cdot 8{,}314\ J(mol\,K)^{-1}} = \underline{\underline{279\,K}}$$

$w = \Delta u \Rightarrow$ saj je $q = 0$

$$w = \Delta u = n\int_{T_1}^{T_2} C_{vm} \cdot dT = nC_{vm}(T_2 - T_1) = 1\,mol \cdot (c_{pm} - R)(T_2 - T_1) =$$

$$= 1\,mol \cdot (20{,}8\ J(mol\,K)^{-1} - 8{,}314\,J/mol\,K) \cdot (279\,K - 310\,K) =$$

$$= -387\,J = \underline{\underline{-0{,}39\,kJ}}$$

④ $T = 273\,K = 0°C$

$p = 1\,atm$

$d = 1\,\mu m$

$W = ?$

Imamo kapljico, ki zmrzne pri $0°C$. Kolikšno delo se je opravilo?

$$W = -\int_{V_1}^{V_2} p_z\,dV = -p_z(V_2 - V_1) = -1{,}013\cdot 10^5\,Pa\,(5{,}722 - 5{,}236)\cdot 10^{-19}\,m^3 =$$

$$= -4{,}92\cdot 10^{-15}\,J$$

$\rho_l = 1{,}000\,g/cm^3$

$\rho_s = 0{,}915\,g/cm^3$

$$V_2 = V_s = \frac{m}{\rho_s}$$

$$V_1 = V_l = \frac{m}{\rho_l}$$

$$V_s \rho_s = V_l \rho_l \qquad V_s = V_l \cdot \frac{\rho_l}{\rho_s}$$

$$V_l = \frac{4\pi r^3}{3} = \frac{\pi d^3}{6} = \frac{\pi}{6}\cdot (10^{-6}\,m)^3 = 5{,}236\cdot 10^{-19}\,m^3$$

$$V_s = V_l \cdot \frac{\rho_l}{\rho_s} = 5{,}236\cdot 10^{-19}\,m^3 \cdot \frac{1{,}000}{0{,}915} = 5{,}722\cdot 10^{-19}\,m^3$$

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⑤ V 2L posodi je 1 mol $CO_2$ pri $T = 300K$. Plin izotermno stisnemo. Končni volumen bo 0,75L. Izračunaj minimalni tlak!

$V_1 = 2\,L$

$n(CO_2) = 1\,mol$

$T = 300K$

$p = konst.$

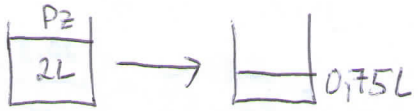
$V_2 = 0{,}75\,L$

$p_{min} = ?$

$W = ?$

$a = 0{,}36551\,\frac{m^6 Pa}{mol^2}$

$b = 4{,}2816\cdot 10^{-5}\,\frac{m^3}{mol}$




$p_z > p_1$

$\boxed{p_z = p_2}$

Izračunati moramo tlak na koncu!

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

$$p_{min} = p_2 = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \qquad V_m = V_{2m} = \frac{0{,}75\,L}{1\,mol} = 0{,}75\,L\,mol^{-1}$$

$$p_{min} = \frac{8{,}314\,J\,(mol\,K)^{-1}\cdot 300\,K}{0{,}75\,L\,mol^{-1} - 4{,}2816\cdot 10^{-5}\,\frac{m^3}{mol}} - \frac{0{,}36551\,\frac{m^6 Pa}{mol^2}}{(0{,}75\,L\,mol^{-1})^2} =$$

$$= 28{,}8\cdot 10^5\,Pa = \underline{28{,}8\,bar}$$

$$W = -\int_{V_1}^{V_2} p_z\,dV = -p_z(V_2 - V_1) = -28{,}8\cdot 10^5\,Pa\,(0{,}75\cdot 10^{-3} - 2\cdot 10^{-3})\,m^3 =$$

$$= 3596\,J = \underline{3{,}6\,kJ}$$

⑥ $\Delta H = q_p$

$\Delta H = ?$

izobarno segrevanje : $p = konst.$

$C_{pm} = a + bT + cT^{-2}$

$n(CO_2) = 1\ mol$

$T_1 = 300\ K$

$T_2 = 2000\ K$

$a = 44,22$

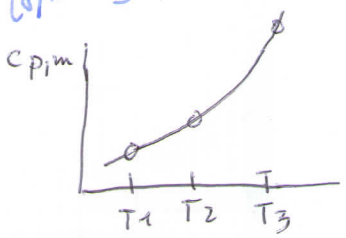
$b = 8,79 \cdot 10^{-3}$

$c = -8,62 \cdot 10^{5}$

interpolacijska funkcija

$C_{pm}(CO_2) = a + bT + cT^{-2}$

$[J/molK]$ $[J/molK^2]$ $[JK/mol]$




$$c_{p,m} = \frac{1}{n}\left(\frac{\partial q}{\partial T}\right)_p = \frac{1}{n}\left(\frac{\partial H}{\partial T}\right)_p$$

