

Show work to receive full credit. Problems 1-3, 4a, 5c,d require numerical answers.

Possibly useful  $\int_0^\infty f'(x)e^{-\alpha f(x)}dx = 1/\alpha$  if  $f(x) \geq 0$  and  $f(0) = 0$  and  $f(x \rightarrow \infty) \rightarrow \infty$ .

- 5 pts    1. At *constant pressure* of 1 bar, you dissociate hydrogen  $H_2 + \text{energy} \rightarrow 2H$ . How much energy must you put in per molecule for this to occur?

- 5 pts    2. You have a device that takes heat from the outside which is at 5.0 °C so that 1 J heat is added to your room where the temperature is 20.0 °C. Suppose this device works at the theoretical optimum efficiency. a) How much heat came from outside? b) What is the minimum energy your device uses to accomplish this?

5 pts    3. The atomic masses of Na and Cl are 23.0 and 35.5. There is 10 g of NaCl in 2.0 kg of water at 25 °C. In water NaCl dissociates to  $\text{Na}^+$  and  $\text{Cl}^-$ . You push the water through a barrier permeable to water but not to  $\text{Na}^+$  and  $\text{Cl}^-$ . How much work do you need to do to get 1.0 kg of pure water?

5 pts    4. A quantum system has energies  $E_n = \epsilon n^3$  with a multiplicity of  $\Omega_n = n^2$  for  $n = 1, 2, 3, \dots$ . a) Give the numerical value of the partition function to 3 significant digits when  $\beta\epsilon = 1/2$ . b) Evaluate the partition function when  $\beta\epsilon \ll 1$ . (Hint: for part b), you should obtain the form  $Z = c\beta^a + d$  where  $a, c, d$  are constants.)

- 10 pts    5. a) At 1 bar and 298 K, which is the stable form:  $\text{NaAlSi}_3\text{O}_8$  or  $\text{NaAlSi}_2\text{O}_6 + \text{SiO}_2$ ?  
b) Give your reason for choosing the form in a). c) At 298 K, at what pressure is the phase transition between the two forms? d) If the temperature were at 308 K, what is the pressure of the phase transition between the two forms? (The answer to b) must be correct to get points for part a).)

- 10 pts    6. A single quantum system has 3 states with energies  $0, \epsilon, 4\epsilon$  with  $\epsilon$  a constant. This system is in contact with a reservoir at temperature  $T$ . a) What is the partition function for a single quantum system? For the rest of the questions, there are  $N$  of these *distinguishable* quantum systems in contact with a reservoir at temperature  $T$ . b) What is the partition function? c) What is the average energy? d) What is the entropy? e) What is the chemical potential?

1) See Prob 1.53 Chap 1 notes

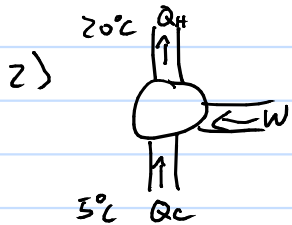
$H_2 + \text{energy} \rightarrow 2H$  at constant  $P$  means use enthalpy info

$$2\Delta H_H - \Delta H_{H_2} = 2 \cdot 217.97 \frac{\text{kJ}}{\text{mol}} - 0 = 435.94 \text{ kJ/mol} = \Delta U + P\Delta V \quad (\text{Eq 1.53})$$

$$P\Delta V = 10^5 \text{ Pa} (V_H - V_{H_2}) = (2 \text{ mol} - 1 \text{ mol}) 8.31 \frac{\text{J}}{\text{mol K}} 298 \text{ K} \Rightarrow 2.48 \text{ kJ/mol}$$

$$\Delta U = 435.94 \text{ kJ/mol} - 2.48 \text{ kJ/mol} = 433.46 \text{ kJ/mol}$$

$$\Delta U_1 = 433.46 \times 10^3 \text{ J} / 6.022 \times 10^{23} = 7.198 \times 10^{-19} \text{ J} \quad (\approx 4.49 \text{ eV})$$



$$Q_H = 1 \text{ J}$$

1<sup>st</sup> Law  $Q_H = W + Q_C \Rightarrow W = Q_H - Q_C$

Theoretical limit  $\frac{Q_C}{Q_H} = \frac{T_C}{T_H} = Q_H \left(1 - \frac{Q_C}{Q_H}\right)$

See HWK Prob 4.15

$$W = 1 \text{ J} \left(1 - \frac{278}{293}\right) = 0.0512 \text{ J} \quad Q_C = Q_H - W = 0.9488 \text{ J}$$

