$R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} = 0.082058 \text{ L atm mol}^{-1} \text{ K}^{-1} = 1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}; \quad 1 \text{ atm} = 1.0133 \times 10^5 \text{ Pa}$

I. (14) Elective Experiments. Do ONE and only one of the following three problems. You must choose one that matches one of your lab electives.

A. **BET Stuff.** In a setup like ours, the volume of the manifold is 64.3 mL, and the cell $V$ is 14.8 mL. The total active volume is the sum of these two, and the room is at 22° C.

1. The system is first evacuated, and the valve to the cell is shut, leaving it at $P \sim 0$. The manifold is charged with N$_2$ to $P = 203$ torr. Then the valve to the cell is opened. What is the new $P$?

2. The cell and manifold are charged with N$_2$ to $P = 195$ torr. With the valve to the cell still open, the "fat" part of the cell is immersed in liquid N$_2$ at 77 K. The pressure drops to 141 torr. Calculate the effective volume (cold volume) that is at 77 K.

3. When you filled the manifold with N$_2$ to a pressure exceeding 800 Torr and then cooled the cell by immersing it in the liquid N$_2$ contained in your dewar, the pressure dropped and then leveled out at a value greater than 760 Torr. What does this tell us?

   1. $P = 165$ Torr
   2. $V_{\text{cold}} = 10.7$ mL
   3. $P > 760$ Torr means that the temperature of the liquified N$_2$ in the cell is > the boiling point $T$. (In fact you were to have used this measurement to determine the $T$.) This can happen when O$_2$ condenses in the Dewar flask, giving a solution that boils above the BP for pure N$_2$. 
B. **Spectro-K.** I$_2$ forms 1:1 complexes with all aromatic substances in a manner similar to that studied for mesitylene. Let us suppose that for such an arene, $K_c = 7.7$ L/mol at 22°C.

1. 5.0 mL of 0.00087 M I$_2$ in heptane is mixed with 10 mL of 2.15 M arene in heptane in a 25.0-mL volumetric flask, and heptane is added to bring the volume to the mark. Calculate the concentrations of all three substances in the equilibrium mixture at 22°C.

2. I$_2$ in heptane has peak absorptivity of 925 L mol$^{-1}$ cm$^{-1}$ at 525 nm. Assuming that only I$_2$ absorbs at this wavelength, calculate the absorbance at 525 nm in a 2.0-cm cuvette of (a) the original I$_2$ stock solution, (b) the I$_2$ in the mix IF there were no reaction with arene, (c) the I$_2$ in the actual equilibrium mixture.

1. $[I_2]_0 = 1.74 \times 10^{-4}$ M, and $[A]_0 = 0.86$ M

Solving for the concentrations at equilibrium, we obtain

$[I_2\cdot A] = 1.512 \times 10^{-4}$ M, $[I_2] = 2.28 \times 10^{-4}$ M, $[A] \approx 0.86$ M

2. $A = \varepsilon c l$

(a) $A = 1.61$

(b) $A = 0.32$

(c) $A = 0.042$
C. Binary. The following data have been obtained for mixtures of water (A) and hydrogen peroxide (B) at 60°C:

<table>
<thead>
<tr>
<th>$x_{A,l}$</th>
<th>$x_{A,v}$</th>
<th>$P$(kPa)</th>
<th>$x_{A,l}$</th>
<th>$x_{A,v}$</th>
<th>$P$(kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.000</td>
<td>2.35</td>
<td>0.700</td>
<td>0.967</td>
<td>12.86</td>
</tr>
<tr>
<td>0.100</td>
<td>0.301</td>
<td>3.00</td>
<td>0.900</td>
<td>0.995</td>
<td>17.77</td>
</tr>
<tr>
<td>0.300</td>
<td>0.696</td>
<td>5.03</td>
<td>1.000</td>
<td>1.000</td>
<td>19.92</td>
</tr>
<tr>
<td>0.500</td>
<td>0.888</td>
<td>8.33</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. For the solution having mole fraction $x_{A,l} = 0.300$, calculate $P_A$, $P_B$, $P_{A,id}$, $P_{B,id}$, $\gamma_A$, and $\gamma_B$ (where "id" stands for ideal).

2. Calculate $a_A$ and $a_B$ for this same mixture.

3.Briefly describe how you determined the compositions of your samples when you did this experiment.

1. $P_A = 3.501$ kPa, $P_{A,id} = 5.976$ kPa, $\gamma_A = 0.586$

2. $P_B = 1.529$ kPa, $P_{B,id} = 1.645$ kPa, $\gamma_B = 0.930$

2. $a_A = 0.176$, $a_B = 0.651$

3. We measured the refractive index of each solution and compared it with a calibration curve of refractive index vs composition, obtained from a series of samples of known prepared composition.
Before beginning Part II, enter here the names of your lab partners and the number of peer points you wish to award to each. The total must not exceed 24, and the maximum to any one partner is 20. If you leave this space blank, your points will be distributed 12:12.

II. (14) Core Experiments.

A. (5) This figure shows the time dependence of T and P in the Triple Point experiment. Tell which curve (I & II) is which, and identify (by letter) points where (1) solid, liquid, and vapor are present simultaneously in equilibrium; (2) solid (only) is in equilibrium with vapor; (3) liquid (only) is in equilibrium with vapor; and (4) supercooled water spontaneously froze.

I is T, II is P.
(1) D  (2) B
(3) F  (4) A

B. (5) The figure to the right represents optical rotation data for a hypothetical sugar we shall call picanose. From this figure, give approximate values for the following quantities: (1) $\alpha_0$, (2) $\alpha_{\infty}$, (3) the inversion time (in s), (4) the half-life of picanose, and (5) the effective rate constant $k_{\text{eff}}$.

(1) 0.9°
(2) $-1.45°$ (1.5° O.K.)
(3) ~100 s
(4) ~140 s
(5) $\sim0.005$ s$^{-1}$
C. (4) The resistance of a thermistor varies approximately exponentially with $T^{-1}$. [Hint: This is the same functional relationship you used to analyze vapor pressure data and estimate kinetics activation energies.] A particular thermistor shows a resistance of 11.27 kΩ at the ice point and 1.872 kΩ at 28.77°C. When immersed in a bath, its resistance is 8.93 kΩ. What is the apparent temperature of the bath?

$$276.567 \text{ K} = 3.42^\circ \text{C}$$

III. (8) Statistics and KaleidaGraph.

A. (4) You desire to fit some data to (1) a cubic polynomial in $x$ with a constant term (4 adjustable parameters), and (2) a declining exponential plus a background (3 parameters). Using $a$, $b$, $c$, and $d$ for the adjustable parameters, and $x$ for the independent variable, write EXACTLY what you might enter in the "Define Fit" box of the General fit routine to execute these fits.

1. $a + b*x + c*x^2 + d*x^3$; $a = 1$; $b = 1$; $c = 1$; $d = 1$ (etc.)
2. $a + b*\exp(-c*x)$; $a = ?$; $b = ?$; $c = ?$

B. (4) On fitting (unweighted) some thermistor calibration data, you obtain the results shown here.

1. If there are 22 data points, how many degrees of freedom are there in this fit?
   $$\nu = 22 - 3 = 19$$
2. If the precision for measuring $T$ is limited by this calibration fit, estimate $s_T$.
   $$s_T = \sqrt{\frac{\text{Chisq}}{\nu}} = 0.0051 \text{ K}$$

3. If this fit is redefined as a quadratic function of $x$ instead of $(x-25)$, which (if any) of the quantities shown in the results box will change and which will not?
   $c$ and its error, Chisq, and $R$ are unchanged; the others all change.