

**Chemistry 366
Thermodynamics
Midterm Exam
April 26, 2006**



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Full credit will be given to correct answers only when ALL the necessary steps are shown. **DO NOT GUESS THE ANSWER.**

This is a closed book exam, and you are responsible to be sure that your exam has no missing pages (5 pages).

If you consider that there is not enough information to solve a problem, you have to specify the missing information and describe the problem solving procedure.

GATE RULES

Rule 1

Life is not fair, get used to it.

Rule 2

The world won't care about your self-esteem. The world will expect you to accomplish something BEFORE you feel good about yourself.

Rule 3

You will not make 50 thousand dollars a year right out of high school. You won't be a vice president with a car phone, until you earn both.

Rule 4

If you think your teacher is tough, wait till you get a boss. He doesn't have tenure.

Rule 5

Flipping burgers is not beneath your dignity. Our grandparents had a different word for burger flipping, they called it opportunity.

Rule 6

If you mess up, it's not your parents' fault, so don't whine about your mistakes, learn from them.

Once you start the exam, you have up to 2 hours to solve it.

Honor Statement

I have neither give nor received aid in this examination.

Full signature _____

P1 Two equal blocks of the same metal, one at T_h and the other at T_c , are placed in contact and come to thermal equilibrium. Assuming the heat capacity to be constant over the temperature range at 24.4 J/(K mol) , calculate the change in entropy. Calculate the value for the case of two 500g blocks of copper, with $T_h=500 \text{ K}$ and $T_c=250 \text{ K}$.

FROM THE SYMMETRICAL CONDITIONS

$$T_f = \frac{T_h + T_c}{2} = \frac{500 \text{ K} + 250 \text{ K}}{2} = 375 \text{ K}$$

$$\Delta S = C_p \ln\left(\frac{T_f}{T_i}\right)$$

$$\Delta S_{\text{total}} = C_p \ln\left(\frac{375}{500}\right) + C_p \ln\left(\frac{375}{250}\right)$$

$$C_p = \frac{500 \text{ g}}{63.55 \frac{\text{g}}{\text{mol}}} \cdot 24.4 \frac{\text{J}}{\text{K mol}} = 192.0 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{\text{total}} = -55.23 \frac{\text{J}}{\text{K}} + 77.85 \frac{\text{J}}{\text{K}} = 22.6 \frac{\text{J}}{\text{K}}$$

P6.24) Calculate the degree of dissociation of N_2O_4 in the reaction $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ at 250 K and a total pressure of 0.500 bar. Do you expect the degree of dissociation to increase or decrease as the temperature is increased to 550 K? Assume that $\Delta H_{\text{reaction}}^\circ$ is independent of temperature.

We set up the following table

	$\text{N}_2\text{O}_4(\text{g})$	\rightarrow	$2\text{NO}_2(\text{g})$
Initial number of moles	n_0		0
Moles present at equilibrium	$n_0 - \xi$		2ξ
Mole fraction present at equilibrium	$\frac{n_0 - \xi}{n_0 + \xi}$		$\frac{2\xi}{n_0 + \xi}$
Partial pressure at equilibrium, $P_i = x_i P$	$\left(\frac{n_0 - \xi}{n_0 + \xi}\right) P$		$\left(\frac{2\xi}{n_0 + \xi}\right) P$

We next express K_p in terms of n_0 , ξ , and P .

$$K_p(T) = \frac{\left(\frac{P \alpha_2}{P^\circ}\right)^2}{\left(\frac{P \alpha_1}{P^\circ}\right)} = \frac{\left[\left(\frac{2\xi}{n_0 + \xi}\right) \frac{P}{P^\circ}\right]^2}{\left(\frac{n_0 - \xi}{n_0 + \xi}\right) \frac{P}{P^\circ}} = \frac{4\xi^2}{(n_0 + \xi)(n_0 - \xi)} \frac{P}{P^\circ} = \frac{4\xi^2}{(n_0)^2 - \xi^2} \frac{P}{P^\circ}$$

We convert this expression for K_p to one in terms of α .

$$K_p(T) = \frac{4\xi^2}{(n_0)^2 - \xi^2} \frac{P}{P^\circ} = \frac{4\alpha^2}{1 - \alpha^2} \frac{P}{P^\circ}$$

$$\left(K_p(T) + 4 \frac{P}{P^\circ}\right) \alpha^2 = K_p(T)$$

$$\alpha = \frac{\sqrt{K_p(T)}}{\sqrt{K_p(T) + 4 \frac{P}{P^\circ}}}$$

$$\begin{aligned}\Delta G_{\text{reaction}}^{\circ} &= 2\Delta G_f^{\circ}(\text{NO}_2, g) - \Delta G_f^{\circ}(\text{N}_2\text{O}_4, g) \\ &= 2 \times 51.3 \times 10^3 \text{ J mol}^{-3} - 99.8 \times 10^3 \text{ J mol}^{-3} = 2.8 \times 10^3 \text{ J mol}^{-3}\end{aligned}$$

