

NAME:

KEY

SID#

Groves Fall 2003
Exam #2

1. (25 pts) A sample of 1.0 mol of a monatomic perfect gas with $\bar{C}_v = 3R/2$, initially at 298 K and 10 L, is expanded, with the surroundings maintained at 298 K, to a final volume of 20 L. Answer the following, and if a numerical answer cannot be obtained from the data, indicate either the direction of change or indeterminate. Misuse or omission of units will be penalized.

- a) Case 1: The expansion occurs isothermally and reversibly. Calculate ΔH , ΔS_{sys} , ΔS_{surr} , and ΔG for the process. Is this process spontaneous? (If yes, explain what thermodynamic quantity (or quantities) you used in determining the spontaneity.)

← only predicts spontaneity at constant T, P.

ΔH	ΔS_{sys}	ΔS_{surr}	ΔG	Spontaneous?
0	+ 5.8 J/K	- 5.8 J/K	- 1.7 kJ	NO

$$\textcircled{1} \Delta H = \Delta \bar{u} + \Delta(PV) = \Delta(nRT) = nR\Delta T = 0$$

$$\textcircled{2} \Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} \text{ (constant } T), q_{\text{rev}} = -w_{\text{rev}} = +nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$\therefore \Delta S_{\text{sys}} = nR \ln\left(\frac{V_2}{V_1}\right) = 8.3145 \text{ J/K} \ln 2 = \underline{5.8 \text{ J/K}}$$

$$\textcircled{3} \Delta S_{\text{surr}} + \Delta S_{\text{sys}} = \Delta S_{\text{universe}} = 0 \text{ (reversible)} \therefore \Delta S_{\text{surr}} = -\Delta S_{\text{sys}} = \underline{-5.8 \text{ J/K}}$$

$$\textcircled{4} \Delta G = \Delta \bar{h} - T\Delta S = \underbrace{(-5.8 \text{ J/K})}_{\text{constant } T} (298 \text{ K}) = \underline{-1.7 \text{ kJ}}$$

$$\textcircled{5} \Delta S_{\text{universe}} = 0 \therefore \text{not spontaneous}$$

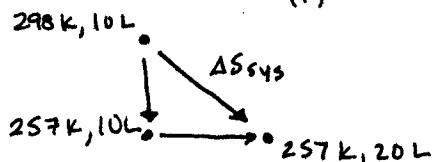
- b) Case 2: The system expands adiabatically against a constant external pressure of 0.5 atm. Calculate ΔU , T_{final} (final temperature of the system as a result of expansion), ΔS_{sys} , and ΔS_{surr} for the process.

ΔU	T_{final}	ΔS_{sys}	ΔS_{surr}
-0.51 kJ	257 K	+ 3.9 J/K	0

$$\textcircled{1} \Delta U = w + q = -P_{\text{ex}} \Delta V = -(0.5 \text{ atm})(10 \text{ L})(101.3 \text{ J/L atm}) = \underline{-51 \text{ kJ}}$$

$$\textcircled{2} \Delta U = \frac{3}{2} nR\Delta T; \Delta T = \frac{2}{3} \Delta U \cdot \frac{1}{nR} \Rightarrow T_f = T_i + \frac{2}{3} (-51 \text{ kJ}) \cdot \frac{1}{8.3145 \text{ J/K}} \\ = (298 - 41) \text{ K} = \underline{257 \text{ K}}$$

$$\textcircled{3} \Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int_{\text{const. } V} \frac{n\bar{C}_v dT}{T} + \int_{\text{const. } T_2} \frac{-dw}{T} = n\bar{C}_v \ln \frac{T_2}{T_1} + \frac{1}{\gamma} nR \ln \frac{V_2}{V_1} \\ = -1.85 \text{ J/K} + 5.76 \text{ J/K} \\ = \underline{+ 3.9 \text{ J/K}}$$



$$\textcircled{4} \Delta S_{\text{surr}} = 0 \text{ since adiabatic process}$$

NAME:

SID#

2. (25 pts)

1 mol NO	0.3 mol O ₂
----------	------------------------

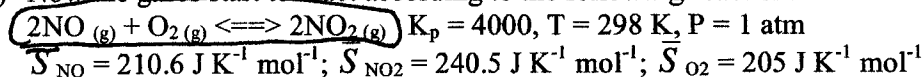
- a) The gases shown above are initially in two separate compartments. The partition is then removed. Calculate ΔS for the two gases mixing together. Assume the gases do not react and closely resemble ideal gases for this step.