3) See HWK Prob 5.76

The pressure you have to apply needs to counterbalance the osmotic pressure Eq 5.78  $\Delta P = N_B kT/V$

$$N_B = 2 \cdot 10 / (23 + 35.5) \cdot 6.022 \times 10^{23} = 2.06 \times 10^{23} \quad (0.342 \text{ mol})$$

$$V_{\text{init}} = 2.0 \text{ kg} / (1000 \text{ kg/m}^3) = 2 \times 10^{-3} \text{ m}^3$$

$$V_{\text{fin}} = \frac{1}{2} V_{\text{init}} = 10^{-3} \text{ m}^3 \quad \text{because } \frac{1}{2} \text{ the water has been pushed through}$$

$$\text{Eq (1.30)} \quad W = -\int_{V_i}^{V_f} P dV = -N_B kT \int_{V_i}^{V_f} \frac{1}{V} dV = N_B kT \ln(V_i/V_f)$$

$$= 2.06 \times 10^{23} \cdot 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} 298 \text{ K} \ln 2 = 587 \text{ J}$$

$$4) \text{ Eq (6.13)} \quad Z = \sum_3 e^{-\beta E(s)} = \sum_{n=1}^{\infty} n^2 e^{-\beta \epsilon n^3}$$

$$a) \quad Z = e^{-\beta \epsilon} + 4 e^{-\beta \epsilon 8} + \underbrace{9 e^{-\beta \epsilon 27}}_{1.2 \times 10^{-5}} = e^{-1/2} + 4 e^{-4} = 6.798 \times 10^{-1} \approx 6.80 \times 10^{-1}$$

$$b) \quad Z = \sum_{n=0}^{\infty} n^2 e^{-\beta \epsilon n^3} \approx \int_0^{\infty} n^2 e^{-\beta \epsilon n^3} dn = \frac{1}{3} \int_0^{\infty} F(n) e^{-\beta \epsilon F(n)} dn = \frac{1}{3} \frac{1}{\beta \epsilon}$$

$F(n) = n^3$

5) See HWK Prob 5.28

a)  $\text{NaAlSi}_3\text{O}_8$  is stable because b)  $\Delta G_{\text{albite}} < \Delta G_{\text{jadeite}} + \Delta G_{\text{quartz}}$

$$\begin{aligned} c) \quad \Delta G(P, T_0) &= \Delta G(P_0, T_0) + \Delta V \cdot (P - P_0) = 0 \text{ at phase trans.} \\ &= -3711.5 \text{ kJ} - (-2852.1 \text{ kJ} - 856.64 \text{ kJ}) + (P - P_0)(100.07 \times 10^{-6} \text{ m}^3 - [60.40 \times 10^{-6} \text{ m}^3 + 22.64 \times 10^{-6} \text{ m}^3]) \\ &= -2.76 \times 10^3 \text{ J} + 16.98 \times 10^{-6} \text{ m}^3 (P - P_0) \\ P - P_0 &= 1.62 \times 10^8 \text{ Pa} \Rightarrow P \approx 1.62 \times 10^8 \text{ Pa} \end{aligned}$$

$$\begin{aligned} d) \quad \Delta G(P, T) &= \Delta G(P_0, T_0) + \Delta V (P - P_0) - \Delta S (T - T_0) \\ \Delta S &= 207.40 \text{ J/K} - (133.5 \text{ J/K} + 41.84 \text{ J/K}) = 32.1 \text{ J/K} \\ \Delta G(P, T) &= 0 = -2.76 \times 10^3 \text{ J} + 16.98 \times 10^{-6} \text{ m}^3 (P - P_0) - 321 \text{ J} \\ P - P_0 &= 1.81 \times 10^8 \text{ Pa} \Rightarrow P \approx 1.81 \times 10^8 \text{ Pa} \end{aligned}$$

6) Combines several HWK and class problems

a) Eg 6.13  $Z(\beta) = 1 + e^{-\beta \epsilon} + e^{-4\beta \epsilon}$

b) Eg 6.67  $Z(\beta, N) = Z^N(\beta) = (1 + e^{-\beta \epsilon} + e^{-4\beta \epsilon})^N$

c) Eg 6.25, 6.19  $U(\beta) = N \epsilon (\epsilon e^{-\beta \epsilon} + 4 \epsilon e^{-4\beta \epsilon}) / Z(\beta)$

d) Eg 6.56, 6.58  $F = -kTN \ln(1 + e^{-\beta \epsilon} + e^{-4\beta \epsilon}) = -\frac{N}{\beta} \ln(1 + e^{-\beta \epsilon} + e^{-4\beta \epsilon})$   
 Eg 6.57  $S = (U - F)/T$   
 $= \frac{N}{T} \frac{\epsilon e^{-\beta \epsilon} + 4 \epsilon e^{-4\beta \epsilon}}{1 + e^{-\beta \epsilon} + 4 e^{-4\beta \epsilon}} + Nk \ln(1 + e^{-\beta \epsilon} + e^{-4\beta \epsilon})$

e) Eg 6.64  $\mu = \left( \frac{\partial F}{\partial N} \right)_{\beta, V} = -kT \ln(1 + e^{-\beta \epsilon} + e^{-4\beta \epsilon})$