The University of Sydney

CHEM1612 - CHEMISTRY 1B (PHARMACY)
SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2006

TIME ALLOWED: THREE HOURS

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

<table>
<thead>
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INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 21 pages of examinable material.

- Complete the examination paper in INK.

- Read each question carefully. Report the appropriate answer and show all relevant working in the space provided.

- The total score for this paper is 100. The possible score per page is shown in the adjacent tables.

- Each new question of the short answer section begins with a •.

- Electronic calculators, including programmable calculators, may be used. Students are warned, however, that credit may not be given, even for a correct answer, where there is insufficient evidence of the working required to obtain the solution.

- Numerical values required for any question, standard electrode reduction potentials, a Periodic Table and some useful formulas may be found on the separate data sheets.

- Pages 17 and 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

<table>
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Short answer section

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The final step in the industrial production of urea, \((\text{NH}_2\text{H})_2\text{CO}\), is:

\[
\text{CO}_2(g) + 2\text{NH}_3(g) \rightarrow \text{H}_2\text{O}(g) + (\text{NH}_2\text{H})_2\text{CO}(s) \quad \Delta H^\circ = -90.1 \text{ kJ mol}^{-1}
\]

Using the following data, calculate the standard enthalpy of formation of solid urea.

\[
\begin{align*}
4\text{NH}_3(g) + 3\text{O}_2(g) &\rightarrow 6\text{H}_2\text{O}(g) + 2\text{N}_2(g) \quad \Delta H^\circ = -1267.2 \text{ kJ mol}^{-1} \\
\text{C}(s) + \text{O}_2(g) &\rightarrow \text{CO}_2(g) \quad \Delta H^\circ = -393.5 \text{ kJ mol}^{-1} \\
2\text{H}_2(g) + \text{O}_2(g) &\rightarrow 2\text{H}_2\text{O}(g) \quad \Delta H^\circ = -483.6 \text{ kJ mol}^{-1}
\end{align*}
\]

The formation of urea in the industrial process is only spontaneous below 821 °C.

What is the value of the entropy change \(\Delta S^\circ\) (in J K\(^{-1}\) mol\(^{-1}\)) for the reaction?

Rationalise the sign of \(\Delta S^\circ\) in terms of the physical states of the reactants and products.
• The specific heat capacity of water is 4.18 J g\(^{-1}\) K\(^{-1}\) and the specific heat capacity of copper is 0.39 J g\(^{-1}\) K\(^{-1}\). If the same amount of energy were applied to a 1.0 mol sample of each substance, both initially at 25 °C, which substance would get hotter? Show all working.

Answer:

• Explain why the acidity of hydrogen halides increases with increasing halogen size \(i.e., K_a (HCl) < K_a (HBr) < K_a (HI)\), while the acidity of hypohalous acids decreases with increasing halogen size \(i.e., K_a (HOCl) > K_a (HOBr) > K_a (HOI)\).
• The $K_a$ of benzoic acid is $6.3 \times 10^{-5}$ M at 25°C.

Calculate the pH of a 0.0100 M aqueous solution of sodium benzoate ($C_6H_5COONa$).

Answer:

A buffer solution is prepared by adding 375 mL of this 0.0100 M aqueous solution of sodium benzoate to 225 mL of 0.0200 M aqueous benzoic acid. Calculate the pH of the buffer solution.

Answer:
“Water gas” is a mixture of combustible gases produced from steam and coal according to the following reaction:

\[
C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \quad \Delta H^\circ = 131 \text{ kJ mol}^{-1}
\]

The equation for the complete combustion of 1 mol of water gas (i.e. 0.5 mol CO(g) and 0.5 mol H_2(g)) can be written as:

\[
\frac{1}{2}CO(g) + \frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g) + \frac{1}{2}H_2O(g)
\]

Calculate the standard enthalpy of combustion of water gas, given the following thermochemical data.

