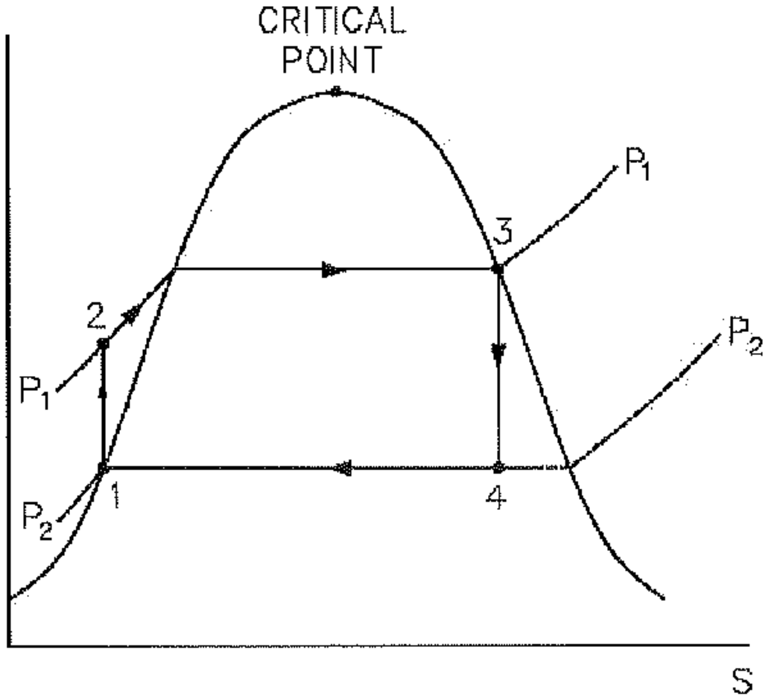
Studienämnden Kf / Kb

Termodynamik

Lösningar

TD



Av: Patrik "Putte" Andersson, kf-06

I.1.1. $T = 100°C = 373.15\ K$

$P = 120\ torr = 16 \cdot 10^3\ Pa$

$\rho = 0.6388\ kg/m^3$

$$\left.\begin{array}{l} PV = nRT \\ V = m/\rho \\ M = m/n \end{array}\right\} \quad M = \frac{R \cdot T \cdot \rho}{P} = 0.124\ kg/mol$$

$M_P = 30.97\ g/mol$

$$\frac{0.124 \cdot 10^3}{30.97} \approx 4$$

$\Rightarrow$ Molekylformeln är $\underline{\underline{P_4}}$

T. 1.4) $T = 298\ K$

a) $\langle v \rangle = \int_0^\infty v f(v)\, dv = \sqrt{\frac{8 k_B T}{\pi m}}$

$m_{He} = \frac{n \cdot M}{N_A} = 6.65 \cdot 10^{-24}\ g$

$m_{Hg} = \frac{n \cdot M}{N_A} = 3.33 \cdot 10^{-22}\ g$

$\langle V_{He} \rangle = 39.7\ m/s$

$\langle V_{Hg} \rangle = 5.6\ m/s$

$\frac{\langle V_{He} \rangle}{\langle V_{Hg} \rangle} \approx \underline{\underline{7.1}}$

b) Ideal gas ⇒ translationsenergi

$\langle E_{Tra} \rangle = \frac{3}{2} k_B T$ samma för He och Hg

$\frac{\langle E_{He} \rangle}{\langle E_{Hg} \rangle} = \underline{\underline{1}}$

T.1.5) CO_2 $T = 300\ K$

$v = 200\ m/s$ $v + dv = 250\ m/s$

$$f(v)\,dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \cdot \exp\left(\frac{-mv^2}{2k_B T}\right) dv$$

$f(v) = \text{konstant}$

$$\int_{v_1}^{v_2} f(v)\,dv \approx f(\langle v\rangle)(v_2 - v_1)$$

$$k_B = \frac{R}{N_A} \qquad \frac{m}{k_B} = \frac{m \cdot N_A}{R} = \frac{M}{R}$$

$$f(v)\,dv = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \cdot \exp\left(\frac{-Mv^2}{2RT}\right) dv$$

$f(225) = 1.915 \cdot 10^{-3}$

$\Rightarrow f(\langle v\rangle) \cdot \Delta v = \underline{\underline{0.096}}$

T.2.1) (5 bar, 2 dm³, 293 K) ⟶ (1 bar, V_2 dm³, 293 K)

a, P_{ex} = konstant = 10^5 Pa

$$w_{ec} = -\int P_{ex}\, dV = -P_{ex} \Delta V$$

För isoterm expansion är $P_1 V_1 = P_2 V_2$

$\Rightarrow V_2 = 10\ dm^3$

$\Rightarrow w_{ec} = \underline{-800}$ J

Systemet uträttar arbetet 800 J på omgivningen

b, 4 delsteg P_{ex} = 4, 3, 2, 1 bar

$$w_{ec} = \sum w_{ec}$$

$$w_{ec1} = -P_{ex1}(V_2 - V_1)$$

$$w_{ec2} = -P_{ex2}(V_3 - V_2)$$

$$w_{ec3} = -P_{ex3}(V_4 - V_3)$$

$$w_{ec4} = -P_{ex4}(V_5 - V_4)$$

$P_i V_i = P_j V_j \Rightarrow V_2 = 2.5\ dm^3$

$\Rightarrow V_3 = 3.3\ dm^3$

$\Rightarrow V_4 = 4.95\ dm^3$

$\Rightarrow V_5 = 9.9\ dm^3$

$$\Rightarrow w_{ec} = -200 - 240 - 330 - 495 = -1265\ J \approx \underline{1.3}\ kJ$$

c, Reversibel expansion

$$\underline{w}_{ec} = -\int P_{ex}\, dV = -\int RT \frac{dV}{\underline{V}} \Rightarrow$$

$$\underline{w}_{ec} = -P_1 \underline{V}_1 \ln\left(\frac{V_2}{V_1}\right) = \underline{\underline{-1.6}}\ \text{kJ}$$

