Name: ______________________________ Test 2

150 points Chemistry 261

Dr. Jay H. Baltisberger April 6, 1998

Answer three of the following four multiple choice questions for 15 points each:

1. How many degrees of freedom are present in an alloy of copper and zinc (only a single homogenous solid phase) .

A) 0 **B)** 1 **C)** 2 **D)** 3 **E)** 4

Since $c = 2$, $p = 1$, from the phase rule $f = c - p + 2 = 2 - 1 + 2 = 3$ (T, p, x_{Cu}). Thus answer D is correct.

2. What is the equilibrium constant (K°_p) for the reaction $N_2 + O_2 \longleftrightarrow 2\,NO$ given the free energy of formation of NO, $\Delta G^\circ_f = 86.55$ kJ/mol?

A) $4.56\text{x}10^{-31}$ **B)** $6.75\text{x}10^{-16}$ **C)** 86.55 **D)** $1.48\text{x}10^{15}$ **E)** $2.19\text{x}10^{30}$

Using the equation $\Delta G^\circ = -RT \ln K^\circ_p$, we solve for $K^\circ_p = \exp(-\Delta G^\circ / RT)$. For this reaction, $\Delta G^\circ = 2\,\Delta G^\circ_{f,NO} - \Delta G^\circ_{f,O2} - \Delta G^\circ_{f,N2} = 173.1$ kJ/mol. Putting this into the equation for $K^\circ_p = \exp(-173100 / 8.31451 / 298) = 4.56\text{x}10^{-31}$ (answer A).

3. Calculate the ΔH_f (in kcal/mol) for FeO given the following equations:

$FeO\,(s) + C\,(s) \longrightarrow Fe\,(s) + CO\,(g)$	37.0 kcal/mol
$2CO\,(g) + O_2\,(g) \longrightarrow 2CO_2\,(g)$	–135.0 kcal/mol
$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$	–94.0 kcal/mol

A) –192.0 **B)** –127.0 **C)** –63.5 **D)** –33.0 **E)** +33.0

We reverse reaction 1, reverse reaction 2 and divide by 2 (to balance CO) and add reaction 3 (to balance CO_2). Net reaction is formation of FeO and has $\Delta H_f = -63.5$ kcal/mol (answer C).

4. What is the entropy change when 180.2 g (10.00 mol) of liquid water is pressurized from 1.00 atm to 21.00 atm at 298 K. For water, assume $\alpha = 3.04\text{x}10^{-4}\ K^{-1}$ and $\rho = 1.00\ g/cm^3$ over the entire pressure range of this problem.

A) –0.111 J / K **B)** –0.00337 J / K **C)** 0.00 J / K **D)** 0.00337 J / K **E)** 0.111 J / K

Using the equation that $dS = -\alpha V\,dP$ and integrating this gives: $\Delta S = -\alpha V \Delta P$ (assuming α and V are constants over pressure range). $\Delta S = -(0.000304\ K^{-1})\,(180.2\ g)\,(1.00\ cm^3 / g)\,(20\ atm)\,[\,(8.31451\ J / mol\ K) / (82.06\ atm\ cm^3 / mol\ K)\,] = -0.111\ J / K$.

Choose three of the following four problems for 35 points each:

5. Calculate ΔG for the isothermal compression of 30.0 g of water from 1.0 atm to 100.0 atm at 25˚C; neglect the variation of V with P.

Using the equation $dG = V\,dP$ and integrating this gives $\Delta G = V\Delta P = (30.0\ cm^3)\,(99\ atm)\,[\,(8.31451\ J / mol\ K) / (82.056\ cm^3\ atm / mol\ K)\,] = 300.9\ J$.

6. For the gas-phase reaction

$$I_2 + \text{cyclopentene} <\!\!\longrightarrow \text{cyclopentadiene} + 2HI$$

measured K°_p values in the range of 450 to 700K are fitted by:

$$\ln K^\circ_p = a + b / T$$

where a = 7.55 and b = -4.83×10^3 K. Calculate ΔG°, ΔH°, and ΔS° for this reaction at 500K. Assume ideal gases.

