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.

<table>
<thead>
<tr>
<th>Page (Possible Points)</th>
<th>Your Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>Page 2 (20)</td>
<td></td>
</tr>
<tr>
<td>Page 3 (30)</td>
<td></td>
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<tr>
<td>Page 4 (20)</td>
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<tr>
<td>Page 5 (30)</td>
<td></td>
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<td>Total (100)</td>
<td></td>
</tr>
</tbody>
</table>

mean 73

Average after Two Tests

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

\[ \text{C}_2\text{H}_2(\text{g}) + 5 \text{N}_2\text{O}(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + \text{H}_2\text{O}(l) + 5 \text{N}_2(\text{g}) \]

Answer the following questions about this chemical reaction.

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

<table>
<thead>
<tr>
<th>Gas:</th>
<th>C(_2)H(_2)</th>
<th>N(_2)O</th>
<th>CO(_2)</th>
<th>N(_2)</th>
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</thead>
<tbody>
<tr>
<td>Partial Pressure (bar):</td>
<td>0.60</td>
<td>1.5</td>
<td>0.85</td>
<td>2.2</td>
</tr>
</tbody>
</table>

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

\[
\Delta_rS = \Delta_rS^0 - R \ln Q
\]

\[
\Delta_rS^0 = 2S^0(\text{CO}_2, \text{g}) + S^0(\text{H}_2\text{O}, \text{l}) + 5S^0(\text{N}_2, \text{g}) - S^0(\text{C}_2\text{H}_2, \text{g}) - 5S^0(\text{N}_2\text{O}, \text{g})
\]

\[
= \left[ 2(214) + 70. + 5(192) - 201 - 5(220) \right] \text{J mol}^{-1}\text{K}^{-1}
\]

\[
= 157 \text{J mol}^{-1}\text{K}^{-1} \quad \text{(or 157)}
\]

\[
Q = \frac{P_{\text{CO}_2}^2 P_{\text{N}_2}^5}{P_{\text{C}_2\text{H}_2} P_{\text{N}_2\text{O}}^5}
\]

\[
= \frac{(0.85)^2(2.2)^5}{(0.60)(1.5)^5} = 8.17
\]

\[
S_0 \Delta_rS^0 = 157 \text{J mol}^{-1}\text{K}^{-1} - \left( \frac{8.315J}{\text{mol K}} \right) \ln (8.17)
\]

\[
= 157 \text{J mol}^{-1}\text{K}^{-1} - 17.5 \text{J mol}^{-1}\text{K}^{-1}
\]

\[
\Delta_rS^0 = 139.5 \text{J mol}^{-1}\text{K}^{-1} \quad \text{(or 140 or 139.5 or 140)}
\]

- 1 sig figs and didn't write \(\Delta_rS^0 = 139.5 \text{J mol}^{-1}\text{K}^{-1}\) *
- most people need 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 \(S^0(\text{H}_2\text{O}, \text{l})\)
- 6 reactants - products
- 2 math error*
- 4 unit error
- 8 No calculation of \(\Delta_rS^0\) (or wrong calc of \(\Delta_rS^0\))

* did not subtract if already at -6

[Question 1 continues on the next page.]

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(b) (10 points) Now assume the identical conditions as in part (a), except that instead of forming H₂O(l), the reaction now forms H₂O(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: \( \Delta S^0 \), since a gas (with Enam) will have a lot more entropy than a liquid, other things \((n, T)\) being equal.

Minor effect: \( \Delta S \) not as much, since \( P_{H_2O} > 1 \) bar, so \( -R \ln Q \) is more negative than before.

- 4 no, incorrect, discussion of \( Q \)
- 6 no, incorrect, discussion of \( \Delta S^0 \)
- 8 both of above errors
- 8 something

(c) (20 points) Calculate the change in internal energy (in J) when 2.50 g of C₂H₂(g) reacts in an excess of N₂O(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.)

\[
\Delta U = BDE(C\equiv C) + 2 \cdot BDE(C-H) + 5 \cdot BDE(N=\text{N}) + 5 \cdot BDE(N=\text{O})
- 4 \cdot BDE(C=O) - 2 \cdot BDE(O-H) - 5 \cdot BDE(N=\text{N})
\]
\[
\Delta U = [839 + 2(413) + 5(201) - 4(799) - 2(467)] \text{KJ mol}^{-1} = -1460 \text{KJ mol}^{-1}
\]

\[
2.50 \text{ g C}_2\text{H}_2 (\text{mol} C_2H_2 \frac{1}{26.038 \text{ g C}_2\text{H}_2}) = 0.0960 \text{ mol}
\]

