

Dec. 12, 2016 4-5:50 pm

Name KEY*An 8" x 11" Sheet of personal notes (both sides) is allowed*

Last,

First

(200 points) Be sure you have 10 problems on 6 pages including Tables A1 and A5.

Read: In this exam, there should be time to avoid nonsensical answers. Most of the answers can be estimated without doing any arithmetic. If you get a quantitative answer which is very far from what you think it should be and cannot find the error, you will be rewarded for pointing out approximately what you expected and why. You will be penalized by 25% on a problem for sign and unit errors that lead to unreasonable results if you do not say why it is unreasonable.

For full credit show all work and put correct units on final answers.

(20 pts)

1. (a) State the 3 Laws of Thermodynamics in words and with a commonly used equation. Define all symbols used.

1st Law: Energy of the universe is conserved $\Delta U = q + w$

7 pts
2nd Law: Entropy of the Universe $(\Delta S + \Delta S_{\text{sum}}) \rightarrow 0$
for all natural processes

3rd. Entropy of a perfect crystal at 0 Kelvin
 $= 0$ And or $S = k_B \ln W$

- (b) How can you tell when work and heat are not zero?

6 pts
 $q \neq 0$ if something in surroundings changes temperature
 $w \neq 0$ if " " " has a mechanical energy change.

- (c) Explain the tremendous importance of the Second Law in terms of when ΔG can and cannot be used as a criterion for a when a process is "spontaneous".

$$\Delta G = -T \Delta S_{\text{universe}} + w_{\text{useful}}$$

7 pts
therefore if $\Delta S_{\text{univ}} > 0$ the process is spontaneous even if ΔG is positive
e.g. by large input of work
 $w_{\text{useful}} = \text{Very } +$

(20 pts)

2. (a) Super saturated water vapor in an isolated constant volume system initially at 100 °C condenses to liquid until equilibrium is reached. Tell whether each of the following thermodynamic variables is +, -, 0, or ?, where the ? means it is not possible to determine anything definite. Explain your reasons briefly for each case.

$q \text{ } \cancel{\text{O}}$ $w \text{ } \cancel{\text{O}}$ $\Delta T \text{ } \cancel{\text{+}}$ $\Delta U \text{ } \overset{\text{isolated}}{\cancel{\text{O}}} \text{ } \Delta H \text{ } ?$ $\Delta S \text{ } \overset{\Delta S_{\text{univ}}}{\cancel{\text{+}}} \text{ } \Delta G \text{ } ?$ $\Delta S_{\text{surr}} \text{ } \cancel{\text{O}}$ $\Delta S_{\text{univ}} \text{ } \cancel{\text{+}}$ happens

$\Delta H = \Delta U + \Delta(PV) = 0 + (P_2 - P_1)V$; hard to know if $P_2 > P_1$

18 pts

$\Delta G = \Delta H - \Delta(TS)$ because liquid smaller than gas
= uncertain but condensation treats the gas.

= uncertain because ΔH is uncertain.

2 pts

- (b) Will the liquid formed ever boil during this process? Provide ample reasoning behind your answer.

NO

super sat. means condensation (NOT evaporation)
process stops when $P_{H_2O \text{ gas}} = \text{vapor pressure}$
i.e. at boiling point.

(20 pts)

3. For the same initial conditions as in prob 2., answer the same questions if the process is isothermal, assuming the initial $p_{H_2O} = 2 \text{ atm}$ and the external pressure is constant at 1 atm and V is constant, and no useful work is done.

$q = w \text{ } \cancel{\text{O}}$ $\Delta T \text{ } \overset{\text{isothermal}}{\cancel{\text{O}}} \text{ } \Delta U \text{ } \cancel{\text{-}} \text{ } \Delta H \text{ } \cancel{\text{-}} \text{ } \Delta S \text{ } \cancel{\text{-}} \text{ } \Delta G \text{ } \cancel{\text{-}} \text{ } \Delta S_{\text{surr}} \text{ } \cancel{\text{+}} \text{ } \Delta S_{\text{univ}} \text{ } \cancel{\text{+}}$ happens
 $\downarrow -P_{\text{ext}} \Delta V = 0, w_{\text{useful}} = 0$

$\Delta U = q + w = q$

$\Delta S = \text{neg.}$ because liquid more ordered and T is constant.

