Chemistry 366
Thermodynamics
Midterm Exam
March 4, 2008

Name _____

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.

But surely this is an old tale you tell, they say;
But surly this is a new tale you tell, other say.
Tell it once again, they say;
Or, do not tell it yet again, others say.
But I have heard all this before, say some;
Or, but this is not how it was before, say the rest

Naqshbandi recital, from The Way of the Sufi, by Idries Shah

Once you start the exam, you have up to 1 hours to solve it.

Honor Statement

I have neither give nor received aid in this examination.

Full signature _____

PROBLEM 1 (25 POINTS)

Calculate the pressure exerted by benzene for a molar volume 1.42 L at 790 K using the Redlich-Kwong equation of state:

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)} = \frac{nRT}{V - nb} - \frac{n^2 a}{\sqrt{T}} \frac{1}{V(V + nb)}.$$ The Redlich-Kwong

parameters a and b for benzene are 452.0 bar dm^6 mol^{-2} K$^{1/2}$ and 0.08271 dm^3 mol^{-1}, respectively. Is the attractive or repulsive portion of the potential dominant under these conditions?

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)}$$

$$= \frac{8.314 \times 10^{-2} \text{bar dm}^3\text{mol}^{-1}\text{K}^{-1} \times 790 \text{ K}}{1.42 \, \text{dm}^3\text{mol}^{-1} - 0.08271 \text{dm}^3\text{mol}^{-1}}$$

$$- \frac{452.0 \, \text{bar dm}^6\text{mol}^{-2}\text{K}^{\frac{1}{2}}}{\sqrt{790 \text{ K}}} \times \frac{1}{1.42 \, \text{dm}^3\text{mol}^{-1} \times \left(1.42 \, \text{dm}^3\text{mol}^{-1} + 0.08271\text{dm}^3\text{mol}^{-1}\right)}$$

$$P = 41.6 \text{ bar}$$

$$P_{ideal} = \frac{RT}{V} = \frac{8.3145 \times 10^{-2} \times \text{L bar mol}^{-1}\text{K}^{-1} \times 790 \text{ K}}{1.42 \text{ L}} = 46.3 \text{ bar}$$

Because $P < P_{ideal}$, the attractive part of the potential dominates.

PROBLEM 2 (25 POINTS)

1 mol of an ideal gas, for which $C_{V,m} = 3/2R$, initially at 20.0°C and 1.00×10^6 Pa undergoes a two-stage transformation. For each of the stages described in the following list, calculate the final pressure, as well as q, w, ΔU, and ΔH. Also calculate q, w, ΔU, and ΔH for the complete process.

a) The gas is expanded isothermally and reversibly until the volume doubles.

b) Beginning at the end of the first stage, the temperature is raised to 80.0°C at constant volume.

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a) $P_2 = \dfrac{P_1 V_1}{V_2} = \dfrac{P_1}{2} = 0.500 \times 10^6$ Pa

$w = -nRT \ln\dfrac{V_2}{V_1} = -8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln 2 = -1.69 \times 10^3$ J

$\Delta U = 0$ and $\Delta H = 0$ because $\Delta T = 0$

$q = -w = 1.69 \times 10^3$ J

b) $\dfrac{T_1}{P_1} = \dfrac{T_2}{P_2}; \quad P_2 = \dfrac{T_2 P_1}{T_1} = \dfrac{353 \text{ K} \times 0.500 \times 10^6 \text{Pa}}{293 \text{ K}} = 6.02 \times 10^5$ Pa

$\Delta U = nC_{V,m}\Delta T = 1.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (353 \text{ K} - 293 \text{ K}) = 748$ J

$w = 0$ because $\Delta V = 0$

$q = \Delta U = 748$ J

$\Delta H = nC_{P,m}\Delta T = n(C_{V,m} + R)\Delta T = \dfrac{3}{2} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (353 \text{ K} - 293 \text{ K})$

$= 1.25 \times 10^3$ J

For the overall process,

$q = 1.69 \times 10^3 \text{ J} + 748 \text{ J} = 2.44 \times 10^3$ J

$w = -1.69 \times 10^3 \text{J} + 0 = -1.69 \times 10^3$ J

$\Delta U = 0 + 748 \text{ J} = 748$ J

$\Delta H = 0 + 1.25 \times 10^3 \text{J} = 1.25 \times 10^3$ J

PROBLEM 3 (25 POINTS)

Use the relation $C_{P,m} - C_{V,m} = T\left(\dfrac{\partial V_m}{\partial T}\right)_P \left(\dfrac{\partial P}{\partial T}\right)_P$, the cyclic rule, and the van der

Waals equation of state to derive an equation for $C_{P,m} - C_{V,m}$ in terms of V_m and the gas constants R, a, and b.