\[
\begin{align*}
\Delta H^\circ_{\text{vap}} (H_2O) &= 44 \text{ kJ mol}^{-1} \\
\Delta H^\circ_{\text{f}} (H_2O(l)) &= -286 \text{ kJ mol}^{-1} \\
\Delta H^\circ_{\text{f}} (CO_2(g)) &= -393 \text{ kJ mol}^{-1}
\end{align*}
\]

Answer:
The CO(g) in water gas can be reacted further with H₂O(g) in the so-called “water-gas shift” reaction:

\[
\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)
\]

At 900 K, \(K_c = 1.56\) for this reaction. A sample of water gas flowing over coal at 900 K contains a 1:1 mole ratio of CO(g) and H₂(g), as well as 0.250 mol L\(^{-1}\) H₂O(g). This sample is placed in a sealed container at 900 K and allowed to come to equilibrium, at which point it contains 0.070 mol L\(^{-1}\) CO₂(g). What was the initial concentration of CO(g) and H₂(g) in the sample?

\[
[\text{CO}] = [\text{H}_2] = \ldots
\]

If the walls of the container are chilled to below 100 °C, what will be the effect on the concentration of CO₂(g)?

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.
• The isomerisation of glucose-6-phosphate (G6P) to fructose-6-phosphate (F6P) is a key step in the metabolism of glucose for energy. At 298 K,

\[ \text{G6P} \rightleftharpoons \text{F6P} \quad \Delta G^\circ = 1.67 \text{ kJ mol}^{-1} \]

Calculate the equilibrium constant for this process at 298 K.

Answer:

What is the free energy change (in kJ mol\(^{-1}\)) involved in a mixture of 3.00 mol of F6P and 2.00 mol of G6P reaching equilibrium at 298 K?

Answer:

Sketch a graph of \(G_{\text{sys}}\) versus “extent of reaction”, with a curve showing how \(G_{\text{sys}}\) varies as G6P is converted to F6P. Indicate the position on this curve corresponding to 3.00 mol of F6P and 2.00 mol of G6P.
• Assume that NaCl is the only significant solute in seawater. A 1.000 L sample of seawater at 25 ºC and 1 atm has a mass of 1.0275 kg and contains 33.0 g of NaCl. At what temperature would this seawater freeze? The freezing point depression constant of water is 1.86 ºC kg mol\(^{-1}\).

Answer:

The vapour pressure above pure H\(_2\)O is 23.76 mmHg at 25 ºC and 1 atm. Calculate the vapour pressure above this seawater under the same conditions.

Answer:

The desalination of seawater by reverse osmosis has been suggested as a way of alleviating water shortages in Sydney. What pressure (in Pa) would need to be applied to this seawater in order to force it through a semi-permeable membrane, yielding pure H\(_2\)O?

Answer:
• The molar solubility of lead(II) fluoride, PbF$_2$, is found to be $2.6 \times 10^{-3}$ M at 25 °C. Calculate the value of $K_{sp}$ for this compound at this temperature.

\[K_{sp} = \]

• Draw all stereoisomers of the complex ion of [Co(en)$_3$]Br$_3$.

(\text{en = ethylenediamine = NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)

• Name the following complexes.

\[
\text{[Co(H}_2\text{O})_4]\text{Br}_2\text{Cl}
\]

\[
\text{K[Au(CN)}_2\text{]}
\]
• Write the chemical equation for the formation of the complex ion [Cd(NH₃)₄]²⁺.

Write the associated stability constant expression ($K_{\text{stab}}$).

• The physiological properties of chromium depend on its oxidation state. Consider the half reaction in which Cr(VI) is reduced to Cr(III).

\[
\text{CrO}_4^{2-} (\text{aq}) + 4\text{H}_2\text{O}(l) + 3e^- \rightarrow \text{Cr}('\text{OH}_3(s) + 5\text{OH}^-(aq) \quad E^0 = -0.13 \text{ V}
\]

Calculate the potential for this half reaction at 25 °C, where pH = 7.40 and [CrO₄²⁻ (aq)] = 1.0 × 10⁻⁶ M.

Answer:
Consider the following reaction at 298 K.

\[
\text{Ni}^{2+}(aq) + \text{Zn}(s) \rightleftharpoons \text{Ni}(s) + \text{Zn}^{2+}(aq)
\]

Calculate \( \Delta G^o \) for the cell. (Relevant electrode potentials can be found on the data page.)

