Name: ANSWER KEY
or Student No.:

CHEM 456
Test I

* Please show your work and show units for partial credit.
* Please note the tables of constants and units conversion factors at end of test. These will be useful in solving some of the problems.
* Please check your test now to make sure that you have a total of 5 pages, including the tables.

15 pts

1. The enthalpy change for the chemical reaction below is -1270 kJ/mol at 298 K when all species are at 1 bar pressure:

$$2\,Ca(s) + O_2(g) \rightarrow 2\,CaO(s).$$

Calculate the molar internal energy change for this reaction at these conditions, stating any assumptions or approximations made.

Initial State: 1 bar, 298 K, 2 mol Ca(s), 1 mol O_2
Final State: 1 bar, 298, 2 mol CaO(s)

$\Delta H = \Delta U + \Delta(PV)$ since $H \equiv U + PV$

At const. P: $\Delta H = \Delta U + P\Delta V \quad \therefore \quad \Delta U = \Delta H - P\Delta V$

$\Delta V = V_{2\,moles\,CaO(s)} - V_{2\,moles\,Ca(s)} - V_{mole\,O_2(g)} \simeq -V_{mole\,O_2(g)}$ since $V_s \ll V_g$.

$\Delta V = -\bar{V}_{O_2(g)} = -\frac{RT}{P}$ (Ideal gas law assumption)

$\Delta U = \Delta H - P\Delta V = \Delta H + P(RT/P) = \Delta H + RT = -1270\,\frac{kJ}{mol} + (8.31\,\frac{J}{mol\,K})(298\,K)$

$\Delta U = -1270$ kJ/mol $+ 2.5$ kJ/mol $=$ **-1267.5 kJ/mol**

2 pts / 8 pts

2. The normal boiling point of $Cl_2(l)$ is -34 °C, where its latent heat of vaporization is 20 kJ/mol.
(a) What is the molar Gibbs free energy change for vaporization at this temperature and 1 ~~bar~~ atm? 0 (since eq bm const. T, P)
(b) Calculate the molar entropy change upon vaporization at this condition.

$$\Delta S = \lambda / T = \frac{20{,}000\ J/mol}{(273 - 34)\ K} = 83.68\ J/mol\,K$$

5 pts

3. Define the chemical potential of species i in phase α with mathematical symbols.

$$\mu_i^\alpha = \bar{G}_i \equiv \left(\frac{\partial G_{TOTAL}}{\partial n_i^\alpha}\right)_{T,P,n_{j\neq i}^\alpha}$$

24pts total - part (a)

4. (a) Calculate q, w, ΔU, ΔH, and ΔS when 1 mole of an ideal monatomic gas ~~changes~~ heating reversibly at 1 bar from (298 K, ~~1 bar~~) to (350 K, ~~1 bar~~). Const. P, reversible. Monatomic, i.gas $\bar{C}_V = \frac{3}{2}R$, $\bar{C}_P = \frac{5}{2}$

5pts. $q = q_{rev} = q_P = C_P \Delta T = \frac{5}{2}nR(350K - 298K) = (\frac{5}{2})(8.31\ J/K)(52K) = \underline{1080.}$

4pts $\Delta H = q_P = \underline{1080\ J}$ for 1 mole

5pts $w = -\int P dV = -P\Delta V = -P\Delta(\frac{nRT}{P}) = -\Delta(nRT) = -nR\Delta T$

$= -(1\ mole)(8.314\ J/mol\ K)(52K) = \underline{-432\ J}$

5pts $\Delta U = q + w = 1080 - 432 = \underline{648\ J}$

5pts $\Delta S = \int C_P \frac{dT}{T} = C_P \ln(\frac{T_2}{T_1}) = \frac{5}{2}nR \ln(\frac{350K}{298K}) =$

$= \frac{5}{2}(1)(8.314\ J/K)(0.161) = \underline{3.34\ J/K}$

5pts (b) Calculate q, w, ΔU, ΔH, and ΔS when the gas changes between the same two conditions, but irreversibly, such that the gas now does 200 J of work on its surroundings.

ΔU, ΔH, ΔS same as above (since STATE FUNCTIONS).

$w = \underline{-200\ J}$ (given)

$q = \Delta U - w = 648\ J - (-200\ J) = \underline{848\ J}$

Here, we are considering methane gas, which we treat as ideal, in two different mixtures. The mixtures are not in equilibrium. (Separate boxes, if you like)

15pts. 5. Calculate the difference in chemical potential for methane gas between two ideal gas mixtures (B-A), both at 500 K and a total pressure of 2 bar. In mixture A, the mole fraction of methane is 0.0001. In mixture B, it is 0.8.

$i = CH_4$

$$\mu_i^A = \mu_i^\circ + RT\ln\left(P_i^A/P^\circ\right) \qquad \mu_i^B = \mu_i^\circ + RT\ln\left(P_i^B/P^\circ\right)$$

$$\mu_i^B - \mu_i^A = RT\ln\left(P_i^B/P^\circ\right) - RT\ln\left(P_i^A/P^\circ\right) = RT\ln\left(P_i^B/P_i^A\right)$$

$$= RT\ln\left(\frac{X_i^B P_{TOT}}{X_i^A P_{TOT}}\right) = RT\ln\left(\frac{X_i^B}{X_i^A}\right) = (8.314\ J/mol\,K)(500K)\ln\left(\frac{0.8}{10^{-4}}\right)$$

$$= \underline{37.36\ kJ/mol}$$

2pts each. 6. Circle the correct words:
(a) The entropy of mixing of ideal solutions is: (positive) or negative.
(b) Entropy increases as the disorder: (increases) or decreases.
(c) The entropy of the universe: (increases) or decreases.
(d) This ~~change~~ quantity depends on the path between two states: ΔH or (work).
(e) A process will occur spontaneously at constant T and P if the Gibbs free energy: increases or (decreases).
(f) A species flows to that phase where its chemical potential is initially: (lower) or higher.
(g) The chemical potential for a species increases as its attractions to other species in that phase: increases or (decreases).
(h) The chemical potential for a species increases as its concentration in that phase: (increases) or decreases.

10pts total 7. (a) [3pts] To good approximation, C_V for a solid metal below 20 K is proportional to T raised to what integer power? <u>3</u>.
(b) [7pts] If the heat capacity of gold is 0.43 J mol^{-1} K^{-1} at 10 K, calculate is its molar entropy at 10 K?

$$\bar{C}_P = \bar{C}_V = aT^3$$

$$\bar{S} = \int_{T=0}^{T=10K} \bar{C}_P\left(\frac{dT}{T}\right) = \int_0^{10K} aT^3\frac{dT}{T} = a\int_0^{10K} T^2\,dT$$

$$= \frac{1}{3}a\left[T^3\right]_0^{10K} = \frac{1}{3}aT^3 = \frac{1}{3}\bar{C}_P$$

(just $\bar{C}_P$)

$$= \frac{1}{3}(0.43\ J/mol\,K) = \underline{0.143\ J/mol\,K}$$

Alternatively, solve for "a" given $C_V = 0.43\ J/mol\,K$ at $T = 10K$, then do integral to calc. S.

$C_V = aT^m$ — Even if you didn't know m=3 in part (a), I would give you credit (7pts) for solving (b) symbolically, in which case: $\bar{S} = \frac{1}{m}(0.43\ \frac{J}{mol\,K})$