Exams are closed book and notes, calculators are required. Obviously, no external communication devices are allowed. A periodic table will be provided.

The universal gas constant, R, is 8.31 J / K mol or 0.0821 L atm / K mol.

1. A CO$_2$(s) block with mass 19 g is placed in a 3.5 L cylinder containing 150 torr of Ar (g). The cylinder is at 30 °C. What is the total cylinder pressure when the CO$_2$ all sublimes?

\[
\begin{align*}
n(\text{CO}_2) &= 19/44 = 0.43 \text{ mol} \\
P(\text{CO}_2) &= nRT / V = (0.43)(0.0821)(303) / 3.5 = 3.1 \text{ atm} \\
P(\text{total}) &= P(\text{CO}_2) + P(\text{Ar}) = 3.1 \text{ atm} + (150 / 760) \text{ atm} = 3.3 \text{ atm}
\end{align*}
\]

2. What are the relative effusion rates of Cl$_2$ (g) and Kr (g) at 400 K?

Effusion rates are inv prop to square root of molecular or atomic masses, thus:

\[
\text{Rate Cl}_2 / \text{ rate Kr} = (\text{at mass Kr} / \text{mol mass Cl}_2)^{0.5} = (84 / 71)^{0.5} = 1.1
\]

3. List the properties of an ideal gas according to the kinetic molecular theory.

Particles (1) occupy negligible volume, (2) in constant straight-line motion, with (3) elastic collisions with container and other particles (i.e. no interparticle forces) and (4) avg KE is proportional to Kelvin temp.

4. Nitric oxide gas (NO) reacts with chlorine gas according to the equation:

\[
\text{NO (g)} + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NOCl (g)}
\]

The following initial rates of reaction have been measured at 300 K for the following initial conditions:

<table>
<thead>
<tr>
<th>Expt. #</th>
<th>Rate (M/hr)</th>
<th>NO (M)</th>
<th>Cl$_2$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.19</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>4.79</td>
<td>1.00</td>
<td>0.50</td>
</tr>
<tr>
<td>3</td>
<td>9.59</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

What is the rate law and the rate constant for this reaction at 300 K?

\[
\text{Rate} = k [\text{NO}]^2[\text{Cl}_2] \\
k = 9.5 \text{ hr}^{-1} \text{ M}^{-2}
\]

5. Experiments show that the rate of disappearance of cyclopropane according to:

\[
\text{cyclopropane} \rightarrow \text{propene}
\]

is first order with a rate constant of 6.2 x 10$^{-4}$ min$^{-1}$ at 700 K. What is the half-life for this reaction?
t_{1/2} = 0.693 / k = 0.693 / 6.2E-4 \text{ min}^{-1} = 1100 \text{ min}

6. For the overall reaction: \( 2 \text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2 \), a proposed mechanism is:

\[
\begin{align*}
\text{NO}_2 + \text{NO}_2 & \quad \Leftrightarrow \quad \text{N}_2\text{O}_4 \quad \text{(fast)} \\
\text{N}_2\text{O}_4 + \text{O}_3 & \quad \rightarrow \quad \text{N}_2\text{O}_5 + \text{O}_2 \quad \text{(slow)}
\end{align*}
\]

If correct, what rate law (in terms of reactants) will be observed?

\[
\text{Rate} = k_2 [\text{N}_2\text{O}_4][\text{O}_3]
\]

But \( k_1 [\text{NO}_2]^2 = k_{-1} [\text{N}_2\text{O}_4] \)

\[
[\text{N}_2\text{O}_4] = \left( \frac{k_1}{k_{-1}} \right) [\text{NO}_2]^2
\]

Plug this into first line to get:

\[
\text{Rate} = (k_2 \frac{k_1}{k_{-1}}) [\text{NO}_2]^2 [\text{O}_3]
\]

7. The equilibrium constant, \( K_c = 5.0 \) for the reaction at 1000 °C:

\[
\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})
\]

If 2.0 moles of \( \text{SO}_2 \) and 1.0 moles of \( \text{NO}_2 \) are placed in a 1.0 L container, what concentration of \( \text{SO}_3 \) will be present at equilibrium at 1000 °C?

<table>
<thead>
<tr>
<th>Compound</th>
<th>Initial conc</th>
<th>change</th>
<th>equilibrium conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_2 )</td>
<td>2.0</td>
<td>- x</td>
<td>2.0 - x</td>
</tr>
<tr>
<td>( \text{NO}_2 )</td>
<td>1.0</td>
<td>- x</td>
<td>1.0 - x</td>
</tr>
<tr>
<td>( \text{SO}_3 )</td>
<td>0</td>
<td>+ x</td>
<td>x</td>
</tr>
<tr>
<td>( \text{NO} )</td>
<td>0</td>
<td>+ x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_c = 5.0 = [\text{SO}_3][\text{NO}] / ([\text{SO}_2][\text{NO}_2]) = x^2 / [(2.0 - x)(1.0 - x)]
\]

Rearranging \( 5.0(x^2 - 3.0x + 2.0) = x^2 \)

\[
4.0x^2 - 15x + 10 = 0
\]

From quadratic, \( x = 2.9 \) or 0.9 but 2.9 is impossible

\[
[\text{SO}_3]_{\text{equ}} = x = 0.9
\]

8. Give an example of a technologically significant reaction that requires a catalyst, indicate both the reaction and catalyst used.

any of the following (there are many other possibilities, too)

- Haber process: \( \text{N}_2 + 3\text{H}_2 = 2\text{NH}_3 \) catalyst is based on Fe(m)
- NO\text{\textsubscript{2}} reduction: \( 2\text{NO}_2 \rightarrow \text{N}_2 + \text{O}_2 \) catalyst is Pt/Rh
- CO oxidation: \( \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \) (same catalyst)
- Polymerization of ethylene: \( n\text{C}_2\text{H}_4 \rightarrow (\text{C}_2\text{H}_4)_n \) catalyst is Pt, Pd, or Ni
9. Explain briefly the changes (increase or decrease) in pressure and temperature that will result in an increase in the mole fraction of NOBr present in the following equilibrium:

\[ 2 \text{NOBr} (g) \rightleftharpoons 2 \text{NO} (g) + \text{Br}_2 (g) \quad (\Delta H_{\text{rxn}} = +30 \text{ kJ/mol}) \]

Since the equilibrium has 2.5 moles of gas on the right side, and only 2 moles on the left side, increased pressure will shift the equilibrium to the left and increase the NOBr mole fraction.

The reaction is endothermic, and absorbs heat going to the right, so decreased temperature will shift the equilibrium to the left (the exothermic direction) and thus increase the mole fraction of NOBr at equilibrium.

10. Copper (II) ion complexes with water and hydroxide ion as shown below.

\[
[\text{Cu(H}_2\text{O)}_4]^{2+} \text{(aq)} + 2 \text{OH}^- \text{(aq)} \rightleftharpoons [\text{Cu(H}_2\text{O)}_2(\text{OH})_2] \text{(s)} + 2 \text{H}_2\text{O} \text{(l)}
\]

Will the addition of nitric acid, $\text{HNO}_3$, result in an increase, decrease, or no change, in the amount of solid present. Explain.

Adding acid will decrease the concentration of the reactant $\text{OH}^-$, therefore driving the equilibrium to the left, and consuming some of the solid product. The amount of solid will therefore decrease.