

Name: KEY

Chemistry 112
Test 1
February 13, 2006

Instructions before starting the test:

1. Your exam booklet should have **seven** pages total, with questions on pages 2-5, and a periodic table and other reference data on pages 6 and 7. Check to see you have seven pages now. If you do not, ask for another copy of the exam.
2. You may remove the last two 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 (24)	
Page 3 (32)	
Page 4 (20)	
Page 5 (24)	
Total (100)	
Estimated Grade	

mean 73

1. (54 points total) Molecular chlorine is one of the most important substances in both the ocean and the atmosphere, and is therefore studied intensely by environmental chemists. Much of its chemistry can be explained using the ideas of molecular thermodynamics.

(a) (12 points) A naturally occurring sample of 500 Cl_2 molecules is exposed to a catalyst which facilitates the exchange of Cl atoms among the molecules. Assuming that naturally occurring chlorine is 76.0% ^{35}Cl and 24.0% ^{37}Cl , compute the most probable distribution of molecules for this sample. (Use probability, not ICE tables, to solve this problem!)

$$P(^{35}\text{Cl}) = 0.760 \quad P(^{37}\text{Cl}) = 0.240$$

$$P(^{35}\text{Cl}_2) = [P(^{35}\text{Cl})]^2 = (0.760)^2 = 0.578$$

$$P(^{37}\text{Cl}_2) = [P(^{37}\text{Cl})]^2 = (0.240)^2 = 0.0576$$

$$P(^{35}\text{Cl}^{37}\text{Cl}) = 1 - P(^{35}\text{Cl}_2) - P(^{37}\text{Cl}_2) = 1 - 0.578 - 0.0576 = 0.364$$

So most prob. dist is

$$500(0.578) = 289 \text{ } ^{35}\text{Cl}_2$$

$$500(0.0576) = 29 \text{ } ^{37}\text{Cl}_2$$

$$500(0.364) = 182 \text{ } ^{35}\text{Cl}^{37}\text{Cl}$$

(-1) not rounded to nearest integer

(-3) didn't report #'s of molecules

(-4) " $^{35}\text{Cl}_2$ " is the most prob. dist

(-4) one value of f (no # of $^{35}\text{Cl}^{37}\text{Cl}$)

(-10) no correct probabilities

(b) (12 points) Can the sample in part (a) ever be said to reach equilibrium? Explain. Your answer should include a clear definition of the term "equilibrium." Note that there is not one right answer to this question—I will grade you on the quality of your reasoning.

(-5) No discuss of the effect of the total # of molecules

(-5) Invalid def'n of equi) (or inapplicable) (or never clearly given)

(-4) Vague def'n of equi)

- (c) (12 points) Consider two flasks, both at 300 K. One flask contains 0.100 mol of $^{35}\text{Cl}_2$, and the other flask contains 0.100 mol of $^{37}\text{Cl}_2$. Assume that $^{35}\text{Cl}_2$ and $^{37}\text{Cl}_2$ have the same bond length. In which flask would you expect the molecules to have more quanta of rotational energy? Justify your answer clearly and completely.

$$\frac{\Delta E_{\text{rot}}(^{37}\text{Cl}_2)}{\Delta E_{\text{rot}}(^{35}\text{Cl}_2)} = \frac{\mu(^{35}\text{Cl}_2) R^2(^{35}\text{Cl}_2)}{\mu(^{37}\text{Cl}_2) R^2(^{37}\text{Cl}_2)} = \frac{(35)(35)}{(37)(37)} = \frac{35}{37} < 1$$

$\therefore \Delta E_{\text{rot}}(^{37}\text{Cl}_2)$ is smaller than $\Delta E_{\text{rot}}(^{35}\text{Cl}_2)$.

And, at the same T, a sample with smaller ΔE has

more excited states populated \Rightarrow $^{37}\text{Cl}_2$ has more quanta

Same T \Rightarrow same total E. Since each quantum of $^{37}\text{Cl}_2$ rot E is smaller, the sample of $^{37}\text{Cl}_2$ need more quanta to have the same total E as $^{35}\text{Cl}_2$.

- 5 smaller $E_{\text{rot}} \Rightarrow ^{37}\text{Cl}_2$ has fewer quanta
- 5 no discussion of # of quanta (but correct reasoning up to that point)
- 7 $^{37}\text{Cl}_2$ has more rot E (no discussion of $\sim \frac{1}{\mu}$)
- 2 Excited e-'s or vibrations
- 7 $^{35}\text{Cl}_2$ has greater reduced mass

- (d) (20 points) At what temperature (in K) would 20% of a sample of $^{35}\text{Cl}_2$ ($k_f = 380 \text{ kg s}^{-2}$) be in its first excited vibrational state? Report the temperature to two significant figures.

$$\frac{n_1}{n_0} = \frac{1}{4} = 0.25 = e^{-(E_1 - E_0)/kT} \Rightarrow \ln\left(\frac{n_1}{n_0}\right) = -\frac{(E_1 - E_0)}{kT}$$

