

Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions.

Part 0: Warmup. 4 points each

- Reactions with a positive ΔH° and a negative ΔS° are
 - spontaneous at all temperatures.
 - non-spontaneous at all temperatures.
 - spontaneous at low temperatures but non-spontaneous at high temperatures. Answer _____
 - non-spontaneous at low temperatures but spontaneous at high temperatures.
- Which of the processes below DOES NOT result in an increase in entropy?
 - $2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)$
 - $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$ (The melting of ice.)
 - $\text{CO}_2(s) \rightarrow \text{CO}_2(g)$ (The sublimation of dry ice.) Answer _____
 - $\text{NH}_4\text{NO}_3(s) \rightarrow \text{N}_2\text{O}(g) + 2 \text{H}_2\text{O}(l)$
- Consider the reaction below. If hydrogen chloride gas is being produced at 1.2 moles per liter per minute (M min^{-1}), at what rate is hydrogen gas being consumed?
$$2\text{ICl}(g) + \text{H}_2(g) \rightarrow \text{I}_2(g) + 2\text{HCl}(g)$$
 - 1.2 M min^{-1}
 - 0.60 M min^{-1}
 - 2.4 M min^{-1}
 - Not enough information to determine. Answer _____

Part I: Complete all of problems 4-9

- Concisely discuss the validity of each of the following statements in a maximum of three sentences each. Clearly justify your reasoning. (12 points)
 - Reactions with a positive ΔH° and a positive ΔS° are always spontaneous.
 - Free energy changes provide a good indication of which reactions are favorable and fast, as well as those that are unfavorable and slow.

5. If even a tiny spark is introduced into a mixture of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$, a highly explosive exothermic reaction occurs. Without the spark, the mixture remains unreacted indefinitely. Explain this observation in terms of the reaction thermodynamics and kinetics. A reaction coordinate diagram may be useful.(8 points)

6. Consider a *first order* reaction: $\text{B} \rightarrow \text{Products}$. An experiment is performed and it is determined that with a starting $[\text{B}] = 0.100 \text{ M}$, it requires 56.2 seconds for the concentration to fall to 0.029 M. What is the rate constant for the reaction (with appropriate units)? How long would it take for the concentration to fall from 0.100 M to 0.0010 M? (14 points)

Answer: Rate constant _____ Time to 0.0010 M _____

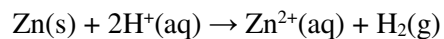
7. How much heat energy is produced when 0.100 kg of gaseous ethane (C_2H_6) undergoes a combustion reaction with excess oxygen gas to produce gaseous carbon dioxide and liquid water? (14 points)

Species	ΔH°_f , kJ mol ⁻¹	Species	ΔH°_f , kJ mol ⁻¹
O(g)	+249.2	H ₂ O(l)	-285.8
O ₂ (g)	0	H ₂ O(g)	-241.8
H(g)	+218.0	C ₂ H ₆ (g)	-84.7
H ₂ (g)	0	CO ₂ (g)	-393.5

Answer _____

Part II. Answer three (3) of problems 8-11. Clearly mark the problem you do not want graded. 14 points each.

8. In a constant-pressure experiment, a coffee-cup calorimeter contains 100.0 mL of 0.300 M HCl at 20.3°C. When 1.82 g zinc metal also at 20.3°C is added and is allowed to react via the net ionic equation below, the temperature rises to 30.5°C. What is the heat of reaction (ΔH_{rxn}) per mole of Zn? Assume no heat is lost to the environment during the course of the reaction and that the heat capacity and the density of the solution is the same as that of pure water (1.00 g/mL and 4.184 J/g°C, respectively).



Answer _____

9. Determine ΔH° for the reaction $\text{N}_2\text{H}_4(\text{l}) + 2\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$ from these data:

Reaction	ΔH°
$\text{N}_2\text{H}_4(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	-622.2 kJ
$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-285.8 kJ
$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$	+173.1 kJ
$\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l})$	-187.8 kJ

Answer _____

10. The reaction $\text{I}^-(\text{aq}) + \text{OCl}^-(\text{aq}) \rightarrow \text{IO}^-(\text{aq}) + \text{Cl}^-(\text{aq})$ was studied and the data below were obtained. Determine the rate law and the value of the rate constant for this reaction.

$[\text{I}^-]_0(\text{mol/L})$	$[\text{OCl}^-]_0(\text{mol/L})$	Initial Rate (mol/Ls)
0.12	0.18	0.00949
0.060	0.18	0.00237
0.030	0.090	0.000296
0.24	0.090	0.0190

Answer _____

11. Consider the reaction $\text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_4\text{NO}_3(\text{s})$ at 298K.

Species	$\Delta\text{H}^\circ_f, \text{kJ mol}^{-1}$	$\text{S}^\circ_f, \text{J mol}^{-1} \text{K}^{-1}$	$\Delta\text{G}^\circ_f, \text{kJ mol}^{-1}$
$\text{O}_2(\text{g})$	0	205.1	0
$\text{H}_2(\text{g})$	0	130.7	0
$\text{NH}_4\text{NO}_3(\text{s})$	-365.6	151.1	-183.9
$\text{N}_2\text{O}(\text{g})$	82.05	219.9	104.2
$\text{H}_2\text{O}(\text{l})$	-285.8	69.91	-237.1
$\text{H}_2\text{O}(\text{g})$	-241.8	188.8	-228.6

a. Is the forward reaction exothermic or endothermic? (5 points)

