

1. a) Starting with $dH = TdS + Vdp$, prove $\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$

Hint: Use one of the partial differential relations derived from $dG = -SdT + Vdp$.

[3]

b) Use the result from part a to show $(\partial H/\partial p)_T = 0$ for an ideal gas.

2. Use the differential $dA = -SdT - pdV$ of the Helmholtz energy to prove:

[3]

a) $(\partial A/\partial V)_T = -p$

b) $(\partial A/\partial T)_V = -S$

c) $(\partial p/\partial T)_V = (\partial S/\partial V)_T$

3. a) 8.00 moles of pure N₂ gas at 300 K and 2.00 bar and 2.00 moles of pure O₂ gas at 300 K and 2.00 bar mix isothermally at constant pressure. Assuming ideal gas behavior, calculate q , w , ΔU , ΔH , ΔG and ΔS for the mixing process.

[7]

b) Is the process described in part a reversible? Justify your answer.

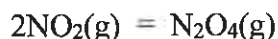
4. A gas mixture at 500 K contains N₂ at 1.50 bar, H₂ at 3.60 bar and NH₃ at 2.00 bar. Is the gas mixture at chemical equilibrium? If not, is the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ spontaneous? Justify your answer. Data at 500 K: $\Delta G_{\text{fm}}^\circ(\text{NH}_3, \text{g}) = 4.80 \text{ kJ mol}^{-1}$

[3]

5. A 50.0 L tank contains a mixture of NO₂(g) and N₂O₄(g) at 25 °C. A gauge indicates a total pressure of 5.76 bar in the tank. Calculate the number of moles of NO₂ and N₂O₄ at equilibrium.

[4]

Assume ideal gas behavior and use equilibrium constant $K = 3.01$ for the reaction



Q1 a) $dH = Tds + Vdp$ ← to get $\left(\frac{\partial H}{\partial P}\right)_T$ divide by dp_T

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V \left(\frac{\partial P}{\partial P}\right)_T = 1$$

$\left(\frac{\partial S}{\partial P}\right)_T$? a more convenient result from $dG = -SdT + Vdp$

$$-S = \left(\frac{\partial G}{\partial T}\right)_P \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

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

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

order of differentiation (T or P first) "doesn't matter"

$$\begin{aligned} \left(\frac{\partial H}{\partial P}\right)_T &= T \left(\frac{\partial S}{\partial P}\right)_T + V = T \left(-\frac{\partial V}{\partial T}\right)_P + V \\ &= -T \left(\frac{\partial V}{\partial T}\right)_P + V = -TV\beta + V = V(1 - \beta T) \end{aligned}$$

$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ (Volumetric thermal expansion coefficient)

"special" case:

b) ideal gas $V = \frac{nRT}{P}$

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

n, R, P constant for $\left(\frac{\partial V}{\partial T}\right)_P$

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

(Explains why $dH = C_p dT$, even if p changes) (IDEAL GAS)

Helmholtz free energy $A(T, V)$

Q2 $dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$ independent variables T, V

compare $dA = -SdT - PdV$

a) $-P = \left(\frac{\partial A}{\partial V}\right)_T$

b) $-S = \left(\frac{\partial A}{\partial T}\right)_V$

c) mathematical property of mixed partial derivatives

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial A}{\partial T} \right)_V \right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial A}{\partial V} \right)_T \right]_V$$

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

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

(minus signs cancel)

Q3 a) isothermal ideal gases U, H depend only on T .

\rightarrow no change in $T \rightarrow$ no change in U, H

$\Delta U = 0$
 $\Delta H = 0$

const. pressure: $\Delta H = q = 0$

$W = -\int_{ext} p dV = -p dV = -p \Delta V = 0$ (volume constant)
(pressure constant)

$V = \frac{(n_{N_2} + n_{O_2}) RT}{P} = \text{const.}$ (n_{N_2}, n_{O_2}, T, P all constant)

$\Delta U = \Delta H = q = W = 0$

?? Is anything happening??

... Yes!

(Q3 a) cont.) $\left(\begin{array}{l} \text{mole fractions:} \\ x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{O_2}} = \frac{8.00 \text{ mol}}{8.00 \text{ mol} + 2.00 \text{ mol}} = 0.800 \\ x_{O_2} = 1 - x_{N_2} = 0.200 \end{array} \right)$
 mix n_{N_2} moles N_2 and n_{O_2} moles O_2 at constant T, P

$$\begin{aligned} \Delta G_{\text{mix}}(T, P) &= n_{N_2} RT \ln x_{N_2} + n_{O_2} RT \ln x_{O_2} \\ &= (8.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln(0.800) \\ &\quad + (2.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln(0.200) \\ &= -4452 \text{ J} - 8029 \text{ J} \end{aligned}$$