$$c_{p,m} = \frac{1}{n}\frac{\partial H}{\partial T} \qquad \partial H = n \cdot c_{p,m} \cdot \partial T$$

$$\Delta H = \int_{T_1}^{T_2} n \cdot c_{p,m} \cdot dT = n \int_{T_1}^{T_2} (a + bT + cT^{-2})\, dT =$$

$$= n\left[aT\Big|_{T_1}^{T_2} + \frac{bT^2}{2}\Big|_{T_1}^{T_2} - \frac{c}{T}\Big|_{1}^{T_2}\right] = 1 \cdot \left[44,22 \cdot 1700K + \frac{8,79 \cdot 10^{-3}\,(2000^2 - 300^2)}{2} - \left(-8,62 \cdot 10^{*5} \cdot \left(\frac{1}{2000} - \frac{1}{300}\right)\right)\right]$$

$$\Delta H = 89\,916\ J \doteq 89,9\ kJ$$

Jo je toplota pri $q_p$.

① $\Delta H_{tv}$ od $N_2O_5$!

1) $2NO + O_2 \rightarrow 2NO_2$ $\quad \Delta H_1^\circ = -114,1\ kJ$

2) $4NO_2 + O_2 \rightarrow 2N_2O_5$ $\quad \Delta H_2^\circ = -110,2\ kJ$

3) $N_2 + O_2 \rightarrow 2NO$

iščemo: $2N_2 + 5O_2 \rightarrow 2N_2O_5$

$N_2 + \frac{5}{2}O_2 \rightarrow N_2O_5 - \Delta_{tv}H$

pri tvorbenih ent. vedno iščemo reakcije nastanka IZ ELEMENTOV

$$\Delta_{tv}H^\circ = \Delta H_1^\circ + \frac{1}{2}\Delta H_2^\circ + \Delta H_3^\circ = 11,3\ kJ$$

② $\Delta$ sež. H (etan) pri 1 bar in 25°C!

$2\,C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

stand. tlak $\rightarrow \Delta_r H^\circ = ?$

iz tabel: $\Delta_r H^\circ = 4\Delta_{tv}H^\circ(CO_2) + 6\Delta_{tv}H^\circ(H_2O) - 2\Delta_{tv}H^\circ(C_2H_6) - 7\Delta_{tv}H^\circ(O_2)$ (0)

$= 4\cdot(-393,509\ kJ/mol) + 6\cdot(-285,83\ kJ/mol) - 2\cdot(-84,0\ kJ/mol) =$

$= -3121,0\ kJ$

$\Delta_{sež.}H^\circ = \frac{\Delta_r H^\circ}{n} = \frac{-3121,0\ kJ}{2\ mol} = -1560,5\ kJ/mol$

③ $CaCO_3$ (kalcit) $\rightarrow$ $CaCO_3$ (aragonit) $\quad \Delta U = 0,21\ kJ$ Izračunaj $\Delta H$!

$p = 1$ bar

$\Delta_r H = ?$

$H = U + pV$

$\Delta H = \Delta U + \Delta(pV) = \Delta U + p\Delta V$

$\rho_{(a)} = 2,93\ g/cm^3$

$\rho_{(k)} = 2,71\ g/cm^3$

$\Delta V = V_a - V_k = \frac{m}{\rho(a)} - \frac{m}{\rho(k)} = m\left(\frac{1}{\rho(a)} - \frac{1}{\rho(k)}\right) =$ (100 g (na mol))

$= 100\,g\cdot\left(\frac{1}{2,93} - \frac{1}{2,71}\right)\frac{cm^3}{g} =$

$= -2,77\ cm^3$

$\Delta H = 0,21\ kJ + 10^5\ Pa\cdot(-2,77\cdot10^{-6})\cdot m^3 =$

$= 209,7\ J$

④ $\frac{3}{2}H_{2(g)} + \frac{1}{2}N_{2(g)} \rightarrow NH_{3(g)}$ Izračunaj $\Delta U$ za sledečo reakcijo!