$(n_1 R T_1 = P_1 \underline{V}_1)$

T.2.2}

$$W_{EC_1} = -\int P\,dV = -P\,\Delta V_1 = -9\cdot10^5\ \text{J}$$

(1 HS): $dU = dQ + dW$

$U = U(T)$ T konstant $\Rightarrow$

$dQ = -dW \Rightarrow$

$Q_1 = \underline{\underline{9\cdot10^5}}\ \text{J}$

$$W_{EC_2} = -P\,\Delta V_2 = 9\cdot10^6\ \text{J} \Rightarrow$$

$Q_2 = \underline{\underline{-9\cdot10^6}}$

$$W_{EC,min} = W_{EC,rev} = -\int P\,dV = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow W_{EC,min} = -P_1V_1\ln\left(\frac{V_2}{V_1}\right)$$

$P_1 = 10^5\ \text{Pa}$

$V_1 = 10\ \text{m}^3$

$\Rightarrow W_{EC,min} = \underline{\underline{2,3}}\ \text{MJ}$

T.2.3) $298\,K < T < 2000\,K$

$$C_p = a + bT + \frac{c}{T^2} \qquad a = 44.22 \ J/Kmol$$

$$b = 8.79 \cdot 10^{-3} \ J/Kmol$$

$$c = -8.62 \cdot 10^{5} \ JK/mol$$

5 mol CO_2 (g) vid 1 bar värms från 298K till 373K

$$C_p = \left(\frac{dH}{dT}\right)_P \Rightarrow dH = C_p dT \Rightarrow$$

$$\Delta H = \int \left(a + bT + \frac{c}{T^2}\right) dT = \left[aT + \frac{bT^2}{2} - \frac{c}{T}\right]_{T_1}^{T_2} \Rightarrow$$

$$\Delta H = 2956 \ J/mol$$

$$\Delta \underline{H} = n \cdot \Delta H = \underline{\underline{14.78}} \ kJ$$

$$\Delta \underline{U} = \Delta \underline{H} - P\Delta \underline{V} = \Delta \underline{H} - nR\Delta T = \underline{\underline{11.67}} \ kJ$$

T.2.4) $\Delta H = 1344.9$ kJ $\Delta H_{vap} = 1406$ kJ/kg

a, $H_2O((\ell), 0°C, 1 bar) \longrightarrow H_2O((\ell), 300°C, 85.927 bar)$

$\Delta U = \Delta H - \Delta(PV) = \Delta H - P_2V_2 + P_1V_1$

$\rho_1(H_2O(\ell), 0°C, 1 bar) = 0.998$ kg/dm³ $\Rightarrow$ $\underline{V_1} = 1,002\ dm^3$

p.s.s $\Rightarrow$ $\underline{V_2} = 1.404\ dm^3$

$\Rightarrow$ $\Delta U = \underline{1332.9}$ kJ

b, $H_2O((\ell), 300°C, 85.927 bar) \longrightarrow H_2O((g), 300°C, 85.927 bar)$

isobar och isoterm process!

$V_1 = 1.404\ dm^3$

$\rho_2(H_2O(g), 300°C, 85.927 bar) = 0,04619$ kg/dm³ $\Rightarrow V_2 = 21.65\ dm^3$

$\Delta U = \Delta H_{vap} - \Delta(PV) = \Delta H_{vap} - P\Delta V \Rightarrow$

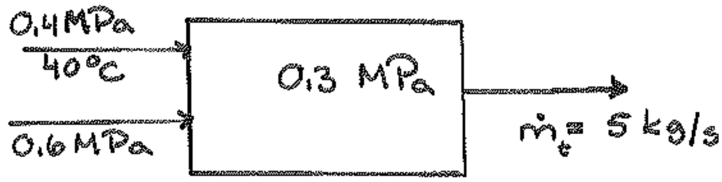
$\Delta U = \underline{1232}$ kJ

c, ideal ånga $PV = nRT$ $n = m/M = 55.5$ mol $\Rightarrow$

$\underline{V_2} = 30.8\ dm^3$

$\Delta U = \Delta H_{vap} - P\Delta V = \underline{1153}$ kJ

T. 2.7)



Energibalans

$$\dot{m}_L H^L + \dot{m}_V H^V = \dot{m}_t H^V = \dot{m}_t H(0{,}3\,MPa)$$

Massbalans

$$\dot{m}_L + \dot{m}_V = \dot{m}_t$$

$$H^V = H(0{,}6\,MPa) = 2756{,}9\ kJ/kg$$

$$H^L = H(40°C) + V^L \Delta P = H(40°C) + V^L(4 - P(40°C)) = 167{,}9\ kJ/kg$$

$$H(0{,}3\,MPa) = 2725{,}4\ kJ/kg$$

$$\dot{m}_V = \dot{m}_t - \dot{m}_L \Rightarrow$$

$$\dot{m}_L H^L + (\dot{m}_t - \dot{m}_L) H^V = \dot{m}_t H(0{,}3\,MPa) \Rightarrow$$

$$\dot{m}_L = \dot{m}_t \frac{(H(0{,}3\,MPa) - H^V)}{H^L - H^V} = 0{,}06\ kg/s$$

$$\dot{m}_V = \dot{m}_t - \dot{m}_L = \underline{4{,}96}\ kg/s$$

T. 3.1)

$S(25°C, 1 bar, (l)) \xrightarrow{1} S(25°C, P^{sat}, (l)) \xrightarrow{2}$
$S(25°C, P^{sat}, (g)) \xrightarrow{3} S(25°C, 1 bar, (g))$