$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2 - P_1)V$

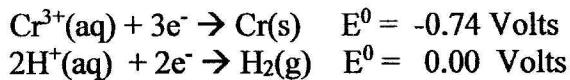
$P_2 < P_1$ because decrease mols of gas.

both $\Delta U \text{ } \& \text{ } \Delta(PV)$ are neg. so ΔH is neg.

$\Delta G = \Delta H - T\Delta S$ (Can't tell because $-T\Delta S$ opposite sign from ΔH)

or $\Delta G = - = -T\Delta S_{\text{univ}}^2 + w_{\text{useful}}$ zero

(20 pts) 4. (a) Given the following information from a table of reduction potentials,



What is the standard cell potential for the conversion of 2 moles of $\text{Cr}^{3+}(\text{aq})$ to $\text{Cr}(\text{s})$ by reacting with $\text{H}_2(\text{g})$? electrons start on H_2 end on $\text{Cr}(\text{s})$

$$E_{\text{final}}^\circ - E_{\text{initial}}^\circ = -0.74 - (0) = \boxed{-0.74 \text{ volts}}$$

(b) What is ΔG° for this process in (a)?

2 moles of Cr^{3+} requires 6e^- $n = 6$

$$\Delta G^\circ = -n F E^\circ = -6 (96,500) (-0.74) \\ = +428,460 \text{ J} = \boxed{+428.4 \text{ kJ}}$$

intensive, so
of moles
not relevant

(c) Qualitatively, how would ΔG° for this process be different from ΔG° ?

Biological Standard state $[\text{H}^+] = 10^{-7} \text{ M}$

Reaction is $3\text{H}_2(\text{g}) + 2\text{Cr}^{3+} \rightarrow 6\text{H}^+(\text{aq}) + 2\text{Cr}(\text{s})$

Reaction will be more spontaneous (product at 10^{-7} M instead of 1M)
the E° will be less negative (ΔG° more neg.) Le Chatelier

(20 pts) 5. (a) Using only the data found in Table A.5, calculate the equilibrium constant for the reaction $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$ at 25°C , including correct units,

$$K = e^{-\frac{\Delta G^\circ}{RT}} \quad \Delta G^\circ = -228.57 - (-237.129) = +8.559$$

7 pts $K = \boxed{0.0316 \text{ bar/mol fraction}}$

(b) What is the equilibrium concentration in mol L^{-1} of the vapor at 25°C ?

$$P_V = n_{\text{H}_2\text{O}} RT \quad \frac{n}{V} = [\text{H}_2\text{O(g)}] = \frac{P_{\text{H}_2\text{O}}}{RT} = \frac{0.0316 \text{ bar}}{0.083145 \frac{\text{bar L}}{\text{K mol}}} \frac{298 \text{ K}}{1 \text{ mol}} \\ = \boxed{0.00128 \text{ M}}$$

8 pts (c) What is the vapor pressure of pure water at 25°C and at 37°C ?

$$\text{at } 25^\circ \text{C} \quad \text{Vapor Pressure} = K_{25} = 0.0316 \text{ bar}$$

$$\text{at } 37^\circ \text{C} = 310 \text{ K} \quad \text{need } \Delta H_{\text{vap}}^\circ = -241.818 - (-285.83) = 44.01 \frac{\text{kJ}}{\text{mol}}$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = -\frac{44010}{8.3145} \left(\frac{1}{310} - \frac{1}{298} \right) = 0.685$$

$$\frac{K_2}{K_1} = e^{0.685} = 1.974$$

$$3 \quad \text{V.P.} @ 37^\circ \text{C} = 1.974 \times 0.0316 \\ = \boxed{0.0624 \text{ bar}}$$

(20 pts) 6. If $[H^+] = 10^{-5} M$ on one side of a membrane and $10^{-7} M$ on the other side, and if the electric potential difference is 50 mV more positive on the $10^{-7} M$ side:

(a) calculate the Gibbs energy change for the transfer of 2 moles of H^+ from the 10^{-5} to the $10^{-7} M$ side for $T=300 K$.

$$\Delta G = nRT \ln \frac{C_2}{C_1} + nFE(\phi_2 - \phi_1)$$

$$= 2 \left[(8.3145)(300) \ln \frac{10^{-7}}{10^{-5}} + (+)(96,500 \frac{C}{mol} \times 0.050 V) \right]$$

$$= 2(-11,490 \text{ J/mol} + 4825 \text{ J/mol}) = \boxed{-13330 \text{ J}}$$

(b) True or false: This is the mechanism for production of most of the ~50 kg of ATP our bodies process during a day.

28^{ts}

TRUE!

