PHYSICAL CHEMISTRY 5200

MIDTERM EXAM

October 24, 2019

Please write neatly and clearly, and show all working. Allocate time to each question in proportion to the available credit. Keep any explanations brief and clear.

Your name: _____

SOME POSSIBLY USEFUL INFORMATION:

N_A or L = 6.022 x 10^{23} mol^{-1} R = 8.314 J K^{-1} mol^{-1}

k or $k_B = R/N_A$

$dU = dq + dw$ $dS = dq_{rev}/T$

$dw = -p_{ex}\, dV$ $\gamma = C_p/C_v$

Perfect gas: $pV = nRT$ and $C_p - C_v = nR$

van der Waals gas: $p = nRT/(V-b) - a(n/V)^2$

Adiabat: pV^{γ} is constant Heat engine $\varepsilon = (T_h - T_c)/T_h$

$H = U + pV$ $A = U - TS$ $G = H - TS$

MULTIPLE CHOICE SECTION (7 questions, 5 points each, 35% total credit)
No work need be shown. ***Circle the best answer.***

Information for questions 1 and 2, all at 298 K and 10^5 Pa:

compound	**S^o / J K^{-1} mol^{-1}**	**$\Delta_f G^o$ / kJ mol^{-1}**
SO_2 (g)	248	-350
O_2 (g)	205	
SO_3 (g)	257	-371

1) At 298 K, the Gibbs energy change (ΔG^o) for 2 SO_2 (g) + O_2 (g) → 2 SO_3 (g) is

A. +42 kJ mol^{-1} B. -21 kJ mol^{-1} C. -42 kJ mol^{-1}
D. more information needed

2) At 298 K, the enthalpy change (ΔH^o) for 2 SO_2 (g) + O_2 (g) → 2 SO_3 (g) is, in kJ mol^{-1},

A. -98 B. -47
C. +14 D. more information needed

3) 0.5 mol of O_2 (g), originally at p = 5 x 10^5 Pa and V = 5 x 10^{-3} m^3, is expanded reversibly and isothermally until p = 10^5 Pa. The entropy change (ΔS^o) is, in J K^{-1}

A. +6.7 B. +13.4 C. -6.7 D. +4030

4) The melting point of toluene (the system) at 10^5 Pa is -95 °C, and the enthalpy of fusion is 6.6 kJ mol^{-1}. What is ΔS for the <u>system</u> when 1 mol of liquid toluene freezes solid at -95 °C, in J K^{-1} ?

A. +69 B. +37 C. -69 D. -37

5) The boiling point of toluene (the system) at 10^5 Pa is 111 °C, and the enthalpy of vaporization is 39.2 kJ mol^{-1}. What is ΔS for the <u>surroundings</u> when 1 mol of liquid toluene vaporizes at 111 °C, in J K^{-1} ?

A. +102 B. +35 C. -102 D. -353

6) When 1.4 mol of C_3H_8 (g) is mixed with 0.8 mol of C_5H_{12} (g) at 298 K, the entropy of mixing ($\Delta_{mix}S$) is approximately, in J K^{-1}:

A. -3.6 B. +12.0 C. +5.5 D. -12.0

7) An ideal gas is taken through a cyclic process. Certain thermodynamic quantities will be zero: choose the answer for which <u>all</u> the listed quantities <u>must</u> be zero.

A. w, U, H, G B. q, S, U, G

C. w, H, A, S D. S, U, H, A

PROBLEM SECTION (3 questions, 65% total)

Show your work for these questions

8) *15 points*

Consider a system where $C_p = a + b/T$ where a and b are constants. In terms of a and b, calculate ΔS for the system for heating from T_1 to T_2 at constant pressure p. If this change is made irreversibly, what can you say about ΔS for the surroundings compared to ΔS_{sys}?

9) *25 points*

Given the general relation $dp/dT = \Delta S/\Delta V$ for a phase change, show that for vaporization of a liquid to a perfect gas, we expect the pressure of the vapor p approximately to follow the form

$$\ln p = -\Delta_{vap}H/(RT) + \text{constant}$$

where $\Delta_{vap}H$ is the enthalpy of vaporization.

The vapor pressure of a compound is measured to follow

$$\ln (p \text{ in bar}) = 8.7 - 2380/T$$

where 1 bar = 10^5 Pa and T is the temperature in K. Deduce the normal boiling point T_b and $\Delta_{vap}H$.

10) 25 *points*

Consider G as a function of T and p, and expand dG in terms of T, p, V and S, to derive the results

$$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \text{and} \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

Hence show that $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

Use one of these equations to determine ΔG for an isothermal pressure change of a perfect gas from p_1 to p_2. Hence show that with $p_1 = p^o$ where G is G^o, and p_2 a general value p, that G at any pressure can be written as

$$G = G^o + RT \ln(p/p^o)$$

What is ΔG for the isothermal pressure change of a *non-ideal* gas from p_1 to p_2, whose equation of state is $pV = n(RT-aV)$?

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