$S^{\ominus}(g) = \Delta S_1 + \Delta S_2 + \Delta S_3 + S^{\ominus}(l)$

95.18 torr = 0.13 bar

$\Delta S_1 \approx 0$ kondenserad fas

$\Delta S_2 = \Delta H_{trs} \cdot T_{trs}^{-1} = 113.5$ J/mol K

$\Delta S_3 = -R \ln\left(\frac{1 bar}{p^{sat}}\right) \approx -1.7$ J/mol K

$\Rightarrow S^{\ominus}(g) = \underline{\underline{269.5}}$ J/mol K

T. 3.2)

$$A(s1, 0K) \xrightarrow{1} A(s1, 13.8K) \xrightarrow{2} A(s1, 201.4K) \xrightarrow{3}$$
$$A(s2, 201.4K) \xrightarrow{4} A(s2, 240.2K) \xrightarrow{5} A(s3, 240.2K) \xrightarrow{6}$$
$$A(s3, 292.25K) \xrightarrow{7} A(l, 292.25K) \xrightarrow{8} A(l, 298.15K)$$

$$S(T) = \int_0^T C_p \cdot T^{-1} dT + \sum \Delta H_{trs} \cdot T_{trs}^{-1}$$

$$C_p = \alpha T^3 \Rightarrow$$

$$\Delta S = \left[\alpha \frac{T^3}{3}\right]_0^T + \sum \Delta H_{trs} \cdot T_{trs}^{-1}$$

$$\Rightarrow \Delta S = \frac{C_p(T)}{3} + \sum \Delta H_{trs} \cdot T_{trs}^{-1}$$

$$\Delta S_1 = 3.142/_3 = 1.047 \text{ J/mol K}$$

$$\Delta S_2 = \int_{13.8}^{201.4} \frac{C_p(T)^{s1}}{T} dT = 115.39 \text{ J/mol K}$$

$$\Delta S_3 = \Delta H_{trs}(s_1 \rightarrow s_2) \cdot T_{trs}^{-1} = 5.45 \text{ J/mol K}$$

$$\Delta S_4 = \int_{201.4}^{240.2} \frac{C_p(T)^{s2}}{T} dT = 23.89 \text{ J/mol K}$$

$$\Delta S_5 = \Delta H_{trs}(s_2 \rightarrow s_3) \cdot T_{trs}^{-1} = 32.37 \text{ J/mol K}$$

$$\Delta S_6 = \int_{240.2}^{292.25} \frac{C_p(T)^{s3}}{T} dT = 28.45 \text{ J/mol K}$$

$$\Delta S_7 = \Delta H_{trs}(s_3 \rightarrow l) \cdot T_{trs}^{-1} = 8.38 \text{ J/mol K}$$

$$\Delta S_8 = \int_{292.25}^{298.15} \frac{C_p(T)^l}{T} dT = 3.245 \text{ J/mol K}$$

$$\Rightarrow S^{\ominus}(l, 25°c) = \sum_1^8 \Delta S_i = 218.222 \text{ J/mol K}$$

$A(l, 298.15K, P^{\ominus}) \xrightarrow{9} A(l, 298.15K, P^*) \xrightarrow{10}$

$A(g, 298.15K, P^*) \xrightarrow{11} A(g, 298.15K, P^{\ominus}) \xrightarrow{12}$

$A(g, 373.15, P^{\ominus})$

$\Delta S_9 \approx 0$ kondenserad fas

$$\Delta S_{10} = \Delta H_{trs}(l \rightarrow g) \cdot T_{trs}^{-1} = 143.38 \text{ J/mol K}$$

ΔS_{11} : tryckförändring, isotermt, ideal gas

$$\Rightarrow \Delta S_{11} = \int_{P^*}^{P^{\ominus}} \left(\frac{\partial S}{\partial P}\right)_T dP = -\int_{P^*}^{P^{\ominus}} \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$V = \frac{RT}{P} \Rightarrow \frac{\partial V}{\partial T} = \frac{R}{P} \Rightarrow$$

$$\Delta S_{11} = -\int_{P^*}^{P^{\ominus}} \frac{R}{P} dP = -37.014 \text{ J/mol K}$$

$$\Delta S_{12} = \int_{298.15}^{373.15} \frac{C_p(T)^g}{T} dT = 30.105 \text{ J/mol K}$$

$$\Rightarrow S^{\ominus}(g, 100°c) = \sum_1^{12} \Delta S_i = \underline{\underline{354.693}} \text{ J/mol K}$$

T. 3. 3) Försummar avvikelser från idealitet och den kondenserade fasens tryckberoende

$$\Delta S = \int \frac{C_P}{T} dT = \sum \frac{\Delta H_{vap}}{T} - R \int \frac{dP}{P}$$

$$\Delta S_a = -R \int \frac{dP}{P} = -R \ln\left(\frac{P_3}{P^{\ominus}}\right) = 38.4 \text{ J/mol K}$$

$$\Delta S_b = \frac{\Delta H_{vap} + \Delta H_{sub}}{T_3} = -199.8 \text{ J/mol K}$$

$$\Delta S_c = \int \frac{C_P}{T} dT = -31.657 \text{ J/mol K}$$

$$\Delta S_D \approx 0$$

$$S^{\ominus} A_{(s)}(25°C, 1atm) = S A_{(g)}(T_3, 1atm) + \sum \Delta S_i =$$

$$360.40976 + 38.4 - 199.8 - 31.657 = 167.35 \text{ J/mol K}$$

$$167.35 \text{ J/mol K} = 40 \text{ cal/mol K}$$

T. 3.4) Clausius - Clapeyron

$$\frac{dP^*}{dT} = \frac{\Delta_{sub}H}{T \cdot \Delta V}$$

Antar: $\Delta_{sub}H$ oberoende av T (ideal gas)

$$\Delta V = V^g - V^s \approx V^g = \frac{RT}{P}$$

$$\Rightarrow \quad \frac{dP}{P} = \frac{\Delta_{sub}H}{R} \frac{dT}{T^2}$$

$$\Rightarrow \quad \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{sub}H}{R}\left(T_1^{-1} - T_2^{-1}\right)$$

$$\Rightarrow \quad \Delta_{sub}H = \underline{\underline{90.4}} \text{ kJ/mol}$$

$S^\ominus$ ((s), 1atm, 25°C) S - tillståndsfunktion

Utgå från känt tillstånd o välj beräkningsväg

((g), 25°C, 1atm) ⇝ ((s), 25°C, 1atm)

↓ A C ↑

((g), 25°C, P*) —B→ ((s), 25°C, P*)