(20 pts) 7. For the reaction $A + B \rightarrow C$ (stoichiometric), the rate of disappearance of A is directly proportional to amount of A, but completely insensitive to the amount of B:

(a) Write the general rate law that describes the decrease of the grams per of A in time.

$$\frac{d \text{ grams } A}{dt} = -k s^{-1} (\text{grams } A)$$

(b) If the initial rate of decrease = 0.01 grams per second when 10 grams of A is present, calculate the rate constant for this process, including the units.

$$0.01 \text{ g s}^{-1} = k \text{ s}^{-1} / 10 \text{ g}$$

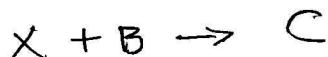
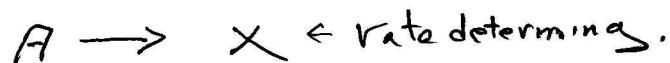
$$k = \frac{0.01 \text{ g s}^{-1}}{10 \text{ g}} = 10^{-3} \text{ s}^{-1}$$

(c) How much will remain after 1000 seconds?

$$f = e^{-10^3 s^{-1} / 1000 s} = e^{-1} = 0.367$$

$$0.367 \times 10 \text{ g} = \boxed{3.67 \text{ grams}}$$

(d) Suggest a plausible mechanism involving 2 elementary steps and the rate determining step that would be consistent with this rate law.



- (20 pts) 8. If the diffusion coefficient is $1 \times 10^{-11} \text{ m}^2\text{s}^{-1}$, and the effective mass = 100 kg, calculate the sedimentation coefficient in Svedbergs at T= 300K.

$$S = \frac{\text{mass}}{\text{frictional coef}} = \frac{m}{f}$$

$$= \frac{\text{effective mass } D}{K T} = \frac{100 \text{ kg mol}^{-1} (1 \times 10^{-11}) \text{ m}^2\text{s}^{-1}}{(18.3145 \text{ kg m}^2\text{s}^{-2}\text{mol}^{-1} \text{ K}^{-1}) 300 \text{ K}} \times 10^{+13} \frac{\text{Sved}}{\text{s}}$$

$$= \boxed{4 \text{ Svedbergs}}$$

- (20 pts) 9. Calculate the ratio of molecules in the excited state to those in the ground state when: $T = 300 \text{ K}$

a. the upperstate is 2000 cm^{-1} above the ground state.

using $K_B = 0.695 \text{ cm}^{-1} \text{ K}^{-1}$

$$\frac{N_{\text{excited}}}{N_{\text{ground}}} = e^{-\frac{2000 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1} 300}} = \boxed{6.83 \times 10^{-5}}$$

b. frequency to excite from ground to excited state = 600 MHz (as in NMR)

$$\nu = 600 \text{ MHz} = \frac{6 \times 10^8 \text{ s}^{-1}}{3 \times 10^{10} \text{ cm s}^{-1}} = 2 \times 10^{-2} \text{ cm}^{-1}$$

$$\frac{N_{\text{excited}}}{N_{\text{ground}}} = e^{-\frac{0.02 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1} 300 \text{ K}}} = \boxed{0.9999}$$

OR USE
 $e^{-\frac{\Delta E (J)}{K_B \frac{J}{\text{mol K}}}}$

$$\Delta E = h\nu = 2.3 \text{ cm}^{-1}$$

$$K_B = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ mol}^{-1}$$

- (20 pts) 10. For the reaction $A(\text{aq}) \rightleftharpoons B(\text{s}) + C(\text{g})$ which is exothermic, what will happen if:

(a) The concentration of A is decreased?

\rightarrow Reaction will proceed LEFT (increase A)

(b) The amount of B(s) is increased?

\rightarrow Nothing is No concentrations changed.

(c) The temperature is increased?

\rightarrow Will proceed LEFT (endothermic direction to USE added heat)

$$\ln \frac{k_2}{k_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

neg if $T_2 > T_1$

\rightarrow so $k_2 < k_1$ and more reactants at equilibrium.