NOT A MISTAKE! Say there are 5 molecules total: 4 in ground state, 1 in 1st excited state. Indeed, $\frac{\# \text{ in 1st excited state}}{\text{total \#}} = \frac{1}{5} = 20\%$. But $\frac{\# \text{ in 1st excited state}}{\# \text{ in ground state}} = \frac{n_1}{n_0} = \frac{1}{4}$

$$\Rightarrow T = \frac{-(E_1 - E_0)}{k \ln\left(\frac{n_1}{n_0}\right)} \quad \text{and} \quad E_1 - E_0 = \frac{3}{2} h\nu - \frac{1}{2} h\nu = h\nu = \frac{h}{2\pi} \sqrt{\frac{k_f}{\mu}}$$

($\nu = 1.82 \times 10^{13} \text{ s}^{-1}$)

$$\mu = \frac{(35)(35)}{35+35} \text{ amu} \left(\frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}} \right) = 2.9 \times 10^{-26} \text{ kg}$$

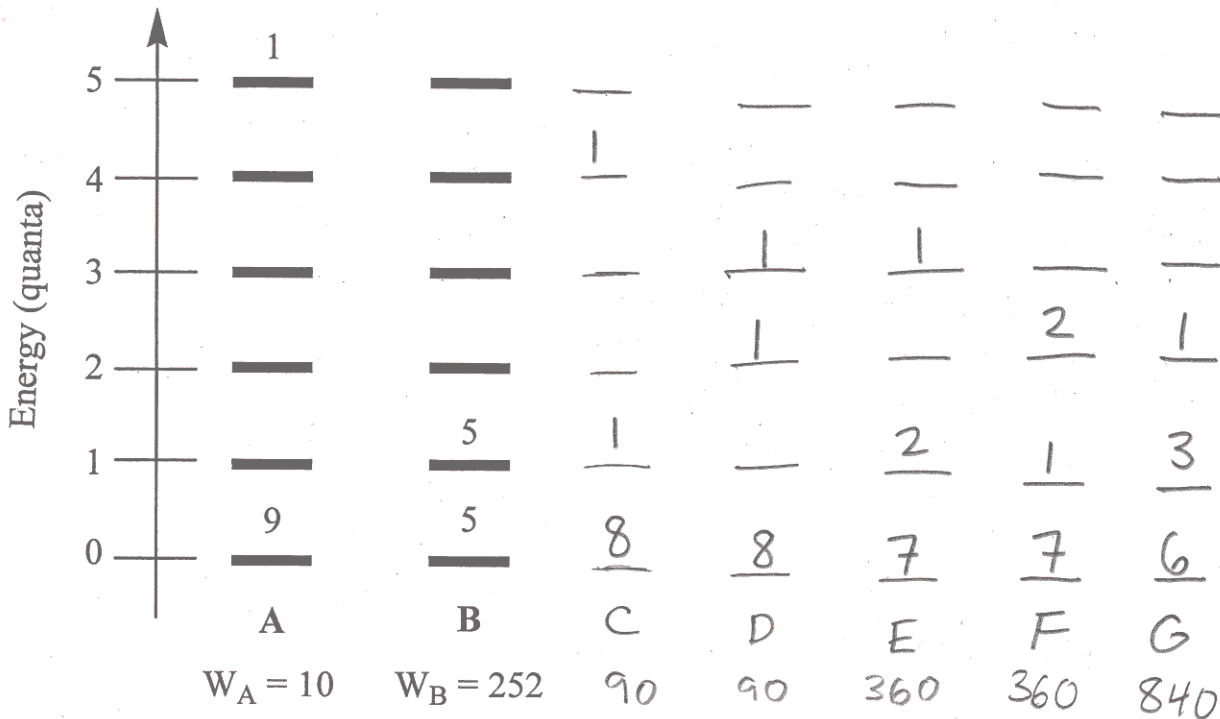
$$E_1 - E_0 = \left(\frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{2\pi} \right) \sqrt{\left(\frac{380 \text{ kg}}{\text{s}^2} \right) \left(\frac{1}{2.9 \times 10^{-26} \text{ kg}} \right)} = 1.2 \times 10^{-20} \text{ J}$$

(or other incorrect ratio)

$$\text{So } T = \frac{-(1.21 \times 10^{-20} \text{ J})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) (\ln(0.25))} = \boxed{630 \text{ K}}$$

- 5 540 K if used $n_1/n_0 = 0.20$
- 2 math error in addn to big error
- 3 math error only (minor)
- 5 used E_{vib} instead of ΔE_{vib}
- 5 Didn't convert amu to kg
- +5 Something correct

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 2. (26 points total) Consider a system with ten particles and five quanta of energy. Two possible energy distributions, along with their thermodynamic probabilities, are shown below:



(a) (15 points) Draw in the other possible distributions, and compute their thermodynamic probabilities. Show your work for the W calculations below.

$$W_C = \frac{10!}{8!1!1!1!1!} = \frac{10 \cdot 9 \cdot 8!}{8!} = 90$$

$$W_D = W_C = 90$$

$$W_E = \frac{10!}{7!2!} = \frac{10 \cdot 9 \cdot 8 \cdot 7!}{7! \cdot 2} = 360$$

$$W_F = W_E = 360$$

$$W_G = \frac{10!}{6!3!} = \frac{10 \cdot 9 \cdot 8 \cdot 7 \cdot 6!}{6! \cdot 3 \cdot 2} = 840$$

-3 per missing or incorrect distribution

-2 per wrong W (if distribution is right)

(b) (5 points) What is the probability (to three decimal places) of the least probable energy distribution?

$$W_{TOT} = 10 + 252 + 90 + 90 + 360 + 360 + 840 = 2002$$

$$SO P_A = \frac{W_A}{W_{TOT}} = \frac{10}{2002} = 0.005$$

-4 incorrect (unless self-consistent w/ part (a))


[Problem 2 continues on the next page.]