A: Isoterm tryckändring

$$\Delta S = -R \ln\left(\frac{P^*}{P^\ominus}\right)$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{sub}H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Rightarrow$$

$$P^* = P_1 \cdot \exp\left(\frac{\Delta_{sub}H}{R}\left(T_1^{-1} - T_2^{-1}\right)\right) = 1.558 \cdot 10^{-5} \text{ torr}$$

$$\Rightarrow \Delta S = 147.18 \text{ J/mol K}$$

B: Fasövergång

$$\Delta S = \frac{\Delta_{sub}H}{T} = -303.2 \text{ J/mol K}$$

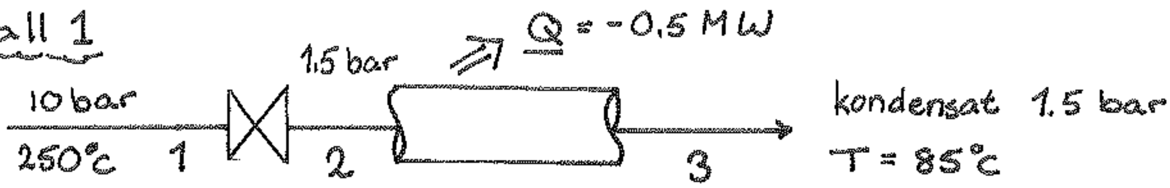
C: Isoterm tryckändring

$\Delta S \approx 0$ för kondenserade faser

$$S^\ominus(\text{(s)}, 25°\text{C}, 1\text{atm}) = S^\ominus(\text{(g)}, 25°\text{C}, 1\text{atm}) + \Delta S_A + \Delta S_B + \Delta S_C$$

$$S^\ominus(\text{(s)}, 25°\text{C}, 1\text{atm}) = \underline{\underline{180.1}} \text{ J/mol K}$$

T. 3.5} Fall 1



$H_1 = H(10\text{ bar}, 250°C) = 2943.1$ kJ/kg

$H_2 = H_1$ strypventil är isentalp

$H_3 = H(\ell, 85°C, 1.5\text{ bar})$

$\Delta H \approx V\Delta P$ för kondenserade faser $T_r < 0.75$

$V^L(85°C, P^*) = 0.001032\ m^3/kg$ oberoende av P

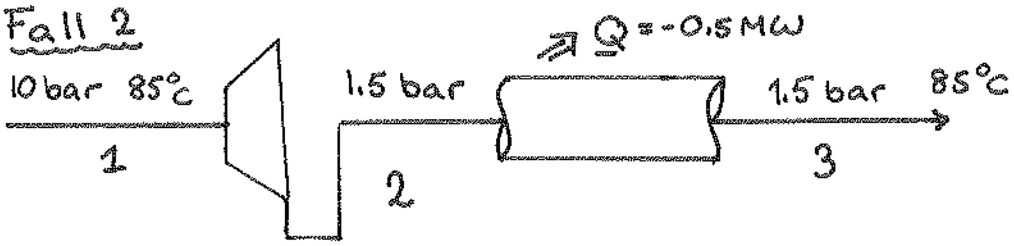
$P^*(85°C) = 0.0579 \cdot 10^6$ Pa

$H^L(85°C, P^*) = 356.01$ kJ/kg

$H_3 = H^L + V\Delta P = 356.1$ kJ/kg

Energibalans för värmeväxlaren:

$Q = \dot{m}\Delta H \Rightarrow \dot{m} = 0.193$ kJ/kg s



$H_1 = 2943.1 \text{ kJ/kg}$

$S_1 = S(10 \text{ bar}, 250\,°C) = 6.9265 \text{ kJ/kg K}$

$S_2' = S_1$

$S_2' = S_2'^L + q(S_2'^V - S_2'^L)$

$S_2'^L(1.5 \text{ bar}, T^*) = 1.4165 \text{ kJ/kg K}$

$S_2'^V(1.5 \text{ bar}, T^*) = 7.2429 \text{ kJ/kg K}$

$$q = \frac{S_2' - S_2'^L}{S_2'^V - S_2'^L} = 0.9457$$

$$\left.\begin{aligned} H_2' &= H_2'^L + q(H_2'^V - H_2'^L) \\ H_2'^L &= 461.1 \text{ kJ/kg} \\ H_2'^V &= 2690.6 \text{ kJ/kg} \end{aligned}\right\} \quad H_2' = 2569.5 \text{ kJ/kg}$$

$$\eta = \frac{\Delta H}{\Delta H'} \Rightarrow H_2 = H_1 + \eta(H_2' - H_1) = 2625.5 \text{ kJ/kg}$$

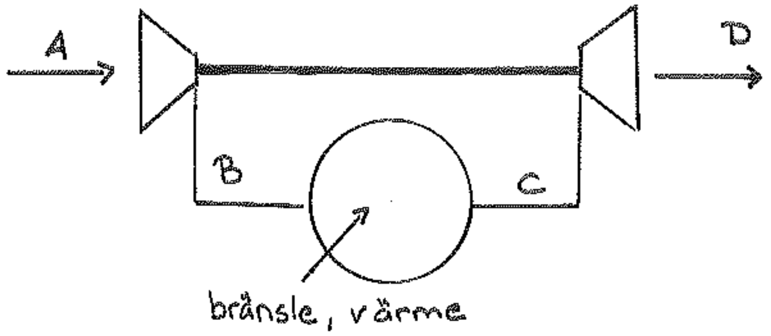
$H_3 = 356.1 \text{ kJ/kg}$

$\dot{Q} = \dot{m}_2 \Delta H \Rightarrow \dot{m} = 0.22 \text{ kg/s}$

a) $\dot{\omega}_{turb} = \dot{m}_2(H_2 - H_1) = \underline{-70} \text{ kW}$

b) $\dot{m}_2 / \dot{m}_1 \approx 1.14 \Rightarrow$ <u>14% ökning</u>

T. 4.2)



$$\omega_{s,net} = \dot{m}(\omega_{sk} + \omega_{st})$$

Energibalans:

$$\omega_{sk} = H_B - H_A$$

$$\omega_{st} = H_D - H_C$$

C_p är konstant med avseende på temperaturen T $\Rightarrow$

$$\Delta H_{AB} = C_p(T_B - T_A) = 180 \text{ kJ/kg} \Rightarrow$$

$$\omega_{sk} = 180 \text{ kJ/kg}$$

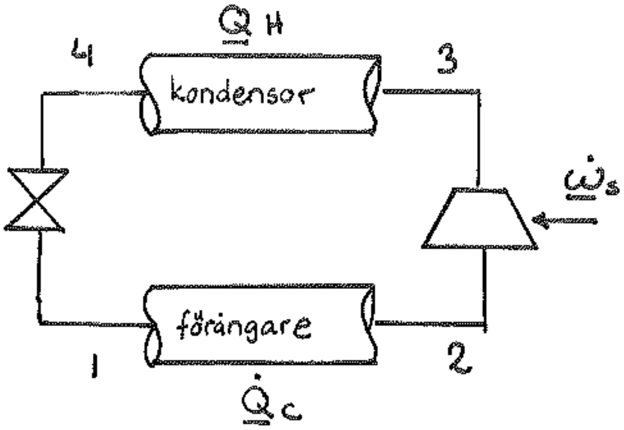
$$T'_D = T_C \left(\frac{P_D}{P_C}\right)^{R/C_p} \quad \text{molflöde} \Rightarrow$$

$$T'_D = T_C \left(\frac{P_D}{P_C}\right)^{1-K^{-1}} = 672{,}8 \text{ K}$$

$$\omega_{st} = \eta \Delta H_{D'C} = \eta C_p (T'_D - T_C) = -301 \text{ kJ/kg}$$

$$\omega_{s,net} = \underline{\underline{-7{,}26}} \text{ MW}$$

T. 4.3)



$\eta = 0.6$

$\dot{V}_2 = 0.5 \text{ m}^3\text{gas/s}$

a, $T_H = 284 \text{ K}$

Energibalans: $\dot{Q}_C = \dot{m}\Delta H$

$H_4 = H(\text{mättad vätska, } 284\text{K}) = 214.74 \text{ kJ/kg}$

$H_1 = H_4 = 214.74 \text{ kJ/kg}$

$H_2 = H(\text{mättad ånga, } 252\text{K}) = 385.84 \text{ kJ/kg}$

$\dot{m} = \dot{V} \cdot \rho$

$\left.\begin{array}{l} \dot{V}_2 = 0.5 \text{ m}^3/\text{s} \\ \rho_2 = 6.4715 \text{ kg/m}^3 \end{array}\right\} \dot{m} = 3.23575 \text{ kg/s}$

$\dot{Q}_C = \dot{m}\Delta H_{21} = \underline{\underline{553.6}} \text{ kJ/kg}$

Energibalans: kompressor

$$\underline{W}_s = \dot{m}\,\Delta H_{32}$$

$P_4 = P(\text{mättad vätska}, 284\,K) = 0.42651\ MPa$

Mollierdiagram ger $H_3' = 410\ kJ/kg$

$$\eta = \frac{H_3' - H_2}{H_3 - H_2} \Rightarrow \Delta H_{32} = 40.266\ kJ/kg$$

$$\underline{W}_s = \dot{m}\,\Delta H_{32} = \underline{\underline{130.3}}\ kW$$

T.5.1)
$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P = \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial V}{\partial T}\right)_P - T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \quad \Rightarrow$$

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right) \quad \text{V.S.V}$$

T. 5.2)

1HS: $dU = dQ + dW$

2HS: $TdS = dQ$

$$\Rightarrow \quad dU = TdS + dW = TdS - PdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T \qquad \text{V.S.V}$$

Ideal gas: $PV = RT \quad \Rightarrow \quad P = RT/V$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T \cdot \frac{R}{V} - P =$$

$$\frac{TR}{V} - \frac{TR}{V} = 0 \qquad \text{V.S.V}$$

T. 5.3} $dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$

Kedjeregeln: $\left(\frac{\partial X}{\partial Y}\right)_F = \left(\frac{\partial X}{\partial Z}\right)_F \left(\frac{\partial Z}{\partial Y}\right)_F$

$$\left(\frac{\partial S}{\partial P}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V = \frac{C_V}{T}\left(\frac{\partial T}{\partial P}\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = \frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P$$

$$\Rightarrow dS = \frac{C_V}{T}\left(\frac{\partial T}{\partial P}\right)_V dP + \frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P dV \qquad \text{V.S.V}$$

T.5.4) Ideal gas: $V = RT/p$

a, $\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{VP} = T^{-1}$

$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{V}\frac{RT}{P^2} = P^{-1}$

b, $\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H \qquad C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p$

$$\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial P}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_P = -1$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu_{JT} = \frac{-1}{\left(\frac{\partial P}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_P} = \left(\frac{\partial H}{\partial P}\right)_T C_p^{-1} \quad \text{V.S.V}$$

c, $PV = RT \qquad U = U(T) \Rightarrow H = U(T) + RT$

dvs $H = H(T)$ ej tryckberoende $\Rightarrow$

$\mu_{JT} = \left(\frac{\partial H}{\partial P}\right)_T = 0$

d, $C_p = C_v + R \qquad \alpha_p = T^{-1} \qquad K_T = P^{-1} \Rightarrow$

$$\alpha_p^2 \frac{TV}{K_T} = \frac{TVP}{T^2} = \frac{PV}{T} = R \Rightarrow$$

$C_p = C_v + R$ V.S.V

T.5.5) $H = U + PV$

$dH = dU + PdV + VdP$

1HS: $dU = dQ + dW$

2HS: $dQ = TdS$

$\Rightarrow dH = TdS + VdP$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{Maxwell relation}$$

$A = U - TS$

$dA = dU - TdS - SdT = -SdT - PdV$

$$dA = \underbrace{\left(\frac{\partial A}{\partial T}\right)_V}_{-S} dT + \underbrace{\left(\frac{\partial A}{\partial V}\right)_T}_{-P} dV$$

$$\frac{\partial^2 A}{\partial V \partial T} = -\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T$$

$$K_T = -V^{-1}\left(\frac{\partial V}{\partial P}\right)_T \quad \Rightarrow$$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - K_T^{-1} \qquad \text{V, S. V}$$

