

1. Nova Scotia Power charges residential customers \$0.156 per kW hr of electrical energy. How much will it cost to provide 1.00 GJ of heat to keep a house warm using:

[3] a) electric baseboard heaters

b) an electrical heat pump operating reversibly between $T_H = 293$ K and $T_C = 270$ K.

2. a) Starting with $dU = TdS - pdV$, use a Maxwell relation to derive the thermodynamic equation of state

[2]
$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

b) Use the thermodynamic equation of state to prove $(\partial U/\partial V)_T = 0$ for an ideal gas.

3. 10.0 moles of pure O_2 and 40.0 moles of pure N_2 mix at 300 K and 1.00 bar.

[5] a) Calculate q , w , ΔU , ΔH , ΔS and ΔG assuming the gases behave ideally.

b) Prove this mixing process is spontaneous.

4. For the Gibbs energy function $G(T,p)$, mathematics gives

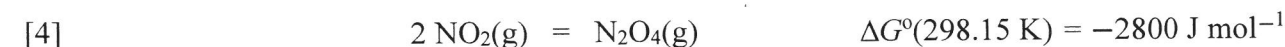
$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

[3] a) Give a more practical equation for dG suitable for calculating changes in the Gibbs energy from experimental data.

b) Derive a Maxwell relation from the expression for dG .

5. A 50.0 L tank contains 2.00 moles of NO_2 gas and 3.00 moles of $N_2O_4(g)$ gas at 25 °C.

a) Show the gas mixture is not at chemical equilibrium with respect to the dimerization reaction



b) Give the equilibrium composition of the gas mixture.

6. Solid water (ice) and liquid water are in equilibrium at 0 °C and 1.00 bar:



a) Calculate $\Delta G_{\text{fusion,m}}^\circ(H_2O, s)$ at 0 °C.

[3] b) Show $H_2O(s) \rightarrow H_2O(l)$ is spontaneous at 1.00 bar and temperatures higher than 0 °C.

c) Show $H_2O(s) \rightarrow H_2O(l)$ is impossible at 1.00 bar and temperatures lower than 0 °C.

Hint: $(\partial G/\partial T)_p = -S$ and therefore $(\partial \Delta G/\partial T)_p = -\Delta S$

- (Q1) a) Cost of 1.00 GJ heat from an electrical baseboard heater? In this case 1.00 GJ of electrical energy is converted to 1.00 GJ heat.

$$\text{\$ } 0.156 \text{ per kW hr} = \text{\$ } 0.156 \text{ for } \left(\frac{1000 \text{ J}}{\text{s}} \right) (3600 \text{ s})$$

$$\begin{array}{l} \text{electricity} \\ \text{cost} \\ \text{for 1.00 GJ} \\ \text{heat} \end{array} = \frac{0.156 \text{ \$}}{3.60 \times 10^6 \text{ J}} 1.00 \times 10^9 \text{ J}$$

$$= \boxed{43.3 \text{ \$}}$$

- b) Cost of 1.00 GJ heat from an electrical heat pump operating reversibly with $T_c = 270 \text{ K}$ and $T_H = 293 \text{ K}$?

$$q_H = -1.00 \text{ GJ} \quad (\text{heat pumped into house at } 293 \text{ K})$$

$$\varepsilon = 1 - \frac{T_c}{T_H} = 1 - \frac{270 \text{ K}}{293 \text{ K}} = 0.0785$$

$$\varepsilon = - \frac{W}{q_H} \quad W = -\varepsilon q_H = \begin{array}{l} \text{electrical work} \\ \text{required to} \\ \text{operate the heat pump} \end{array}$$

$$W = (-0.0785)(-1.00 \text{ GJ}) = 0.0785 \text{ GJ}$$

$$\begin{array}{l} \text{cost } (\text{\textcircled{a}} \text{ } 43.3 \text{ \$ per GJ} \\ \text{from a)} \end{array} = (0.0785)(43.3 \text{ \$}) \\ = \boxed{3.40 \text{ \$}} \quad \text{much cheaper!}$$

Q2 a) Use $dU = TdS - pdV$ to derive the thermodynamic equation of state.

$$dU = TdS - pdV \quad \div dV \text{ at constant } T$$

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

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \quad \text{but what is } \left(\frac{\partial S}{\partial V}\right)_T$$