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

If \( 5 \text{ N-O-N} \), \( \Delta U = -5160 \text{ KJ mol}^{-1} \) and \( \Delta U = -4.95 \times 10^5 \text{ J} \)

If \( 5 \text{ N=O=N} \), \( \Delta U = -1100 \text{ KJ mol}^{-1} \) and \( \Delta U = -1.06 \times 10^5 \text{ J} \)

If \( 5 \text{ N-N=O} \), \( \Delta U = -3335 \text{ KJ mol}^{-1} \) and \( \Delta U = -3.20 \times 10^5 \text{ J} \)

If \( 5 \text{ N=O=N} \), \( \Delta U = -3130 \text{ KJ mol}^{-1} \) and \( \Delta U = -3.01 \times 10^5 \text{ J} \)

If \( 5 \text{ N=N=O} \), \( \Delta U = -2045 \text{ KJ mol}^{-1} \) and \( \Delta U = -1.96 \times 10^5 \text{ J} \)

Test 2--Page 3 of 8
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.

\[ W = -P \Delta V = -n \, R \Delta T = -(0.100 \text{ mol}) \left( \frac{8.315 \text{ J}}{\text{mol} \cdot \text{K}} \right) (355 - 285) \text{ K} \]

\[ = -58.2 \text{ J} \]

Or you could have solved for initial and final volumes \( V_1 = 2.49 \text{ L} \) \( V_2 = 3.11 \text{ L} \) and used conversion \( 1 \text{ L} \cdot \text{bar} = 100 \text{ J} \)

- 1 (dropped 319 on top)
- 1 (dropped 319 on top)
- 1 (dropped 319 on top)
- 1 (dropped 319 on top)
- 2 (more error)
- 2 (unit error)
- 2 (didn’t convert to J)
- 2 (ΔV = 0)

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

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

\[ \uparrow T \Rightarrow \uparrow V \Rightarrow \uparrow S \text{ also since } \Delta E_{\text{trans}} \sim \frac{1}{V^{2/3}} \text{, and } \downarrow \Delta E_{\text{trans}} \text{ more } E_{\text{trans}} \text{ levels being populated} \]

- 5 (no discussion of direct impact of \( T \) on \( S \))
- 5 "" "" "" impact of \( V \) on \( S \) (or incorrect discussion)
- 3 \( \uparrow T \) decreases \( \Delta E \)
- 3 no explanation why \( \uparrow T \Rightarrow \uparrow S \) (or other incorrect explanation)
- 3 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:

<table>
<thead>
<tr>
<th>Gas</th>
<th>CH₄</th>
<th>CO₂</th>
<th>Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar Heat Capacity (J mol⁻¹ C⁻¹)</td>
<td>35.31</td>
<td>37.11</td>
<td>33.91</td>
</tr>
</tbody>
</table>

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.

\[ \Delta U_T = C \Delta T \Rightarrow \Delta T = \frac{\Delta U_T}{C} \]

For a given \( \Delta U_T \), the gas with largest \( C \) will give the lowest \( \Delta T \).

- Choose gas with highest specific heat, \( \text{CH}_4 \)
- Choose \( \text{Cl}_2 \) for the wrong reason
- Incorrect discussion of \( \Delta U_T = C \Delta T \)
- \( \Delta U_T \) smaller

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

\[ \Delta E_{\text{trans}} \sim \frac{1}{m}, \quad \text{and} \quad \Delta E_{\text{vib}} \sim \frac{1}{m}. \]

Larger \( \Delta E \)'s \( \Rightarrow \) smaller pop. of excited states \( \Rightarrow \) lower \( S^{\circ} \).

- No discussion of \( E_{\text{trans}} \) (\( \text{Cl}_2 \))
- Said mass \( \Rightarrow \) higher \( \Delta E \) (\( \text{Cl}_2 \))
- \( \text{Cl}_2 \) because it has no smallest \( \Delta E \)
- \( \text{Cl}_2 \) because it has the largest \( \Delta E \)
- No valid reasoning, wrong choice

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 but system and surroundings) or insulate (i.e. materials like styrofoam but system and surroundings).

Isolation works because with no atoms/molecules, there can be no \( \text{Ex}_{\text{fer}} \) (there is nothing to collide with). Insulation works because the vibrations are of very low amplitude \( \Rightarrow \) little \( \text{Ex}_{\text{fer}} \).