Ideal gas: $PV = nRT$

$$\left(\frac{\partial V}{\partial P}\right) = -\frac{nRT}{P^2} \quad \Rightarrow \quad K = P^{-1}$$

$$\left(\frac{\partial P}{\partial T}\right) = \frac{nR}{V} \Rightarrow T\left(\frac{\partial P}{\partial T}\right) = \frac{nRT}{V} = P$$

$$\left(\frac{\partial H}{\partial V}\right)_T = P - P = 0$$

Entalpin beror enbart av T

T.5.6} $\alpha_p = V^{-1}\left(\frac{\partial V}{\partial T}\right)_p \Rightarrow \frac{C_p}{TV\alpha_p} = \frac{C_p}{T\left(\frac{\partial V}{\partial T}\right)_p}$ (*)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$ Maxwell relation

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\left(\frac{\partial S}{\partial V}\right)_P\left(\frac{\partial V}{\partial T}\right)_P\right) \Rightarrow$$

$$(*) = \frac{T\left(\frac{\partial S}{\partial V}\right)_P\left(\frac{\partial V}{\partial T}\right)_P}{T\left(\frac{\partial V}{\partial T}\right)_P} = \left(\frac{\partial S}{\partial V}\right)_P \overset{\text{Maxwell}}{=} \left(\frac{\partial P}{\partial T}\right)_P$$

T.5.7) $\rho(C_6H_6(l), 20°C, 1bar) = 0.8765\ g/cm^3$

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P = 12.4\cdot10^{-4}\ K^{-1}$$

$$dG = VdP - SdT \Rightarrow \Delta G = \Delta H - T\Delta S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\left(-SdT + VdP\right)\right)_T = \frac{\partial}{\partial P}(VdP)$$

$$\Rightarrow \Delta G = \int\left(\frac{\partial G}{\partial P}\right)_T dP = \int VdP = V\Delta P$$

$$V = M\cdot\rho^{-1} = 89.12\cdot10^{-6}\ m^3/mol \Rightarrow$$

$$\Delta G = \underline{\underline{80.208}}\ J/mol$$

$$\Delta S = \int\left(\frac{\partial S}{\partial P}\right)_T dP = -\int\left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\left(\frac{\partial V}{\partial T}\right) = V\cdot\alpha_P \Rightarrow$$

$$\Delta S = -\int V\alpha_P dP = -V\alpha_P\Delta P = -\underline{\underline{0.099}}\ J/molK$$

$$\Delta H = \Delta G + T\Delta S = \underline{\underline{51.2}}\ J/mol$$

T.5.8) $Sn(\beta) \rightarrow Sn(\alpha)$

Spontan reaktion : $\Delta G < 0$

$\Delta G = \Delta H - T\Delta S = 89{,}29 \ J/mol \quad > 0$

$\therefore$ $Sn(\beta)$ stabilast vid 25°C

Vid jämvikt är $\Delta G = 0$

$\Delta H = T\Delta S \Rightarrow \quad T = \underline{\underline{12{,}95}}\ °C$

T.6.13 $PV = RT + BP \Rightarrow V = \frac{RT}{P} + B$

$dH = TdS + VdP \Rightarrow$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\Delta H = \int\left(\frac{\partial H}{\partial P}\right) dP = \int V - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT} = \frac{R}{P} - \frac{\beta\gamma e^{\gamma/T}}{T^2} \Rightarrow$$

$$\Delta H = \int B + \frac{\beta\gamma e^{\gamma/T}}{T} dP =$$

$$\left[\alpha + \beta e^{\gamma/T}\left(1 + \frac{\gamma}{T}\right)\right] \Delta P = \underline{\underline{-1294}} \text{ J/mol}$$

T. 6.2)

$$\frac{PV}{RT} = 1 - \frac{a}{V} \Rightarrow P = \frac{RT}{V} - \frac{aRT}{V^2}$$

$$\left.\begin{aligned} dA &= -SdT - PdV \\ dG &= -SdT + VdP \end{aligned}\right\} T \text{ konstant} \Rightarrow \begin{aligned} dA &= -PdV \\ dG &= VdP \end{aligned}$$

$$\Delta A = \int \left(\frac{\partial A}{\partial V}\right)_T dV = -\int P dV \Rightarrow$$

$$\Delta A = \int \left(\frac{aRT}{V^2} - \frac{RT}{V}\right) dV = aRT\left(\frac{1}{V_1} - \frac{1}{V_2}\right) + RT \ln\left(\frac{V_1}{V_2}\right) \Rightarrow$$

$$\Delta A = \underline{\underline{7273}} \ J/mol$$

$$\Delta G = \Delta A + \Delta(PV)$$

$$\left.\begin{aligned} P_1 &= 110.6 \text{ kPa} \\ P_2 &= 8498 \text{ kPa} \end{aligned}\right\} \Delta G = \underline{\underline{6888.7}} \ J/mol$$

$$\Delta A^{ig} = -\int P dV = -\int \frac{RT}{V} dV = 7657 \ J/mol$$

$$\frac{\Delta A^{ig}}{\Delta A} = 1.053 \Rightarrow \underline{\underline{5.3\%}}$$

T. 8. 13 $H_2O\,(l) \rightleftharpoons H_2O\,(g)$

$$\ln\left(\frac{P^{sat}}{P_R^{sat}}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right) \qquad (8\text{-}9) \quad \Rightarrow$$

ΔH_{vap} = <u>440.4</u> kJ/mol

T. 8. 2} $H_2O(s) \rightleftharpoons H_2O(g)$ $H_2O(l) \rightleftharpoons H_2O(g)$ $H_2O(s) \rightleftharpoons H_2O(l)$

(a) (b) (c)