We use the cyclic rule to evaluate $\left(\dfrac{\partial V_m}{\partial T}\right)_P$.

$$\left(\frac{\partial V_m}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_{V_m} \left(\frac{\partial P}{\partial V_m}\right)_T = -1$$

$$\left(\frac{\partial V_m}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_{V_m} \left(\frac{\partial V_m}{\partial P}\right)_T$$

$$C_{P,m} - C_{V,m} = T\left(\frac{\partial V_m}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_{V_m} = -T\left[\left(\frac{\partial P}{\partial T}\right)_{V_m}\right]^2 \left(\frac{\partial V_m}{\partial P}\right)_T = -T\frac{\left[\left(\frac{\partial P}{\partial T}\right)_{V_m}\right]^2}{\left(\frac{\partial P}{\partial V_m}\right)_T}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{R}{V_m - b}$$

$$\left(\frac{\partial P}{\partial V_m}\right)_T = \frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = \frac{-RTV_m^3 + 2a(V_m - b)}{V_m^3(V_m - b)^2}$$

$$C_{P,m} - C_{V,m} = -T\frac{\left(\dfrac{R}{V_m - b}\right)^2}{\dfrac{-RT}{(V_m - b)^2} + \dfrac{2a}{V_m^3}} = -T\frac{R}{-T + \dfrac{2a(V_m - b)^2}{RV_m^3}} = \frac{R}{1 - \dfrac{2a(V_m - b)^2}{RTV_m^3}}$$

In the ideal gas limit, $a = 0$, and $C_{P,m} - C_{V,m} = R$.

PROBLEM 4 (25 POINTS)

Calculate the standard enthalpy of formation of $FeS_2(s)$ at 300°C from the following data at 25°C. Assume that the heat capacities are independent of temperature. You are also given that for the reaction $2FeS_2(s) + 11/2O_2(g) \rightarrow Fe_2O_3(s) + 4 SO_2(g)$, $\Delta H°_{reaction} = -1655$ kJ mol^{-1}.

Substance	Fe(s)	FeS₂(s)	Fe₂O₃(s)	S(rhombic)	SO₂(g)
$\Delta H°_f$ (kJ mol^{-1})			−824.2		−296.81
$C_{P,m}/R$	3.02	7.48		2.72	

$\Delta H°_{reaction} = \Delta H°_f (Fe_2O_3, s) + 4\Delta H°_f (SO_2, g) - 2\Delta H°_f (FeS_2, s)$
$= -824.2$ kJ mol^{-1} -1655 kJ mol^{-1} -1655 kJ mol^{-1} -1655 kJ mol^{-1}

$2FeS_2(s) + 11/2O_2(g) \rightarrow Fe_2O_3(s) + 4SO_2(g)$ $\Delta H°_{reaction} = -1655$ kJ mol^{-1}
-1655 kJ mol^{-1} $= \Delta H°_f (Fe_2O_3, s) + 4\Delta H°_f (SO_2, g) - 2\Delta H°_f (Fe_2S_2, s)$

$\Delta H°_f (Fe_2S_2, s, 298 \text{ K}) = \dfrac{1655 \text{ kJ mol}^{-1} + \Delta H°_f (Fe_2O_3, s) + 4\Delta H°_f (SO_2, g)}{2}$

$= \dfrac{1655 - 824.2 - 4 \times 296.81 \text{ kJ mol}^{-1}}{2}$

$= -178.2$ kJ mol^{-1}

The enthalpy of formation at 300°C is given by

$$\Delta H°_f (FeS_2(s), 573 \text{ K}) - \Delta H°_f (FeS_2(s), 298 \text{ K}) + \int_{298 \text{ K}}^{573 \text{ K}} \Delta C_p(T) dT$$

Because the heat capacities are assumed to be independent of T,

$\Delta H°_f (FeS_2(s), 573 \text{ K}) = \Delta H°_f (FeS_2(s), 298 \text{ K})$
$+ [C_{P,m}(FeS_2, s) - C_{P,m}(Fe, s) - 2C_{P,m}S(s)][573 \text{ K} - 298 \text{ K}]$
$= -178.2$ kJ mol^{-1} $+ 8.314$ JK^{-1} mol$^{-1} \times (7.48 - 3.02 - 2\times2.70) \times [573 \text{ K} - 298 \text{ K}]$
$= -180.0$ kJ mol^{-1}