$\Delta_{tv}H^\circ_{(NH_3)} = -46,1\ kJ/mol$ ; $T = 25°C$

$\Delta U = ?$

$\Delta U = \Delta H - \Delta(pV) =$ (plini se obnašajo idealno) $= \Delta H - \Delta(nRT) =$

$= \Delta H - RT\Delta n = -46,1\ kJ/mol - RT(-1\ mol) = \Delta H + RT =$

$= -46\,100\ J + 8,314\ \frac{J}{mol\,K} \cdot 298\ K =$

$\Delta n = n(pr.) - n(reakt.) = 1\ mol - \left(\left(\frac{3}{2}+\frac{1}{2}\right)mol\right) = -1\ mol$

$= -43\,621\ J =$

$= \underline{\underline{-43,6\ kJ}}$

⑤ $3H_{2(g)} + N_{2(g)} \rightarrow 2NH_{3(g)}$ $\quad \Delta_r U^\circ(T(25°)) = -87,424\ kJ$

a) Izračunaj $\Delta_r H^\circ\ (T = 25°C) = ?$ $\quad \Delta_r U^\circ$

b) Izračunaj $\Delta_r H^\circ(T = 1500\ K) = ?$

Kirchoffov z.: $\Delta H_{(T=1500K)} = \Delta H_{(T=298K)} + \int_{298}^{1500} \Delta c_p \cdot dT$

$c_{pm}(NH_3) = a_1 + b_1 T + c_1 T^2$

$a_1 = 25,464$

$b_1 = 36,863 \cdot 10^{-3}$ } v $J/mol\,K$

$c_1 = -6,301 \cdot 10^{-6}$

$c_{pm}(H_2) = a_2 + b_2 T + c_2 T^2$

$a_2 = 29,066$

$b_2 = -0,837 \cdot 10^{-3}$

$c_2 = 2,013 \cdot 10^{-6}$

$c_{pm}(N_2) = a_3 + b_3 T + c_3 T^2$

$a_3 = 27,286$

$b_3 = 5,230 \cdot 10^{-3}$

$c_3 = -0,04 \cdot 10^{-6}$

$\Delta_r H^\circ = \Delta_r U^\circ + \Delta_r(pV) =$

$= \Delta_r U^\circ + \Delta_r(nRT) =$

$= \Delta_r U^\circ + \Delta n(2\ mol - 4\ mol)RT =$

$= \Delta_r U^\circ - 2\ mol\ RT =$

$= -87\,426\ kJ - 2\ mol \cdot 8,314\ \frac{J}{mol\,K} \cdot 298\ K =$

$= \underline{-92,382\ kJ}$

$R \xrightarrow{\Delta H(1500K)} P$

$c_p(r) \downarrow \qquad \uparrow c_p(p)$

$R \xrightarrow{\Delta H(298K)} P$

$\Delta_r H^\circ_{(1500K)} = \Delta_r H^\circ_{(298K)} + \int_{298}^{1500} \Delta c_p\, dT =$

$\boxed{\text{o - } p = 1\ bar}$

$= \Delta_r H^\circ_{(298K)} + \int_{298}^{1500} (\Delta a + \Delta b T + \Delta c T^2)\, dT =$

$\boxed{\Delta c_p} = 2 \cdot c_{pm}(NH_3) - 3 \cdot c_{pm}(H_2) - c_{pm}(N_2) =$

$= 2 \cdot (a_1 + b_1 T + c_1 T^2) - 3 \cdot (a_2 + b_2 T + c_2 T^2) - (a_3 + b_3 T + c_3 T^2) = \underbrace{2a_1 - 3a_2 - a_3}_{\Delta a = -63,566} + T\underbrace{(2b_1 - 3b_2 - b_3)}_{\Delta b = 7,102 \cdot 10^{-2}} + \underbrace{T^2(2c_1 + 3c_2 - c_3)}_{\Delta c = -1,86 \cdot 10^{-5}}$

$$= \Delta_r H^\circ(298) + \Delta a \, T\Big|_{298}^{1500} + \Delta b \, \frac{T^2}{2}\Big|_{298}^{1500} + \Delta c \, \frac{T^3}{3}\Big|_{298}^{1500} =$$

$$= \Delta_r H^\circ(298) + \Delta a \, (1500 - 298) + \frac{\Delta b}{2}(1500^2 - 298^2) + \frac{\Delta c}{3}(1500^3 - 298^3) =$$

$$= -112\,799\ \text{J} = \underline{-112{,}8\ \text{kJ}}$$