Using $\Delta G^\circ = -RT \ln K^\circ_p = -(8.31451\ J/mol\ K)(500\ K)(7.55 - (4830/500)) = +8771\ J/mol$. For ΔH° and ΔS° we need to use $\ln K^\circ_p = -\Delta H^\circ/RT + \Delta S^\circ/R$. Thus $a = \Delta S^\circ/R$ giving $\Delta S^\circ = 7.55\ (8.31451\ J/mol\ K) = 62.77\ J/mol\ K$ and $b = -\Delta H^\circ/R$ gives $\Delta H^\circ = 4830\ K\ (8.31451\ J/mol\ K) = 40{,}159\ J/mol$.

7. The normal melting point of Ni is 1452˚C. The vapor pressure of liquid Ni is 0.100 torr at 1606˚C and 1.00 torr at 1805˚C. The molar heat of fusion of Ni is 4.2 kcal/mol. Making reasonable approximations, estimate the triple point and vapor pressure of solid Ni at 1200 ˚C.

The first step is determining the triple point. The liquid/solid slope will be nearly infinite so the triple point temperature will be basically identical to the normal melting point (1452 ˚C). The heat of vaporization is determined using the Clapeyron equation applied to the liquid/vapor transition (the two other data points given in the problem). Integrating this equation gives

$$\ln(P_2/P_1) = \ln(1\ torr / 0.1\ torr) = -(\Delta H/R)(1/T_2 - 1/T_1)$$

$$2.302 = -(\Delta H / (8.31451\ J/mol\ K))(1/2078K - 1/1879K)$$

$$\Delta H_{vap} = 375544\ J/mol$$

Using this enthalpy, we may calculate the pressure at the triple point using the same equation:

$$\ln(p_2 / 0.1\ torr) = -(375544\ J/mol / (8.31451\ J/mol\ K))(1/1725K - 1/1879K)$$

$$p_2 = 0.011\ torr$$

From this point we need to extrapolate back to 1200 ˚C using the Clapeyron equation, $d \ln P / dT = \Delta H / RT^2$. We need to know the ΔH_{sub}, which is essentially the $\Delta H_{vap} + \Delta H_{fus}$. This yields a value of $\Delta H_{sub} = 375544\ J/mol + [4200\ cal/mol\ (4.184\ J/cal)] = 393117\ J/mol$. Lastly, using the Clapeyron equation you may back calculate the vapor pressure from the triple poin (1452˚C & 0.011 torr).

$$\ln(p_2 / 0.011\ torr) = -(393117\ J/mol / (8.31451\ J/mol\ K))(1/1473K - 1/1725K)$$

$$p_2 = 0.000101\ torr$$

8. For CH_3OH (l) at 25˚C, the vapor pressure is 125 torr, ΔH_m of vaporization is 37.9 kJ/mol, ΔH_f is –238.7 kJ/mol, and S°_m is 126.8 J/mol K. Making reasonable approximations, find ΔH°_f and S°_m of CH_3OH (g).

To get the ΔH°_f of CH_3OH (g) we need to determine the enthalpy of the vaporization at 1 bar and 25˚C. This should be basically the same as the enthalpy of vaporization at the normal boiling point or 37.9 kJ/mol (since ΔH° is relatively temperature independent, assuming the heat capacities of liquid and gas are similar). The ΔH°_f will be $-238.7 + 37.9\ kJ/mol = -200.8\ kJ/mol$. To determine the$S^\circ_m$ we need the normal boiling point temperature. From the Clapeyron equation:

$$\ln(P_2/P_1) = \ln(750\ torr / 125\ torr) = -(\Delta H/R)(1/T_2 - 1/T_1)$$

$$1.792 = -(37900 / (8.31451\ J/mol\ K))(1/T_2 - 1/298K)$$

$$T_2 = 337.5\ K = 64.5^\circ C$$

The $\Delta S^\circ_{vap} = (37900\ J/mol) / (337.5\ K) = 112.3\ J/mol\ K$. Again, assuming that ΔS° due to the temperature difference is negligible (good approximation if the heat capacities of the liquid and gas are similar) then $S^\circ_m = 126.8 + 112.3\ J/mol\ K = 239.1\ J/mol\ K$.