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Answer:

What is the value of the equilibrium constant for the reaction at 298 K?

Answer:

Express the overall reaction in voltaic cell notation.

Using a current of 2.00 A, how long (in minutes) will it take to plate out all of the silver from 0.250 L of a \( 1.14 \times 10^{-2} \) M \( \text{Ag}^+(aq) \) solution?

Answer:
• If a medical procedure calls for 2.0 mg of $^{48}$V, what mass of isotope would be required to be able to use it exactly one week later? The half life of $^{48}$V is 1.61 days.

Answer:

• Describe how hydrophilic and hydrophobic colloids are stabilised in water.

• Calculate the standard free-energy change for the following reaction at 298 K.

\[
2\text{Au}(s) + 3\text{Mg}^{2+}(1.0\text{ M}) \rightarrow 2\text{Au}^{3+}(1.0\text{ M}) + 3\text{Mg}(s)
\]

Answer:
The major pollutants NO(g), CO(g), NO₂(g) and CO₂(g), which are emitted by cars, can react according to the following equation.

\[ \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \]

The following rate data were collected at 225 °C.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[NO₂]₀ (M)</th>
<th>[CO]₀ (M)</th>
<th>Initial rate (d[NO₂]/dt, M s⁻¹)</th>
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<tbody>
<tr>
<td>1</td>
<td>0.263</td>
<td>0.826</td>
<td>1.44 × 10⁻⁵</td>
</tr>
<tr>
<td>2</td>
<td>0.263</td>
<td>0.413</td>
<td>1.44 × 10⁻⁵</td>
</tr>
<tr>
<td>3</td>
<td>0.526</td>
<td>0.413</td>
<td>5.76 × 10⁻⁵</td>
</tr>
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</table>

Determine the rate law for the reaction.

Calculate the value of the rate constant at 225 °C.

\[ \text{Answer:} \]

Calculate the rate of appearance of CO₂ when [NO₂] = [CO] = 0.500 M.

\[ \text{Answer:} \]

Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.
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DATA SHEET

Physical constants
Avogadro constant, \( N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \)
Faraday constant, \( F = 96485 \text{ C mol}^{-1} \)
Planck constant, \( h = 6.626 \times 10^{-34} \text{ J s} \)
Speed of light in vacuum, \( c = 2.998 \times 10^8 \text{ m s}^{-1} \)
Rydberg constant, \( E_R = 2.18 \times 10^{-18} \text{ J} \)
Boltzmann constant, \( k_B = 1.381 \times 10^{-23} \text{ J K}^{-1} \)
Gas constant, \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)
\( \quad = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \)
Charge of electron, \( e = 1.602 \times 10^{-19} \text{ C} \)
Mass of electron, \( m_e = 9.1094 \times 10^{-31} \text{ kg} \)
Mass of proton, \( m_p = 1.6726 \times 10^{-27} \text{ kg} \)
Mass of neutron, \( m_n = 1.6749 \times 10^{-27} \text{ kg} \)

Properties of matter
Volume of 1 mole of ideal gas at 1 atm and 25 °C = 24.5 L
Volume of 1 mole of ideal gas at 1 atm and 0 °C = 22.4 L
Density of water at 298 K = 0.997 g cm\(^{-3}\)

Conversion factors
1 atm = 760 mmHg = 101.3 kPa
0 °C = 273 K
1 L = 10\(^{-3}\) m\(^3\)
1 Å = 10\(^{-10}\) m
1 eV = 1.602 \times 10^{-19} \text{ J}
1 Ci = 3.70 \times 10^{10} \text{ Bq}
1 Hz = 1 s\(^{-1}\)

