

Name: KEY

Chemistry 112
Test 2
March 3, 2006

Instructions before starting the test:

1. Your exam booklet should have **eight** pages total, with questions on Pages 2-5, and a periodic table and other reference data on Pages 6-8. Check to see you have eight pages now. If you do not, ask for another copy of the exam.
2. You may remove the last three pages.
3. Write your name in the space above and on the backs of Pages 2-5.
4. This exam is closed-everything.
5. You may use programmable calculators, but chemical data should not be stored in them.
6. You have up to **90 minutes** to work on this exam, if you start work at 8:00 a.m.

<u>Page (Possible Points)</u>	<u>Your Score</u>
Page 2 (20)	
Page 3 (30)	
Page 4 (20)	
Page 5 (30)	
Total (100)	

mean 73

Average after Two Tests	
Midterm Grade	

1. (50 points total) Consider the combustion of acetylene in nitrous oxide:



Answer the following questions about this chemical reaction.

(a) (20 points) Calculate the change in entropy (in $\text{J mol}^{-1} \text{K}^{-1}$) for the above reaction, assuming the following partial pressures:

Gas:	C_2H_2	N_2O	CO_2	N_2
Partial Pressure (bar):	0.60	1.5	0.85	2.2

It will be necessary to use some of the reference data in back to solve this problem.

$$\Delta_r S = \Delta_r S^\circ - R \ln Q$$

$$\begin{aligned} \Delta_r S^\circ &= 2S^\circ(\text{CO}_2, \text{g}) + S^\circ(\text{H}_2\text{O}, \text{l}) + 5S^\circ(\text{N}_2, \text{g}) - S^\circ(\text{C}_2\text{H}_2, \text{g}) - 5S^\circ(\text{N}_2\text{O}, \text{g}) \\ &= [2(214) + 70. + 5(192) - 201 - 5(226.)] \text{J mol}^{-1} \text{K}^{-1} \\ &\quad \text{(or 70)} \quad \text{(or 220)} \end{aligned}$$

$$\Delta_r S^\circ = 157 \text{J mol}^{-1} \text{K}^{-1} \quad (\text{or } 157)$$

$$Q = \frac{P_{\text{CO}_2}^2 P_{\text{N}_2}^5}{P_{\text{C}_2\text{H}_2} P_{\text{N}_2\text{O}}^5} = \frac{(0.85)^2 (2.2)^5}{(0.60)(1.5)^5} = 8.17$$

$$\begin{aligned} \text{So } \Delta_r S &= 157 \text{J mol}^{-1} \text{K}^{-1} - \left(\frac{8.315 \text{J}}{\text{mol K}} \right) \ln(8.17) \\ &\quad (157) \\ &= 157 \text{J mol}^{-1} \text{K}^{-1} - 17.5 \text{J mol}^{-1} \text{K}^{-1} \end{aligned}$$

$$\Delta_r S = 139.5 \text{J mol}^{-1} \text{K}^{-1} \quad (\text{or } 140 \quad \text{or } 139.5 \quad \text{or } 140)$$

-1 2 sig figs and didn't write $\Delta_r S^\circ$ as $157 \text{J mol}^{-1} \text{K}^{-1}$ *
(most people used 2 sig figs incorrectly - because Q has 2 sig figs)

-2 more than 3 sig figs *

-6 wrong Q expression for Q, misuse of Q

-6 left out $S^\circ(\text{H}_2\text{O}, \text{l})$

-6 reactants - products

-2 math error *

-4 unit error

-8 ~~total~~ No calculation of $\Delta_r S$ (or very wrong calc of $\Delta_r S^\circ$)

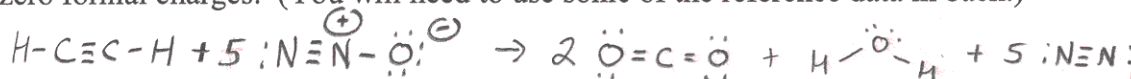
[Question 1 continues on the next page.] * did not subtract if already at -6

- (b) (10 points) Now assume the identical conditions as in part (a), except that instead of forming $\text{H}_2\text{O}(l)$, the reaction now forms $\text{H}_2\text{O}(g)$ at a partial pressure of 2.0 bar. Discuss completely, but qualitatively, how this would affect the change in entropy for the reaction.