$$\Delta S_{\text{mix}} = nR (X_1 \ln X_1 + X_2 \ln X_2) \quad X_1 = \frac{.3}{1.3} \quad X_2 = \frac{1}{1.3}$$

$$= 5.84 \text{ J/K}$$

(also: $\Delta S_{\text{mix}} = -R n_A \ln X_A - R n_B \ln X_B = n_A R \ln \left(\frac{V_{\text{Tot}}}{V_A} \right) + n_B R \ln \left(\frac{V_{\text{Tot}}}{V_B} \right)$)

- b) Now the gases start to react according to the following reaction:



Calculate the ΔS , ΔH , and ΔG for this reaction (label units).

$$\Delta \bar{S}_{\text{rxn}} = \sum_i \bar{S}_{\text{products}} - \sum_i \bar{S}_{\text{reactants}} = 2\bar{S}_{\text{NO}_2} - 2\bar{S}_{\text{NO}} - \bar{S}_{\text{O}_2} = -145.2 \text{ J/(K mol)}$$

$$\Delta \bar{G}_{\text{rxn}} = -RT \ln K_p = -20,549 \frac{\text{J}}{\text{mol}} = -20.5 \text{ kJ/mol}$$

$$\Delta \bar{H}_{\text{rxn}} = \Delta \bar{G}_{\text{rxn}} + T \Delta \bar{S}_{\text{rxn}} = -63.8 \text{ kJ/mol}$$

- c) What is ΔG for the entire process (mixing plus reacting)?

$$\Delta G = \Delta G_{\text{rxn}} + \Delta G_{\text{mix}}$$

$$= T \Delta S_{\text{mix}} + \Delta G_{\text{rxn}} = -(5.85 \text{ J/K})(298 \text{ K}) + (-20549 \frac{\text{J}}{\text{mol}})(.3 \text{ mol})$$

$$= -7.9 \text{ kJ}$$

- d) At what temperature does the reaction become nonspontaneous? For T greater than the temperature you just found, qualitatively describe the state of the system before and after it mixes as described above. In other words, tell us exactly what species are present at both stages.

$$\Delta \bar{G}_{\text{rxn}} = \Delta \bar{H}_{\text{rxn}} - T \Delta \bar{S}_{\text{rxn}} = 0 \quad \rightarrow \quad T = \frac{\Delta \bar{H}_{\text{rxn}}}{\Delta \bar{S}_{\text{rxn}}} = \frac{-63.8 \text{ kJ/mol}}{-145 \text{ J/K mol}}$$

$$T = 439 \text{ K}$$

Before mixing: just have NO and O₂ or above

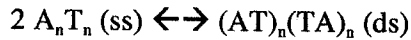
After: The reaction is not spontaneous at this temperature ($T \geq 439 \text{ K}$) so have mainly NO and O₂. Nevertheless at least some NO₂ will exist at a given time.

NAME:

KEY

SID#

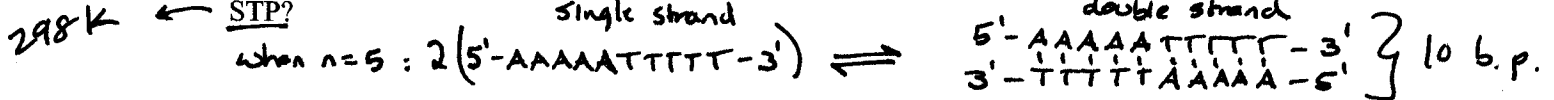
3. (25 pts) Self-complementary DNA sequences can form dimeric double helices with antiparallel strands. Hybridization between single strands containing n A residues followed by n T residues ($3' - A_n T_n - 5'$) can be expressed as the following reaction:



- a) Write an expression for the equilibrium constant (K_{eq}) in terms of concentrations of single stranded (ss) and double stranded (ds) DNA.

$$K_{eq} = \frac{[(AT)_n (TA)_n]}{[A_n T_n]^2} = \frac{[DS]}{[SS]^2}$$

- b) When $n = 5$ the K_{eq} for hybridization is $5 \times 10^3 M^{-1}$. What is ΔG° of hybridization at STP?



$$\Delta \bar{G}^\circ = -RT \ln K_{eq} = -(8.3145 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln (5 \times 10^3 \text{ M}^{-1})$$

$$= -21.1 \text{ kJ/mol}$$

- c) If the initial concentration of single stranded DNA is 1 M, what will be the concentration of each species at equilibrium?