$$\boxed{\Delta G_{(T, P)} = -12480 \text{ J}}$$

$$\begin{aligned} \Delta G &= \Delta(U + PV - TS) = \Delta(H - TS) = \cancel{\Delta H} - \overset{T \text{ const.}}{\Delta(TS)} \\ \Delta G &= -T\Delta S \quad \Rightarrow \quad \Delta S = -\Delta G/T \end{aligned}$$

$$\Delta S = -\left(\frac{-12480 \text{ J}}{300 \text{ K}}\right) = \boxed{41.6 \text{ J K}^{-1}}$$

b) $\Delta G_{T, P} = 0$ reversible process

$\Delta G_{T, P} < 0$ irreversible process

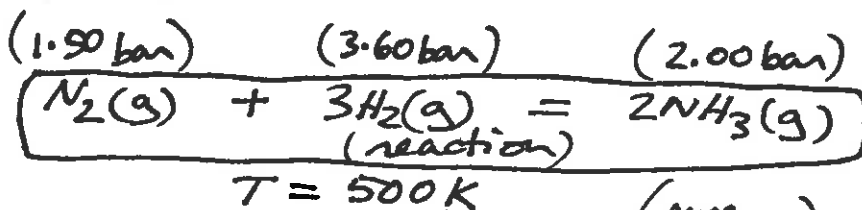
here $\Delta G_{T, P} < 0 \quad \therefore$ mixing the gases is spontaneous

also, the system ($N_2 + O_2$) is isolated

$$\Delta V = 0 \quad \Delta U = 0$$

$\left(\Delta S_{U, V} > 0 \right)$ another criterion for an irreversible process

Q4



$$T = 500 \text{ K}$$

$$\begin{aligned} \Delta G^\circ &= 2\Delta G_{\text{fm}}^\circ(\text{NH}_3, \text{g}) - \cancel{\Delta G_{\text{fm}}^\circ(\text{N}_2, \text{g})} - 3\cancel{\Delta G_{\text{fm}}^\circ(\text{H}_2, \text{g})} \\ &= 2(4.80 \text{ kJ K}^{-1} \text{ mol}^{-1}) = 9.60 \text{ kJ mol}^{-1} \end{aligned}$$

$$K = \left(\frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} \right)_{\text{at equilibrium}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{9600 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (500 \text{ K})}\right)$$

$$\boxed{K = \exp(-2.309)} = 0.0993$$

reaction quotient $Q = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$

$$\boxed{Q = \frac{(2.00)^2}{(1.50)(3.60)^3} = 0.0572 < K}$$

$$\boxed{Q < Q_{\text{equilibrium}} (= K)}$$

too little products
and/or too much reactants

spontaneous
reaction:



// or // Show $\Delta G_r = \Delta G^\circ + RT \ln\left(\frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}\right)$

$$\Delta G_r = 9600 \frac{\text{J}}{\text{mol}} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(500 \text{ K}) \ln\left(\frac{2.00^2}{(1.50)(3.60^3)}\right)$$

$$\Delta G_r = (9600 - 11900) \frac{\text{J}}{\text{mol}} = -2300 \frac{\text{J}}{\text{mol}}$$

$\Delta G_r < 0$
reactants \rightarrow products
spontaneous

Q5



I equilibrium constant $K = \left(\frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} \right)_{\text{equilibrium}} = 3.01 \text{ (at } 25^\circ\text{C)}$

II total pressure (from pressure gauge) $P = P_{\text{NO}_2} + P_{\text{N}_2\text{O}_4} = 5.76 \text{ bar}$

two equations (I) and (II) and two unknowns (P_{NO_2} and $P_{\text{N}_2\text{O}_4}$)
Solve!

equilibrium constant $K = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = \frac{P - P_{\text{NO}_2}}{P_{\text{NO}_2}^2}$

$$3.01 = \frac{5.76 - P_{\text{NO}_2}}{P_{\text{NO}_2}^2}$$

$$3.01 P_{\text{NO}_2}^2 = 5.76 - P_{\text{NO}_2} \quad (\div 3.01)$$

$$P_{\text{NO}_2}^2 + \frac{P_{\text{NO}_2}}{3.01} - \frac{5.76}{3.01} = 0 \Rightarrow P_{\text{NO}_2}^2 + 0.3322 P_{\text{NO}_2} - 1.914$$

Solve quadratic equation

$$P_{\text{NO}_2} = \frac{-0.3322 \pm \sqrt{0.3322^2 - 4(-1.914)}}{2}$$

only the positive root is acceptable

$$P_{\text{NO}_2} = 1.227 \text{ bar} \quad P_{\text{N}_2\text{O}_4} = P - 1.227 \text{ bar} = 4.532 \text{ bar}$$

$$n_{\text{NO}_2} = \frac{P_{\text{NO}_2} V}{RT} = \frac{(1.227 \text{ bar})(50.0 \text{ L})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 2.47 \text{ mol NO}_2$$

$$n_{\text{N}_2\text{O}_4} = (4.532)(50.0) / [(0.08314)(298.15)] = 9.14 \text{ mol N}_2\text{O}_4$$