Major effect: $\uparrow \Delta_r S^\circ$, since a gas (with E_{trans}) will have a lot more entropy than a liquid, other things (n, T) being equal.
 Minor effect: $\uparrow \Delta_r S$ not as much, since $P_{\text{H}_2\text{O}} > 1 \text{ bar}$, so $-R \ln Q$ is more negative than before.

- 4 no, or incorrect, discussion of Q
- 6 no, or incorrect, discussion of $\Delta_r S^\circ$
- 8 both of above errors
- 8 something

- (c) (20 points) Calculate the change in internal energy (in J) when 2.50 g of $\text{C}_2\text{H}_2(g)$ reacts in an excess of $\text{N}_2\text{O}(g)$ according to the equation at the top of the previous page. Your answer must include the Lewis structures of all species, showing all lone pairs and non-zero formal charges. (You will need to use some of the reference data in back.)



$$\Delta_r U = \text{BDE}(\text{C}\equiv\text{C}) + 2 \text{BDE}(\text{C}-\text{H}) + 5 \text{BDE}(\text{N}=\text{N}) + 5 \text{BDE}(\text{N}-\text{O}) - 4 \text{BDE}(\text{C}=\text{O}) - 2 \text{BDE}(\text{O}-\text{H}) - 5 \text{BDE}(\text{N}=\text{N})$$

$$\Delta_r U = [839 + 2(413) + 5(201) - 4(799) - 2(467)] \text{ kJ mol}^{-1} = -1460 \text{ kJ mol}^{-1}$$

$$2.50 \text{ g C}_2\text{H}_2 \left(\frac{\text{mol C}_2\text{H}_2}{26.038 \text{ g C}_2\text{H}_2} \right) = 0.0960, \text{ mol}$$

$$\text{so } \Delta U = \left(\frac{-1460 \text{ kJ}}{\text{mol}} \right) (0.0960, \text{ mol}) \left(\frac{10^3 \text{ J}}{\text{kJ}} \right) = -1.40, \times 10^5 \text{ J}$$

If 5 N-O-N, $\Delta_r U = -5160 \text{ kJ mol}^{-1}$ and $\Delta U = -4.95 \times 10^5 \text{ J}$

If 5 N=O=N, $\Delta_r U = -1100 \text{ kJ mol}^{-1}$ and $\Delta U = -1.06 \times 10^5 \text{ J}$

If 5 N-N=O, $\Delta_r U = -3335 \text{ kJ mol}^{-1}$ and $\Delta U = -3.20 \times 10^5 \text{ J}$

If 5 N-O=N, $\Delta_r U = -3130 \text{ kJ mol}^{-1}$ and $\Delta U = -3.01 \times 10^5 \text{ J}$

If 5 N=N=O, $\Delta_r U = -2045 \text{ kJ mol}^{-1}$ and $\Delta U = -1.96 \times 10^5 \text{ J}$

not showing lone pairs here

~~scribble~~
 -5 no ΔU for 2.50 g
 -3 wrong ΔU
 -3 bad Lewis for N_2O
 -1 per wrong formal charge
 -3 per other bad Lewis structures

~~scribble~~

-2 unit error
 -2 sigfig*

-5 wrong method for $\Delta_r U$
 math error*
 -2

* not if already at -5
 * not if already -5 for wrong $\Delta_r U$ method

2. (20 points total) A 0.100 mol sample of Ne(g) starts at 0.950 bar and 285 K. The sample is then heated to 355 K at a constant pressure of 0.950 bar.

(a) (10 points) Calculate the work (in J) for the above process.

$$W = -P\Delta V = -nR\Delta T = -(0.100 \text{ mol}) \left(\frac{8.315 \text{ J}}{\text{mol K}} \right) (355 - 285) \text{ K}$$

70. 2 sig figs!

$$= \boxed{-58.2 \text{ J}}$$

or you could have solved for initial and final volumes

$$(V_1 = 2.49 \text{ L} \quad V_2 = 3.11 \text{ L}) \text{ and used conversion } 1 \text{ L}\cdot\text{bar} = 100 \text{ J}$$

-1 sf
-1 dropped E sign
-2 math error
~~-2 conversion error~~
-3 unit error
-2 didn't convert to J
-7 $\Delta V = 0$

no more than -3 for all 3 errors

(b) (10 points) Discuss qualitatively how the above process changed the entropy of the sample. Consider all relevant factors.