Clapeyron (8.6)

$$\frac{dP}{dT} = \frac{\Delta H_{trans}}{T(V^v - V^l)}$$

a, $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} = 51.075$ kJ/mol

$V^v = \frac{RT}{P} = 3.716\ m^3/mol$ ⇒

$$\frac{dP}{dT} = \frac{\Delta H_{sub}}{T(V^v - V^s)} = \underline{\underline{50.3}}$$

b, $$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T(V^v - V^l)} = \underline{\underline{44.4}}$$

c, $$\frac{dP}{dT} = \frac{\Delta H_{fus}}{T(V^l - V^s)} = \underline{\underline{-13,57 \cdot 10^6}}$$

T.8.3) $\ln\left(\frac{P^{sat}}{P_R^{sat}}\right) = -\frac{\Delta H_{trans}}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)$

a, $H_2O(l)$

$\ln(P^{sat}) = \ln(P_R^{sat}) - \frac{\Delta H_{vap}}{R}\left(\frac{1}{263.15} - \frac{1}{273.16}\right) = 0.767$

$\Rightarrow P^{sat} = \underline{2.15}$ torr

b, $H_2O(s)$

$\ln(P^{sat}) = \ln(P_R^{sat}) - \frac{\Delta H_{sub}}{R}\left(\frac{1}{263.15} - \frac{1}{273.16}\right) = 0.667$

$\Rightarrow P^{sat} = \underline{1.949}$ torr

T.8.4) Clapeyron: $\frac{dP}{dT} = \frac{\Delta H_{trs}}{T \Delta V}$

a, $\ln(P_s) = 22.8371 - 3155.6 \cdot T^{-1}$ (torr) $\Rightarrow$

$P_s = \exp\left(22.8371 - 3155.6 \cdot T^{-1}\right)$

$\frac{dP}{dT} = 3155.6 \cdot T^{-1} \cdot \exp\left(22.8371 - 3155.6 \cdot T^{-1}\right) = 261.4 \text{ torr/K}$

$261.4 \text{ torr/K} = 34.850 \cdot 10^3 \text{ Pa/K}$

$\Delta H_{sub} = T(V_v - V_s) \cdot \frac{dP}{dT} = \underline{\underline{23.77}} \text{ kJ/mol}$

$\Delta H_{vap} = T(V_v - V_L) \frac{dP}{dT} = \underline{\underline{15.17}} \text{ kJ/mol}$

Antag ideal gas & $V_v \gg V_L$

$\frac{dP}{dT} = \frac{\Delta H_{trs}}{T \Delta V} \approx \frac{\Delta H_{trs}}{T V_v} = \frac{\Delta H_{trs} \cdot P}{R T^2}$

$\left\{ \frac{d \ln P}{dP} = P^{-1} \Rightarrow dP = P \cdot d\ln(P) \right\} \Rightarrow$

$\frac{d \ln(P) \cdot P}{dT} = \frac{\Delta H_{trs} \cdot P}{R T^2} \Rightarrow$

$\frac{d \ln(P_s)}{dT} = \frac{3155.6}{T^2}$ $\qquad \frac{d \ln(P_L)}{dT} = \frac{2018.8}{T^2}$

$$\Delta H_{sub}^{ig} = \frac{RT^2 \cdot 3155.6}{T^2} = 23.23 \text{ kJ/mol}$$

$$\Delta H_{vap}^{ig} = R \cdot 2018.8 = 16.78 \text{ kJ/mol}$$

$$\frac{\Delta H_{sub}^{ig}}{\Delta H_{sub}} = 0.977 \Rightarrow \underline{2.3\%} \text{ fel}$$

$$\frac{\Delta H_{vap}^{ig}}{\Delta H_{vap}} = 1.106 \Rightarrow \underline{10.6\%} \text{ fel}$$

b, $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \Rightarrow$

$$\Delta H_{fus} = \underline{8.6} \text{ kJ/mol}$$

c, $\dfrac{dP_s}{dT} = \dfrac{\Delta H_{fus}}{T(V_l - V_s)} \Rightarrow$

$$\Delta P = \frac{\Delta H_{fus}}{\Delta V} \cdot \ln\left(\frac{T_2}{T_1}\right)$$

$$T_2 = T_1 \exp\left(\frac{\Delta P \Delta V}{\Delta H_{fus}}\right)$$

$$P_1 = \exp\left(22.8371 - \frac{3155.6}{216.55}\right) \cdot \frac{101325}{760} = 518042 \text{ Pa} \Rightarrow$$

$$T_2 = \underline{238} \text{ K}$$

T. 8.6) $CBr_4(s)_I \rightleftharpoons CBr_4(s)_{II}$

a, $P = 1$ atm

Clapeyron

$$\frac{dP}{dT} = \frac{\Delta H_{trs}}{\Delta V\, T_{trs}} \Rightarrow \Delta H_{trs} = \frac{dP}{dT} \cdot \Delta V\, T_{trs}$$

$$P = \frac{T_{trs} - a}{b} \Rightarrow \frac{dP}{dT} = \frac{1}{b} \Rightarrow$$

$\Delta H_{trs} = 21061$ J/kg (tänk på enhet: atm → Pa)

$M = 331.627 \cdot 10^{-3}$ kg/mol $\Rightarrow$

$\Delta H^{M}_{trs} = \Delta H_{trs} \cdot M = \underline{\underline{6984}}$ J/mol

b, $P = 2000$ atm

$\Delta V = 15.3$ cm/kg $\Rightarrow$

$\Delta H_{trs} = 18819.8$ J/kg $\Rightarrow$

$\Delta H^{M}_{trs} = \underline{\underline{6241}}$ J/mol

T. 8.8)

$$\left(\frac{H-H^{ig}}{RT}\right) = -\int T\left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$$\left(\frac{S-S^{ig}}{R}\right) = -\int\left[(Z-1) + T\left(\frac{\partial Z}{\partial T}\right)_P\right]\frac{dP}{P}$$

a, $G = H - TS \qquad Z = PV(RT)^{-1}$

$$G - G^{ig} = (H-H^{ig}) - T(S-S^{ig}) = RT\int(Z-1)\frac{dP}{P} =$$

$$\int\left(V - \frac{RT}{P}\right)dP = RT\ln(\varphi) \quad (8.22) \quad \text{V.S.V}$$