→ independent variables T, V suggests using the Helmholtz function

$$dA = -SdT - pdV \quad \text{with Maxwell relation}$$

$$-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_V \quad \text{or} \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

replacing $\left(\frac{\partial S}{\partial V}\right)_T$ with $\left(\frac{\partial p}{\partial T}\right)_V$ gives conveniently in terms of P, V, T (easy to measure)

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

$$\text{b) ideal gas: } \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial \frac{nRT}{V}}{\partial T}\right)_V - p$$

$$= T \frac{nR}{V} \left(\frac{\partial T}{\partial T}\right)_V - p = \frac{nRT}{V} - p = p - p = 0$$

Q3) 10.0 moles of pure O_2 and 40.0 moles of pure N_2 mix at 300 K and 1.00 bar.

a) Fixed T, P $V = (n_{O_2} + n_{N_2}) \frac{RT}{P}$

\therefore the volume is constant (no work is done)

$$w = - \int p dV = 0$$

isothermal ideal gas

$$dU = C_V dT = 0$$

$$dH = C_P dT = 0$$

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

$$q = \Delta H = 0 \quad (\text{constant pressure})$$

$$\Delta S = \Delta S_{\text{mix}} = -n_{O_2} R \ln x_{O_2} - n_{N_2} R \ln x_{N_2}$$

$$= -(10.0 \text{ mol}) \frac{8.314 \text{ J}}{\text{K mol}} \left(\ln \frac{10.0}{10.0+40.0} \right) - (40.0 \text{ mol}) \frac{8.314 \text{ J}}{\text{K mol}} \ln \frac{40.0}{10.0+40.0}$$

$$\Delta S = 208 \text{ J K}^{-1}$$

$$\Delta G = \Delta(H - TS) = \Delta H - \Delta(TS) = \Delta H - T\Delta S = -T\Delta S$$

$$\Delta G = -62400 \text{ J}$$

b) $\Delta G_{T,P} < 0 \quad \therefore$ spontaneous

$\Delta S_{U,V} > 0$ (isolated system = $q=0, w=0$) \therefore spontaneous

Q4 a) $dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$

for calculating Gibbs energy changes, more convenient to use

$$dG = -SdT + VdP$$

Why? S and V are available or can be measured

b) Maxwell (2nd-derivative) relation from dG ?

comparing $dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$

$$dG = -SdT + VdP$$

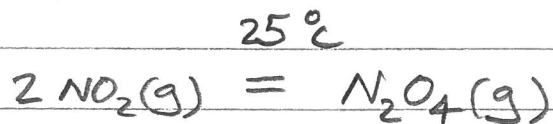
shows $\left(\frac{\partial G}{\partial T}\right)_P = -S$ and $\left(\frac{\partial G}{\partial P}\right)_T = V$

since $\left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right)_P\right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right)_T\right]_P$ order of differentiation "doesn't matter"

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

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

(Q5)



$$K = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = e^{-\Delta G^\circ/RT} = e^{-2800/(8.314)298.15}$$

$$K = 3.09 \quad (-\Delta G^\circ = 2800 \text{ J mol}^{-1})$$

a) A 50.0 L tank holds 2.00 moles of NO_2 and 3.00 moles of N_2O_4 .

$$P_{\text{NO}_2} = \frac{n_{\text{NO}_2} RT}{V} = \frac{2.00(0.08314)298.15}{50.0} = 0.992 \text{ bar}$$

$$P_{\text{N}_2\text{O}_4} = \frac{n_{\text{N}_2\text{O}_4} RT}{V} = \frac{3.00(0.08314)298.15}{50.0} = 1.487 \text{ bar}$$

reaction quotient $Q = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2}$

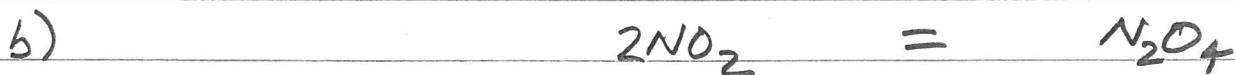
$$= \frac{1.487 \text{ bar}}{(0.992 \text{ bar})^2}$$

$$= 1.511 \text{ bar}^{-1}$$

notice $Q \neq K$ system is not at chemical equilibrium

($Q < K$ not enough N_2O_4 product
too much NO_2 reactant)

(Q5 cont.)



initial pressure: $P_{\text{NO}_2} = 0.992 \text{ bar}$ $P_{\text{N}_2\text{O}_4} = 1.487 \text{ bar}$

at equilibrium = $P_{\text{NO}_2} - 2x$ $P_{\text{N}_2\text{O}_4} + x$

At constant volume (in a 50.0 L tank), the change in the number of moles of a gas is proportional to the change in the partial pressure of the gas.