Rxn:	2 SS	⇌	DS
initial:	1 M		0
change:	-x		+x/2
final:	1-x		x/2

$$K_{eq} = \frac{[DS]}{[SS]^2} = \frac{x/2}{(1-x)^2} = 5 \times 10^3$$

$$[DS] = \frac{x}{2} = .453 \text{ M}$$

$$[SS] = 1-x = 0.095 \text{ M}$$

$$2(5 \times 10^3 - 2 \cdot 5 \times 10^3 x + 5 \times 10^3 x^2) - x = 0$$

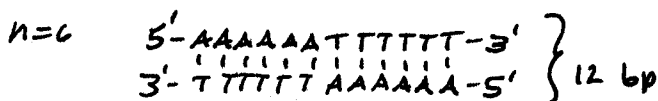
div. by 10×10^3 : $x^2 - 2.01x + 1 = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \{1.11, 0.905\}$$

- c) When $n = 6$ K_{eq} increases to $2 \times 10^5 M^{-1}$. Calculate the additional free energy per base pair added to the double helix at STP.

$$\Delta \bar{G}^\circ (n=6) = -RT \ln K_{eq}(n=6) = -RT \ln (2 \times 10^5) = -30.2 \text{ kJ/mol}$$

$$\Delta(\Delta \bar{G}^\circ) = \Delta \bar{G}^\circ_{n=6} - \Delta \bar{G}^\circ_{n=5} = -30.2 \frac{\text{kJ}}{\text{mol}} - (-21.1 \text{ kJ/mol}) = -9.1 \text{ kJ/mol}$$



Free energy for 2 base pairs →

$$\Delta \Delta \bar{G}^\circ_{1 \text{ base pair}} = \frac{\Delta \bar{G}^\circ_{n=6} - \Delta \bar{G}^\circ_{n=5}}{2} = \frac{-4.6 \text{ kJ/mol}}{2} \text{ per base pair}$$

okay if multiplied by NA

NAME:

KEY

SID#

4. (25 pts) In class, we derived the following expression for the free energy of mixing when there are interactions between the components (e.g. $\Delta H_{\text{mix}} \neq 0$):

$$\Delta \bar{G}_{\text{mix}} = k_B T X_1 \ln X_1 + k_B T X_2 \ln X_2 + \gamma X_1 X_2$$

where γ ($\Delta H/2$) represents the differential pair interaction energy and is assumed to be a constant, independent of temperature.

- a. As T rises, do you expect more or less mixing? Explain your answer quantitatively, based on the equation for $\Delta \bar{G}_{\text{mix}}$ above.

$$\frac{d \Delta \bar{G}_{\text{mix}}}{dT} = k_B (X_1 \ln X_1 + X_2 \ln X_2) \Rightarrow \text{always } \ominus$$

\downarrow \downarrow \downarrow \downarrow
 \oplus \ominus \oplus \ominus

$$d \Delta \bar{G}_{\text{mix}} = \left(\frac{d \Delta \bar{G}_{\text{mix}}}{dT} \right) dT \Rightarrow \text{as } T \text{ increases, } d \Delta \bar{G} \text{ becomes more negative, therefore increased mixing occurs}$$

- b. If you calculate $\Delta \bar{G}_{\text{mix}} > 0$ for a particular composition, T , and γ , what can you predict about the behavior of the mixture?

$\Delta \bar{G}_{\text{mix}} > 0$ implies $\Delta \bar{G}_{\text{demix}} < 0$, so demixing (i.e. phase separation) is spontaneous.

Predict phase separation.

- c. Derive an expression for the temperature (in terms of X_1 , X_2 , γ , and k_B) at the point where $\Delta \bar{G}_{\text{mix}}$ changes from negative to positive (e.g. $\Delta \bar{G}_{\text{mix}} = 0$). What happens at this temperature?

$$\Delta \bar{G}_{\text{mix}} = 0 = k_B T X_1 \ln X_1 + k_B T X_2 \ln X_2 + \gamma X_1 X_2$$

$$T (k_B X_1 \ln X_1 + k_B X_2 \ln X_2) = -\gamma X_1 X_2$$

$$T = \frac{-\gamma X_1 X_2}{k_B (X_1 \ln X_1 + X_2 \ln X_2)} = \frac{\Delta H_{\text{mix}}}{\Delta S_{\text{mix}}}$$

This T is the lowest temperature at which a mixture can remain mixed. It is the transition temperature for phase separation.