b, $V = \frac{RT}{P} + B \Rightarrow \varphi = \exp\left(\frac{1}{RT}\int B\,dP\right) \Rightarrow$

$$\varphi = \exp\left(\frac{BP}{RT}\right)$$

Maclaurinutveckling: $e^x = 1 + x + \mathcal{O}(x) \Rightarrow$

$$\varphi = 1 + \frac{BP}{RT} \quad \text{V.S.V}$$

T. 9.1) Vatten (1) + n-propanol (2)

a, $\mu_i^*(l) = \mu_i^*(g)$, $\mu_i(l) = \mu_i(g)$

$$\mu_i^*(l) = \mu_i^\ominus + RT\ln(P_i^*/P^\ominus) \qquad (a)$$

$$\mu_i(l) + RT\ln(a_i) = \mu^\ominus + RT\ln(P_i/P^\ominus) \qquad (b)$$

$$(b)-(a) \Rightarrow RT\ln(a_i) = RT\ln(P_i/P_i^*) \Rightarrow$$

$$a_i = \frac{P_i}{P_i^*} \equiv \gamma_i x_i$$

$$P_i = y_i P \Rightarrow \gamma_i = \frac{y_i P}{x_i P_i^*}$$

$$\gamma_1 = \frac{(1-y_2)P}{(1-x_2)P_1^*} = \underline{1.265}$$

$$\gamma_2 = \frac{y_2 P}{x_2 P_2^*} = \underline{2.177}$$

b, $\Delta G_{mix} = \sum n_i\mu_i - \sum n_i\mu_i^* = \sum n_i(\mu_i^* + RT\ln(a_i)) - \sum n_i\mu_i^* =$
$\sum n_i RT\ln(a_i) = nRT\sum x_i\ln(a_i) = nRT\sum x_i\ln(\gamma_i x_i)$

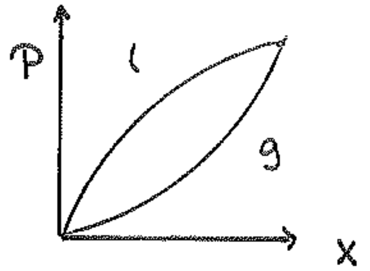
$n = 1$ mol $\Rightarrow \Delta G_{mix} = \underline{-593}$ J

$$\Delta S_{mix} = \left(\frac{\partial \Delta G_{mix}}{\partial T}\right)$$

$$\Delta S_{mix}^{ig} = -nRT\sum x_i\ln x_i = 4.76 \text{ J/K} \qquad (\gamma_i = 1)$$

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} = \underline{1134} \text{ J}$$

T. 9.3)



$$T_r = \frac{T}{T_c} \qquad y_1 = y_2 = 0.5$$

a)

	Pentan 1	Hexan 2
P_c	3.369 MPa	3.012 MPa
ω	0.249	0.305
T_c	469.7 K	507.4 K

$$K = \frac{P_c \cdot 10^{7/3(1+\omega)(1-T_r^{-1})}}{P}$$

$$\sum \frac{y_i}{K_i} = 1 \Rightarrow \frac{y_1}{K_1} + \frac{y_2}{K_2} = 1$$

Testa olika T tills $\sum y_i/K_i = 1 \Rightarrow T_d = \underline{329\ K}$

$$\left. \begin{array}{l} K_i = \frac{P_i^{sat}}{P} \\ y_i P = x_i P_i^{sat} \end{array} \right\} K_i = \frac{y_i}{x_i}$$

$$x_2 = \frac{y_2}{K_2} = \frac{0.5}{0.6726} = \underline{0.743}$$

b/ $$K_i = \frac{P_c \cdot 10^{7/3(1+\omega)(1-T_r^{-1})}}{P}$$

$$\sum K_i x_i = 1$$

Testa olika T tills $\sum K_i x_i = 1 \Rightarrow T_b = \underline{\underline{321\ K}}$

$$y_2 = x_2 K_2 = 0.5 \cdot 0.5137 = \underline{\underline{0.26}}$$

T. 14.1)

$$a(P) = \exp\left(\frac{1}{RT}\int V dP\right) = \exp\left(\frac{V\Delta P}{RT}\right)$$

molvolymen är tryckberoende

$$V = \frac{V}{n} = \frac{V}{\frac{m}{M}} = \frac{M}{\rho}$$

$$\left.\begin{aligned} M &= 18\cdot 10^{-3}\ kg/mol \\ \rho &= 1000\ kg/m^3 \end{aligned}\right\} \quad V = 1.8\cdot 10^{-5}\ m^3/mol \quad \Rightarrow$$

$$a = \exp\left(\frac{V(10-1)\cdot 10^5}{RT}\right) = \underline{\underline{1.007}}$$

T. 14.3} $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$\Delta H^{\ominus} = \sum \nu_i H_i^{\ominus} \Rightarrow$

$\Delta H^{\ominus}_{298} = -9.48 \text{ kJ/mol}$

$\Delta S^{\ominus} = \sum \nu_i S_i^{\ominus} \Rightarrow$

$\Delta S^{\ominus}_{298} = 21.28 \text{ J/mol K}$

$\Delta C_p = \sum \nu_i C_{pi}^{\ominus} \Rightarrow$

$\Delta C_{p298} = -7.4 \text{ J/mol K}$

$\Delta H^{\ominus}_{500} = \Delta H^{\ominus}_{298} + \Delta C^{\ominus}_{p298}(500-298) = -10974.8 \text{ J/mol}$

$\Delta S^{\ominus}_{500} = \Delta S^{\ominus}_{298} + \Delta C_{p298} \cdot \ln\left(\frac{T_2}{T_1}\right) = 17.98 \text{ J/mol K}$

$\Delta G^{\ominus}_{500} = \Delta H^{\ominus}_{500} - T_2 \Delta S^{\ominus}_{500} = -19965 \text{ J/mol}$

$K_a = \exp\left(-\frac{\Delta G^{\ominus}_{500}}{R T_2}\right) = 122$