From stoichiometry, if the NO_2 pressure changes by $2x$, then the N_2O_4 pressure changes by x .

$$K = \left(\frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} \right)_{\text{at equilibrium}} = \frac{P_{\text{N}_2\text{O}_4} + x}{(P_{\text{NO}_2} - 2x)^2} = \frac{1.487 + x}{(0.992 - 2x)^2}$$

Solve the quadratic

$$K(P_{\text{NO}_2} - 2x)^2 = P_{\text{N}_2\text{O}_4} + x$$

$$K(P_{\text{NO}_2}^2 - 4xP_{\text{NO}_2} + 4x^2) = P_{\text{N}_2\text{O}_4} + x$$

$$4Kx^2 - (4KP_{\text{NO}_2} + 1)x + KP_{\text{NO}_2}^2 - P_{\text{N}_2\text{O}_4} = 0$$

$$x^2 - \frac{4KP_{\text{NO}_2} + 1}{4K}x + \frac{KP_{\text{NO}_2}^2 - P_{\text{N}_2\text{O}_4}}{4K} = 0$$

notice
 $x \leq 0.496$

(Q5 b) cont.)

$$x^2 + 1.0729x + 0.1257 = 0$$

$$x = \frac{1.0729 \pm \sqrt{1.0729^2 - 4(0.1257)}}{2}$$

$$x = \frac{1.0729 \pm 0.8052}{2}$$

$$x = 0.134, 0.939$$

(impossible $x \leq 0.496$)

$$x = 0.134 \text{ bar}$$

always
check: $\frac{1.621}{0.724^2} = 3.09 = K$

at equilibrium:

$$P_{\text{NO}_2} = 0.992 \text{ bar} - 2x = 0.724 \text{ bar}$$

$$P_{\text{N}_2\text{O}_4} = 1.487 \text{ bar} + x = 1.621 \text{ bar}$$

equilibrium gas composition

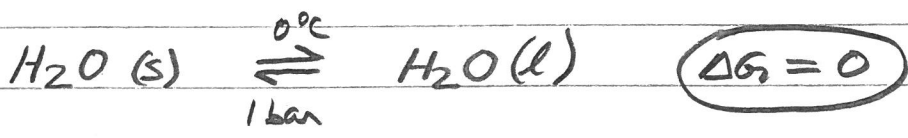
$$n_{\text{NO}_2} = \left(\frac{P_{\text{NO}_2} V}{RT} \right)_{\text{eq}} = \frac{0.724 (50.0)}{0.08314 (298.15)} = \boxed{1.46 \text{ mol}}$$

$$n_{\text{N}_2\text{O}_4} = \left(\frac{P_{\text{N}_2\text{O}_4} V}{RT} \right)_{\text{eq}} = \frac{1.621 (50.0)}{0.08314 (298.15)} = \boxed{3.27 \text{ mol}}$$

Q6

Solid and liquid water are in equilibrium

at 0°C and 1.00 bar.



a) Remove heat, some liquid water is reversibly frozen, add heat, some ice is reversibly melted

$$\Delta G_{\text{fusion,m}}^\circ = G_m^\circ(\text{H}_2\text{O,l}) - G_m^\circ(\text{H}_2\text{O,s})$$

$$\Delta G_{T,P} = 0$$

Because the melting is reversible at 0°C, 1 bar

$$\Delta S_{\text{fus,m}}^\circ = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fusion,m}}^\circ}{T}$$

$$= \frac{6010 \text{ J mol}^{-1}}{273.15 \text{ K}} = 22.00 \text{ J K}^{-1} \text{ mol}^{-1}$$

superscript "0"
 $P = P^\circ = 1 \text{ bar}$
 constant pressure

b) $\Delta G_{\text{fus,m}}^\circ$ is zero at 0°C

$$\frac{d\Delta G_{\text{fus,m}}^\circ}{dT} = -\Delta S_{\text{fus,m}}^\circ = -22.00 \text{ J K}^{-1} \text{ mol}^{-1}$$

negative slope:

above 0°C, $\Delta G_{\text{fus,m}}^\circ < 0$
 $\therefore \text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)}$ spont.

c) below 0°C, $\Delta G_{\text{fus,m}}^\circ > 0$
 $\text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)}$ impossible