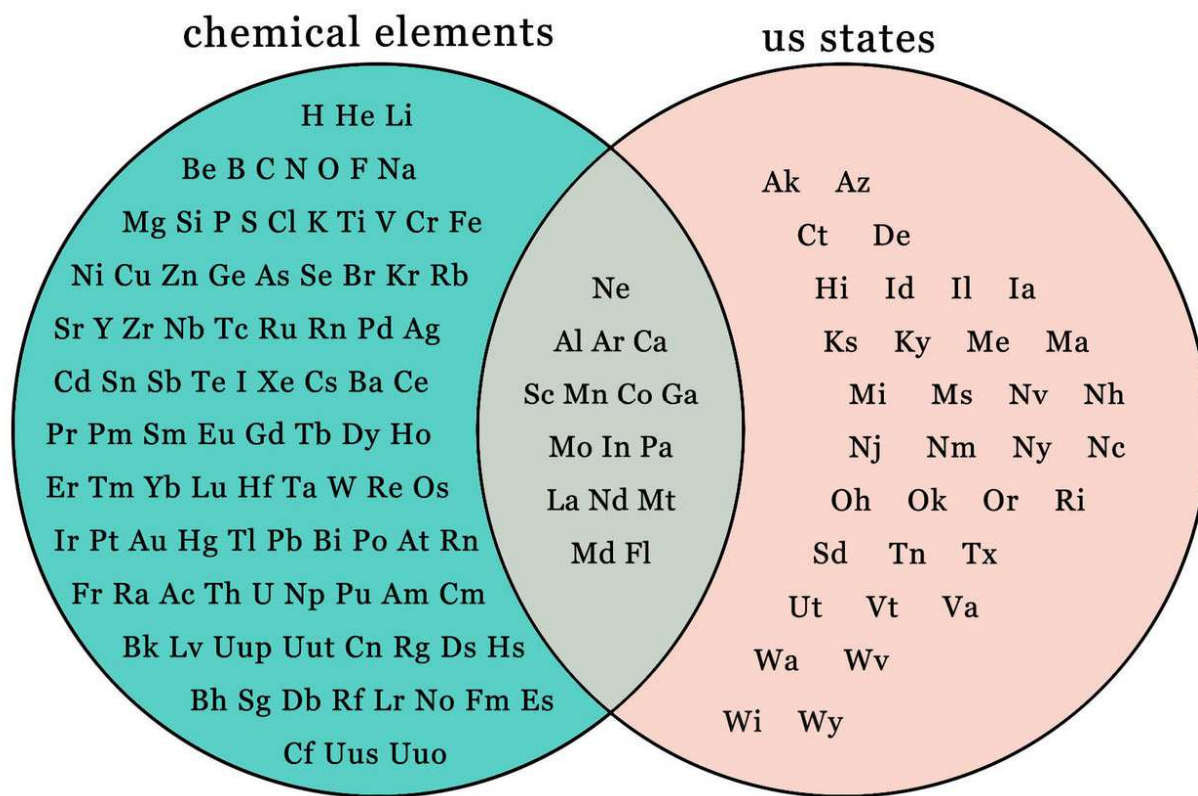
b. What is the value of ΔG° at 298 K? (5 points)

Answer _____

c. Does the reaction occur spontaneously at high temperatures, low temperatures, all temperatures or no temperatures? Justify your answer. (4 points)

Possibly Useful Information

$R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$	$K = ^\circ\text{C} + 273.15$	$q_{\text{released}} = -q_{\text{absorbed}}$
$q = mc\Delta T$	$q = n_{\text{LR}}\Delta H_{\text{rxn}}$	$q = m\Delta H$
$\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \Delta S_{\text{surr}}$	$\Delta G = \Delta H - T\Delta S$	$\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$
$\text{rate} = k[\text{A}]^0$	$[\text{A}]_t = -kt + [\text{A}]_0$	$t_{1/2} = [\text{A}]_0/2k$
$\text{rate} = k[\text{A}]^1$	$\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$	$t_{1/2} = 0.693/k$
$\text{rate} = k[\text{A}]^2$	$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$	$t_{1/2} = 1/(k[\text{A}]_0)$
$k = Ae^{-\left(\frac{E_a}{RT}\right)}$	$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$	$\text{slope} = m = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$



<http://mentalfloss.com/article/61102/12-funny-and-delicious-venn-diagrams>

To save some calculation time, you may round all atomic masses to two (2) decimal points.

1 1A											18 8A										
1 H 1.00794	2 2A										13 3A	14 4A	15 5A	16 6A	17 7A	2 He 4.00260					
3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797				
11 Na 22.9898	12 Mg 24.3050	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B		9 9B	10 10B	11 11B	12 12B	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948			
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9381	26 Fe 55.847	27 Co 58.9332	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80				
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 131.29				
55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)				
87 Fr (223)	88 Ra 226.025	89 †Ac 227.028	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Rg (272)											

*Lanthanide series	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)