Decimal fractions
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<td>10(^{-3})</td>
<td>milli</td>
<td>m</td>
</tr>
<tr>
<td>10(^{-6})</td>
<td>micro</td>
<td>µ</td>
</tr>
<tr>
<td>10(^{-9})</td>
<td>nano</td>
<td>n</td>
</tr>
<tr>
<td>10(^{-12})</td>
<td>pico</td>
<td>p</td>
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Decimal multiples
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<tr>
<td>10(^3)</td>
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<tr>
<td>10(^6)</td>
<td>mega</td>
<td>M</td>
</tr>
<tr>
<td>10(^9)</td>
<td>giga</td>
<td>G</td>
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### Standard Reduction Potentials, $E^\circ$

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<th>Reaction</th>
<th>$E^\circ$ / V</th>
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<tbody>
<tr>
<td>$\text{Co}^{3+}(aq) + e^- \rightarrow \text{Co}^{2+}(aq)$</td>
<td>+1.82</td>
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<tr>
<td>$\text{Ce}^{4+}(aq) + e^- \rightarrow \text{Ce}^{3+}(aq)$</td>
<td>+1.72</td>
</tr>
<tr>
<td>$\text{Au}^{3+}(aq) + 3e^- \rightarrow \text{Au}(s)$</td>
<td>+1.50</td>
</tr>
<tr>
<td>$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-(aq)$</td>
<td>+1.36</td>
</tr>
<tr>
<td>$\text{O}_2 + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>+1.23</td>
</tr>
<tr>
<td>$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-(aq)$</td>
<td>+1.10</td>
</tr>
<tr>
<td>$\text{MnO}_2(s) + 4\text{H}^+(aq) + e^- \rightarrow 2\text{Mn}^{3+} + 2\text{H}_2\text{O}$</td>
<td>+0.96</td>
</tr>
<tr>
<td>$\text{Pd}^{2+}(aq) + 2e^- \rightarrow \text{Pd}(s)$</td>
<td>+0.92</td>
</tr>
<tr>
<td>$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$</td>
<td>+0.80</td>
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<tr>
<td>$\text{Fe}^{3+}(aq) + e^- \rightarrow \text{Fe}^{2+}(aq)$</td>
<td>+0.77</td>
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<tr>
<td>$\text{Cu}^+(aq) + e^- \rightarrow \text{Cu}(s)$</td>
<td>+0.53</td>
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<tr>
<td>$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$</td>
<td>+0.34</td>
</tr>
<tr>
<td>$\text{Sn}^{4+}(aq) + 2e^- \rightarrow \text{Sn}^{2+}(aq)$</td>
<td>+0.15</td>
</tr>
<tr>
<td>$2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$</td>
<td>0 (by definition)</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}(aq) + 3e^- \rightarrow \text{Fe}(s)$</td>
<td>−0.04</td>
</tr>
<tr>
<td>$\text{Pb}^{2+}(aq) + 2e^- \rightarrow \text{Pb}(s)$</td>
<td>−0.13</td>
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<tr>
<td>$\text{Sn}^{2+}(aq) + 2e^- \rightarrow \text{Sn}(s)$</td>
<td>−0.14</td>
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<tr>
<td>$\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$</td>
<td>−0.24</td>
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<td>$\text{Co}^{2+}(aq) + 2e^- \rightarrow \text{Co}(s)$</td>
<td>−0.28</td>
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<td>$\text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s)$</td>
<td>−0.44</td>
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<td>$\text{Cr}^{3+}(aq) + 3e^- \rightarrow \text{Cr}(s)$</td>
<td>−0.74</td>
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<td>$\text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s)$</td>
<td>−0.76</td>
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<tr>
<td>$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$</td>
<td>−0.83</td>
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<td>$\text{Cr}^{2+}(aq) + 2e^- \rightarrow \text{Cr}(s)$</td>
<td>−0.89</td>
</tr>
<tr>
<td>$\text{Al}^{3+}(aq) + 3e^- \rightarrow \text{Al}(s)$</td>
<td>−1.68</td>
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<tr>
<td>$\text{Mg}^{2+}(aq) + 2e^- \rightarrow \text{Mg}(s)$</td>
<td>−2.36</td>
</tr>
<tr>
<td>$\text{Na}^+(aq) + e^- \rightarrow \text{Na}(s)$</td>
<td>−2.71</td>
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<tr>
<td>$\text{Ca}^{2+}(aq) + 2e^- \rightarrow \text{Ca}(s)$</td>
<td>−2.87</td>
</tr>
<tr>
<td>$\text{Li}^+(aq) + e^- \rightarrow \text{Li}(s)$</td>
<td>−3.04</td>
</tr>
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### Useful formulas