- (c) (12 points) Is your answer in part (b) consistent with the second law of thermodynamics? Explain. Your answer should include a clear definition of the second law.

YES. 2nd Law: E naturally disperses among particles. In Dist. A, the E is least dispersed and is also least probable.

~~answer~~ (-4) one mis-statement or incomplete
(-8) incorrect conception of the 2nd Law

3. (12 points) Assuming that the covalent bond in a diatomic molecule behaves as a spring, sketch how the energy of the molecule varies with the distance between the bonded atoms. Explain all key features of your sketch in terms of the electrons and nuclei in the molecule.

(-5) ^(correct) no sketch of energy vs. dist i.e. 

(-6) ^{correct} no discussion of e^- nucleus interaction

(-6) vague " " " " " "

(-4) why is $R > R_0$ bad?

(-2) exponential growth?

(-4) nuclei pulling e^- 's? or no explanation why e^- pull on nuclei
 e^- 's push nuclei away for $R < R_0$?

(-2) Erot invoked

(-5) no discussion of ~~why~~ that $R < R_0$ is bad

(-5) " " " " $R > R_0$ " "

(-11) some discussion

(-4) At $R < R_0$, $k_f \uparrow$

Possibly Useful Information

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

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

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

$$\Delta E = -\mathfrak{R}Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad W = \frac{n!}{n_0! n_1! n_2! \dots}$$

$$\frac{n_j}{n_i} = e^{-(E_j - E_i)/kT} = e^{-\Delta E_{ij}/kT} \quad \frac{n_{j \text{ or above}}}{n} = \frac{n_j}{n_0} e^{-j(E_i - E_0)/kT} = e^{-\Delta E_{ij}/kT}$$

$$c = \lambda \nu \quad \frac{1}{\lambda} \equiv \tilde{\nu} \quad E = h\nu \quad T(\text{K}) = T(^{\circ}\text{C}) + 273.15 \text{ K}$$

$$k = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

$$1 \text{ m} = 10^9 \text{ nm} = 10^{10} \text{ \AA}$$

$$\mathfrak{R} = 2.178 \times 10^{-18} \text{ J}$$

PERIODIC TABLE OF THE ELEMENTS

1A																		8A	
1																			2
H 1.0079																			He 4.0026
3	4											5	6	7	8	9	10		
Li 6.941	Be 9.0122											B 10.81	C 12.011	N 14.007	O 15.999	F 18.998	Ne 20.179		
11	12											13	14	15	16	17	18		
Na 22.990	Mg 24.305											Al 26.982	Si 28.086	P 30.974	S 32.06	Cl 35.453	Ar 39.948		
		3B	4B	5B	6B	7B	8B			1B	2B								
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36		
K 39.098	Ca 40.08	Sc 44.956	Ti 47.88	V 50.942	Cr 51.996	Mn 54.938	Fe 55.847	Co 58.933	Ni 58.69	Cu 63.546	Zn 65.38	Ga 69.72	Ge 72.59	As 74.922	Se 78.96	Br 79.904	Kr 83.80		
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54		
Rb 85.468	Sr 87.62	Y 88.906	Zr 91.22	Nb 92.906	Mo 95.94	Tc (98)	Ru 101.07	Rh 102.91	Pd 106.42	Ag 107.87	Cd 112.41	In 114.82	Sn 118.69	Sb 121.75	Te 127.60	I 126.90	Xe 131.29		
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86		
Cs 132.91	Ba 137.33	*La 138.91	Hf 178.49	Ta 180.95	W 183.85	Re 186.21	Os 190.2	Ir 192.22	Pt 195.08	Au 196.97	Hg 200.59	Tl 204.38	Pb 207.2	Bi 208.98	Po (209)	At (210)	Rn (222)		
87	88	89																	
Fr (223)	Ra 226.03	†Ac 227.03																	

*58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce 140.12	Pr 140.91	Nd 144.24	Pm (145)	Sm 150.36	Eu 151.96	Gd 157.25	Tb 158.93	Dy 162.50	Ho 164.93	Er 167.26	Tm 168.93	Yb 173.04	Lu 174.97
†90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th 232.04	Pa 231.04	U 238.03	Np 237.05	Pu (244)	Am (243)	Cm (247)	Bk (247)	Cf (251)	Es (252)	Fm (257)	Md (258)	No (259)	Lr (260)