$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= 2\Delta H_f^{\circ}(\text{NO}_2, g) - \Delta H_f^{\circ}(\text{N}_2\text{O}_4, g) \\ &= 2 \times 33.2 \times 10^3 \text{ J mol}^{-3} - 11.1 \times 10^3 \text{ J mol}^{-3} = 55.3 \times 10^3 \text{ J mol}^{-3}\end{aligned}$$

$$\ln K_p(T_f) = -\frac{\Delta G_{\text{reaction}}^{\circ}(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_{\text{reaction}}^{\circ}}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(250 \text{ K}) = -\frac{2.8 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} - \frac{55.3 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{250 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(250 \text{ K}) = -5.426$$

$$K_p(250 \text{ K}) = 4.40 \times 10^{-3}$$

$$\alpha = \sqrt{\frac{4.40 \times 10^{-3}}{4.40 \times 10^{-3} + 4 \times 0.500}} = 4.68 \times 10^{-2}$$

Because $\Delta H_{\text{reaction}}^{\circ} > 0$, α increases as T increases.

P7.12) For a van der Waals gas, $z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m}$. Expand the first term of this

expression in a Taylor series in the limit $V_m \gg b$ to obtain $z \approx 1 + \left(b - \frac{a}{RT}\right) \frac{1}{V_m}$.

P7.14) A van der Waals gas has a value of $z = 1.00084$ at 298 K and 1 bar and the Boyle temperature of the gas is 125 K. Because the density is low, you can calculate V_m from the ideal gas law. Use this information and the result of Problem P7.12 to estimate a and b .

$$f(x) = f(0) + \left(\frac{df(x)}{dx}\right)_{x=0} x + \dots \text{ In this case, } f(x) = \frac{1}{1 - \frac{b}{V_m}} \text{ and } x = \frac{b}{V_m}$$

$$z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m} = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RTV_m}$$

$$\frac{1}{1 - \frac{b}{V_m}} \approx \left(1/\left[1 - \frac{b}{V_m}\right]\right)_{\frac{b}{V_m} \rightarrow 0} + \left[\frac{d\left(1/\left[1 - \frac{b}{V_m}\right]\right)}{d\left(\frac{b}{V_m}\right)}\right]_{\frac{b}{V_m} \rightarrow 0} \frac{b}{V_m} = 1 + \frac{b}{V_m}$$

$$z \approx 1 + \frac{b}{V_m} - \frac{a}{RTV_m} = 1 + \frac{1}{V_m} \left(b - \frac{a}{RT}\right)$$

$$z - 1 = \frac{1}{V_m} \left(b - \frac{a}{RT}\right); \quad T_B = \frac{a}{Rb}$$

$$z - 1 = \frac{b}{V_m} \left(1 - \frac{T_B}{T}\right)$$

$$b = \frac{z - 1}{1 - \frac{T_B}{T}} \frac{RT}{P} = \frac{0.00084}{1 - \frac{125 \text{ K}}{298 \text{ K}}} \times \frac{8.314 \times 10^{-2} \text{ dm}^3 \text{ bar mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1 \text{ bar}}$$

$$= 0.0359 \text{ dm}^3 \text{ mol}^{-1} = 3.59 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$a = RbT_B = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.59 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \times 125 \text{ K} = 3.73 \times 10^{-2} \text{ m}^6 \text{ Pa mol}^{-2}$$

P8.20) The vapor pressure of a liquid can be written in the empirical form known as the Antoine equation, where $A(1)$, $A(2)$, and $A(3)$ are constants determined from measurements:

$$\ln \frac{P(T)}{P_a} = A(1) - \frac{A(2)}{\frac{T}{K} + A(3)}$$

Starting with this equation, derive an equation giving $\Delta H_{\text{vaporization}}$ as a function of temperature.

For a liquid-gas equilibrium involving a single species, $K_p = \frac{P}{P^*}$

$$\Delta H = -R \frac{d \ln K_p}{d \left(\frac{1}{T} \right)} = RT^2 \frac{d \ln K_p}{dT} = RT^2 \frac{d \left(A(1) - \frac{A(2)}{\frac{T}{K} + A(3)} \right)}{dT}$$

$$\Delta H = \frac{RT^2 A(2)}{\left[\frac{T}{K} + A(3) \right]^2}$$