#### Quantum Chemistry

- **E** = \( h \nu = hc/\lambda \)
- \( \lambda = h/mv \)
- 4.5\( k_B T = hc/\lambda \)
- \( E = Z^2 E_R (1/n^2) \)
- \( \Delta x \cdot \Delta (mv) \geq h/4\pi \)
- \( q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4 \)

#### Electrochemistry

- **\( \Delta G^\circ = -nFE^\circ \)**
- **Moles of e\(^-\) = It/F**
- \( E = E^\circ - (RT/nF) \times 2.303 \log Q \)
- \( E^\circ = (RT/nF) \times \ln K \)
- \( E = E^\circ - \frac{0.0592}{n} \log Q \) (at 25 °C)

#### Acids and Bases

- **pK\(_w\) = pH + pOH = 14.00**
- **pK\(_w\) = pK\(_a\) + pK\(_b\) = 14.00**
- **pH = pK\(_a\) + \log ([A\(^-\)] / [HA])**

#### Gas Laws

- **PV = nRT**
- \((P + n^2a/V^2)(V - nb) = nRT\)**

#### Colligative properties

- **\( \pi = cRT \)**
- **\( P_{solution} = X_{solvent} \times P^o_{solvent} \)**
- **p = kc**
- **\( \Delta T_f = K_f m \)**
- **\( \Delta T_b = K_b m \)**

#### Kinetics

- **t\(_{1/2}\) = ln2/k**
- **k = Ae^(E_a/RT)**
- **ln[A] = ln[A]\(_o\) - kt**
- **ln\( \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \)**

#### Radioactivity

- **t\(_{1/2}\) = ln2/\( \lambda \)**
- **A = \( \lambda N \)**
- **ln(\( N_0/N_t \)) = \( \lambda t \)**
- **14\(^C\) age = 8033 ln(\( A_0/A_t \))**

#### Polymers

- **\( R_g = \sqrt{\frac{nt_i^2}{6}} \)**

#### Mathematics

- If \( ax^2 + bx + c = 0 \), then \( x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \)
- **ln x = 2.303 log x**
## PERIODIC TABLE OF THE ELEMENTS

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<td><strong>H</strong></td>
<td><strong>He</strong></td>
<td><strong>Li</strong></td>
<td><strong>Be</strong></td>
<td><strong>B</strong></td>
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<td><strong>F</strong></td>
<td><strong>Ne</strong></td>
<td><strong>Na</strong></td>
<td><strong>Mg</strong></td>
<td><strong>Al</strong></td>
<td><strong>Si</strong></td>
<td><strong>P</strong></td>
<td><strong>S</strong></td>
<td><strong>Cl</strong></td>
<td><strong>Ar</strong></td>
</tr>
</tbody>
</table>

**November 2006**

**CHEM1612**

22/32(b)

**LANTHANIDES**

| **La** | **Ce** | **Pr** | **Nd** | **Pm** | **Sm** | **Eu** | **Gd** | ** Tb** | **Dy** | **Ho** | **Er** | ** Tm** | **Yb** | **Lu** |
|138.91 | 140.12 | 140.91 | 144.24 | [144.9] | 150.4 | 151.96 | 157.25 | 158.93 | 162.50 | 164.93 | 167.26 | 173.04 | 174.97 |

**ACTINIDES**

| **Ac** | **Th** | **Pa** | **U** | **Np** | **Pu** | **Am** | **Cm** | **Bk** | ** Cf** | **Es** | **Fm** | **Md** | **No** | **Lr** |
| 227.0 | 232.04 | [231.0] | 238.03 | [237.0] | [239.1] | [243.1] | [247.1] | [252.1] | [257.1] | [259.1] | [260.1] | | | |