	SI units	cgs-eu units
Gas constant	$8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$	$8.3145 \times 10^3 \text{ erg deg}^{-1} \text{ mol}^{-1}$ $1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$ $0.08205 \text{ L atm deg}^{-1} \text{ mol}^{-1}$ $6.0221 \times 10^{23} \text{ molecules mol}^{-1}$
Avogadro's number	$6.0221 \times 10^{23} \text{ mol}^{-1}$	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Boltzmann constant	$1.3807 \times 10^{-23} \text{ J K}^{-1}$	$9.6485 \times 10^3 \text{ C mol}^{-1}$
Faraday constant	$9.6485 \times 10^3 \text{ C mol}^{-1}$	$2.9979 \times 10^9 \text{ cm s}^{-1}$
Speed of light	$2.9979 \times 10^8 \text{ m s}^{-1}$	$6.6261 \times 10^{-29} \text{ erg s}$
Planck constant	$6.6261 \times 10^{-29} \text{ J s}$	$4.8030 \times 10^{-10} \text{ esu}$
Elementary charge	$1.6022 \times 10^{-19} \text{ C}$	$9.1094 \times 10^{-31} \text{ kg}$
Electron mass	$9.1094 \times 10^{-31} \text{ kg}$	$1.6726 \times 10^{-26} \text{ g}$
Proton mass	$1.6726 \times 10^{-26} \text{ g}$	980.66 cm s^{-2}
Standard gravity	9.8066 m s^{-2}	$8.6842 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
Permittivity of vacuum	$8.8542 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$	$\text{C} = \text{coulomb}$ $\text{g} = \text{gram}$ $\text{J} = \text{joule}$ $\text{K} = \text{Kelvin}$ $\text{kg} = \text{kilogram}$ $\text{L} = \text{liter}$ $\text{m} = \text{meter}$ $\text{N} = \text{newton}$ $\text{s} = \text{second}$

	$\Delta H_f^\circ = \bar{H}^\circ$ (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)	$\Delta G_f^\circ = \bar{G}^\circ$ (kJ mol ⁻¹)
Ag(s)	0	42.55	0
Ag ⁺ (aq) [†]	105.579	72.68	77.107
AgCl(s)	-127.068	96.2	-109.789
C(g)	716.682	158.096	671.257
C(s, graphite)	0	5.740	0
C(s, diamond)	1.895	2.377	2.900
Ca(s)	0	41.42	0
CaCO ₃ (s, calcite)	-1206.92	92.9	-1128.79
Cl ₂ (g)	0	223.066	0
Cl ⁻ (aq)	-167.159	56.5	-131.228
CO(g)	-110.525	197.674	-137.168
CO ₂ (g)	-393.509	213.74	-394.359
CO ₂ (aq)	-413.80	117.6	-385.98
HCO ₃ ⁻ (aq)	-691.99	91.2	-586.77
CO ₃ ²⁻ (aq)	-677.14	-56.9	-527.81
Fe(s)	0	27.28	0
Fe ₂ O ₃ (s)	-824.2	87.40	-742.2
H ₂ (g)	0	130.684	0
H ₂ O(g)	→ -241.818	188.825	-228.572
-H ₂ O(l)	→ -285.830	69.91	-237.129
H ⁺ (aq)	0	0	0
OH ⁻ (aq)	-229.994	-10.75	-157.244
H ₂ O ₂ (aq)	-191.17	143.9	-134.03
H ₂ S(g)	-20.63	205.79	-33.56
N ₂ (g)	0	191.61	0
NH ₃ (g)	-46.11	192.45	-16.45
NH ₃ (aq)	-80.29	111.3	-26.50
NH ₄ ⁺ (aq)	-132.51	113.4 [‡]	-79.31
NO(g)	90.25	210.761	86.55
NO ₂ (g)	33.18	240.06	51.31
NO ₃ ⁻ (aq)	-205.0	146.4	-108.74
Na ⁺ (aq)	-240.12	59.0	-261.905
NaCl(s)	-411.153	72.13	-384.138
NaCl(aq)	-407.27	115.5	-393.133
NaOH(s)	-425.609	64.455	-379.494
O ₂ (g)	0	205.138	0
O ₃ (g)	142.7	238.93	163.2
S(rhomboic)	0	31.80	0
SO ₂ (g)	-296.830	248.22	-300.194
SO ₃ (g)	-395.72	256.76	-371.06

* Standard thermodynamic values at 25°C (298 K) and 1 atm pressure. Values for ions refer to an aqueous solution at unit activity on the molarity scale. Standard enthalpy of formation, ΔH_f° , third-law entropies, S° , and standard Gibbs free energy of formation, ΔG_f° , are given.

† The standard state for all ions and for species labeled (aq) is that of a solute on the molarity scale.

Source: Data from *The NBS Tables of Thermodynamic Properties*, D. D. Wagman et al., eds., *J. Phys. Chem. Ref. Data*, 11, Suppl. 2 (1982).