$\uparrow T \Rightarrow \uparrow S$ since by $\frac{n_j}{n_i} = e^{-(E_j - E_i)/kT}$, more excited states are being populated

$\uparrow T \Rightarrow \uparrow V \Rightarrow \uparrow S$ also since $\Delta E_{\text{trans}} \sim \frac{1}{V^{2/3}}$, and $\downarrow \Delta E_{\text{trans}} \Rightarrow$ more E_{trans} levels being populated (or $\Delta S = R \ln \frac{V_2}{V_1}$)

(-5) no discussion of direct impact of T on S

(-5) " " " impact of V on S (or incorrect discussion)

(-3) $\uparrow T$ decreases ΔE

(-3) no explanation why $\uparrow T \Rightarrow \uparrow S$ (or ~~other~~ other incorrect explanation)

(-8) fundamental error

3. (20 points total) Imagine you could re-design the earth with the goal of minimizing temperature fluctuations. You could choose an atmosphere of one of the following gases:

Gas:	CH ₄	CO ₂	Cl ₂
Molar Heat Capacity (J mol ⁻¹ C ⁻¹):	35.31	37.11	33.91

Assume that the total moles of gas in your atmosphere would be the same in all three cases.

(a) (10 points) Which gas would you choose? Justify your choice using one of the equations on p. 6.

CO₂ since $\Delta U_T = C \Delta T \Rightarrow \Delta T = \frac{\Delta U_T}{C} \therefore$ for a given ΔU_T , the gas w/ largest C will give the lowest ΔT .

- (-5) chose gas w/ highest specific heat, CH₄ (+) something
- (-5) chose Cl₂ for the right reason (-5) wrong eqn
- (-4) incorrect discussion of $\Delta U_T = C \Delta T$ (-7) chose CO₂ for the wrong reason
- (-4) ~~(-5)~~ ΔU_T smaller (-2) incorrect discussion of $\Delta U_T = C \Delta T$ w/ CH₄

(b) (10 points) Which of the gases has the lowest standard molar entropy? Explain why in terms of energy levels.

CH₄ since it has the smallest m and μ and $\Delta E_{trans} \sim \frac{1}{m}$, $\Delta E_{rot} \sim \frac{1}{\mu}$, and $\Delta E_{vib} \sim \frac{1}{\mu}$. Larger ΔE 's \Rightarrow smaller pop. of excited states \Rightarrow lower S_{298}° . (Cl₂ arguably has the lowest vibrational contribution to S_{298}° since it has only 1 bond. But $\Delta E_{rot} + \Delta E_{trans}$ must also be considered)

- 6 no discussion of E_{trans} (\therefore Cl₂)
- 7 said ~~more~~ \uparrow mass $\Rightarrow \uparrow \Delta E$ (\therefore Cl₂)
- 7 Cl₂ because it has the smallest \tilde{c}
- 4 Cl₂ " " " " biggest \tilde{c}
- 5 no, or false, justification for CH₄
- 3 correct reasoning, wrong choice
- 9 something
- 3 vague justification

4. (10 points) A "universe" is a system that cannot exchange energy with its surroundings. What is one practical way to make a system behave like a universe in lab, and on an atomic/molecular level, why does the "practical way" you have chosen work?

Isolate (ie vacuum b/tm system and surroundings) or insulate (ie. materials like styrofoam b/tm system and surroundings).
 Isolation works because with no atoms/molecules, there can be no E xfer (there is nothing to collide with). Insulation works because the vibrations are of very low amplitude \Rightarrow little E xfer.

- 6 not a clear explanation why; begging question
- 3 high heat capacity mentioned, but not explained (or other partially correct answers)
- 6 no mass xfer \Rightarrow no E xfer
- 3 no mention of collisions (but other aspects of E xfer mentioned)
- 9 something

Possibly Useful Information

$$E_{vib} = \left(i + \frac{1}{2}\right) h \nu \quad \text{where } \nu = \frac{1}{2\pi} \sqrt{\frac{k_f}{\mu}} \text{ and } i = 0, 1, 2, \dots$$

$$E_{rot} = i(i+1) \frac{h^2}{8\pi^2} \left(\frac{1}{\mu R^2}\right) \quad \text{where } i = 0, 1, 2, \dots$$

$$E_{trans} = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8} \left(\frac{1}{mV^{2/3}}\right) \quad \text{where } n = 1, 2, 3, \dots$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad W = \frac{n!}{n_0! n_1! n_2! \dots}$$