- Not a clear explanation why: begging question
- High heat capacity mentioned, but not explained (or other partially correct answer)
- No mass \( \text{Ex}_{\text{fer}} \) \( \Rightarrow \) no \( \text{Ex}_{\text{fer}} \)
- No mention of collisions (but other aspects of \( \text{Ex}_{\text{fer}} \) mentioned)
- Something
Possibly Useful Information

\[ E_{\text{vib}} = \left( i + \frac{1}{2} \right) \hbar \nu \text{ where } \nu = \frac{1}{2\pi} \sqrt{\frac{k_f}{\mu}} \text{ and } i = 0, 1, 2, \ldots \]

\[ E_{\text{rot}} = i(i + 1) \frac{\hbar^2}{8\pi^2} \left( \frac{1}{\mu R^2} \right) \text{ where } i = 0, 1, 2, \ldots \]

\[ E_{\text{trans}} = \left( n_x^2 + n_y^2 + n_z^2 \right) \frac{\hbar^2}{8} \left( \frac{1}{mV^{2/3}} \right) \text{ where } n = 1, 2, 3, \ldots \]

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \quad \quad W = \frac{n!}{n_0! n_1! n_2! \ldots} \]

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

\[ w = -P\Delta V \quad PV = nRT \quad P\Delta V = nR\Delta T \quad T \text{ (K) } = T \text{ (°C) } + 273.15 \text{ K} \]

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

\[ S_x = S_x^0 - R \ln P_x / \text{bar} \quad S_x = S_x^0 - R \ln [X] / \text{M} \quad \Delta S = \Delta S = \Delta S^0 - R \ln Q \]

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

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

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

\[ 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} \quad 1 \text{ kJ} = 10^3 \text{ J} \quad 1 \text{ m} = 10^9 \text{ nm} = 10^{10} \text{ Å} \]
### Table 5.1. Mean Bond Dissociation Energies (kJ/mol)

<table>
<thead>
<tr>
<th></th>
<th>Single Bonds</th>
<th>Multiple Bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H–H</strong></td>
<td>432</td>
<td>391</td>
</tr>
<tr>
<td><strong>H–F</strong></td>
<td>565</td>
<td>160</td>
</tr>
<tr>
<td><strong>H–Cl</strong></td>
<td>427</td>
<td>201</td>
</tr>
<tr>
<td><strong>H–Br</strong></td>
<td>363</td>
<td>272</td>
</tr>
<tr>
<td><strong>H–I</strong></td>
<td>295</td>
<td>200</td>
</tr>
<tr>
<td><strong>C–H</strong></td>
<td>413</td>
<td>243</td>
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<tr>
<td><strong>C–C</strong></td>
<td>347</td>
<td>467</td>
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<tr>
<td><strong>C–N</strong></td>
<td>305</td>
<td>146</td>
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<tr>
<td><strong>C–O</strong></td>
<td>358</td>
<td>190</td>
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<tr>
<td><strong>C–F</strong></td>
<td>485</td>
<td>203</td>
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<tr>
<td><strong>C–Cl</strong></td>
<td>339</td>
<td>234</td>
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<td><strong>C–Br</strong></td>
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<td><strong>C–I</strong></td>
<td>240</td>
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</tbody>
</table>

### Table 7.1. Standard Molar Entropies (J/mol·K) at 298 K (S°298)

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<th>Solids</th>
<th>Liquids</th>
<th>Gases</th>
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<tr>
<td>C(d)</td>
<td>H₂O(l)</td>
<td>He(g)</td>
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<tr>
<td>C(gr)</td>
<td>Hg(l)</td>
<td>H₂(g)</td>
</tr>
<tr>
<td>P(red)</td>
<td>CH₃OH(l)</td>
<td>HD(g)</td>
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<tr>
<td>P(black)</td>
<td>Br₂(l)</td>
<td>D₂(g)</td>
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<td>Fe(s)</td>
<td>HNO₃(l)</td>
<td>Ne(g)</td>
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<td>Mn(s)</td>
<td>H₂SO₄(l)</td>
<td>Ar(g)</td>
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<tr>
<td>Mg(s)</td>
<td>N₂O₄(l)</td>
<td>Xe(g)</td>
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<td>LiF(s)</td>
<td>CCl₄(l)</td>
<td>HF(g)</td>
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<td>P(white)</td>
<td>Hg(g)</td>
<td>O₃(g)</td>
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<td>SiO₂(q)</td>
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<td>HCl(g)</td>
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<td>I₂(g)</td>
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PERIODIC TABLE OF THE ELEMENTS

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