$$\frac{n_j}{n_i} = e^{-(E_j - E_i)/kT} = e^{-\Delta E_{ij}/kT} \quad \Delta U = \Delta U_C + \Delta U_T = q + w \quad \Delta U_T = C\Delta T$$

$$w = -P\Delta V \quad PV = nRT \quad P\Delta V = nR\Delta T \quad T(\text{K}) = T(^{\circ}\text{C}) + 273.15 \text{ K}$$

$$S = k \ln W \quad \Delta S = nR \ln \frac{V_2}{V_1} \quad \Delta S = -nR \ln \frac{P_2}{P_1} \quad \Delta S = -nR \ln \frac{[X]_2}{[X]_1}$$

$$S_x = S_x^{\circ} - R \ln P_x / \text{bar} \quad S_x = S_x^{\circ} - R \ln [X] / \text{M} \quad \Delta_r S = \Delta_r S^{\circ} - R \ln Q$$

$$h = 6.626 \times 10^{-34} \text{ J s} \quad k = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

$$R = 0.08315 \text{ L bar mol}^{-1} \text{ K}^{-1} = 8.315 \text{ J mol}^{-1} \text{ K}^{-1} \quad 1 \text{ L bar} = 100 \text{ J}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \quad 1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} \quad 1 \text{ kJ} = 10^3 \text{ J} \quad 1 \text{ m} = 10^9 \text{ nm} = 10^{10} \text{ \AA}$$

Table 5.1. Mean Bond Dissociation Energies (kJ/mol)									
Single Bonds						Multiple Bonds			
H-H	432	N-H	391	F-F	154	S-H	347	C=C	614
H-F	565	N-N	160	F-Cl	253	S-C	259	C=N	615
H-Cl	427	N-O	201	F-Br	237	S-F	327	C=O*	799
H-Br	363	N-F	272			S-Cl	253		
H-I	295	N-Cl	200	Cl-Cl	239	S-Br	218	C=C	839
		N-Br	243	Cl-Br	218	S-S	266	C≡N	891
C-H	413			Cl-I	208			C=O	1072
C-C	347	O-H	467			Si-H	393		
C-N	305	O-O	146	Br-Br	193	Si-C	360	N=N	418
C-O	358	O-F	190	Br-I	175	Si-O	452	N=O	607
C-F	485	O-Cl	203			Si-Si	226		
C-Cl	339	O-I	234	I-I	149			N≡N	941
C-Br	276								
C-I	240							O=O	495

Table 7.1. Standard Molar Entropies (J/mol·K) at 298 K (S_{298}°)							
Solids		Liquids		Gases			
C(d)	2.4	H ₂ O(l)	70	He(g)	126	HCN(g)	202
C(gr)	5.7	Hg(l)	76	H ₂ (g)	131	F ₂ (g)	203
P(red)	23	CH ₃ OH(l)	127	HD(g)	143	O ₂ (g)	205
P(black)	23	Br ₂ (l)	152	D ₂ (g)	145	PH ₃ (g)	210
Fe(s)	27	HNO ₃ (l)	156	Ne(g)	146	NO(g)	211
Mn(s)	32	H ₂ SO ₄ (l)	157	Ar(g)	155	CO ₂ (g)	214
Mg(s)	33	N ₂ O ₄ (l)	209	Xe(g)	170		
LiF(s)	36	CCl ₄ (l)	216	HF(g)	174	C ₂ H ₆ (g)	230
P(white)	41			Hg(g)	175	O ₃ (g)	239
SiO ₂ (q)	42					NO ₂ (g)	240
Sn(gray)	44			HCl(g)	187	Br ₂ (g)	245
Sn(white)	52					I ₂ (g)	261
LiCl(s)	58			N ₂ (g)	192	C ₃ H ₁₀ (g)	293
NaCl(s)	72			NH ₃ (g)	193	N ₂ O ₄ (g)	304
KCl(s)	83			CO(g)	198	PCl ₃ (g)	312
KI(s)	106			HBr(g)	199	PCl ₅ (g)	361
I ₂ (s)	116			C ₂ H ₂ (g)	201	N ₂ O(g)	220

PERIODIC TABLE OF THE ELEMENTS

1A												8A					
1 H 1.0079	2A										5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179	
3 Li 6.941	4 Be 9.0122											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
11 Na 22.990	12 Mg 24.305	3B	4B	5B	6B	7B	—8B—			1B	2B						
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 †Ac 227.03															

*58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
†90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	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 (260)