I. (30) Elective Experiments. Do only ONE of the following three problems; pick one that corresponds to your lab work. (Other choices will not be counted.)

A. Equilibrium and spectrophotometry. In experiments like those you performed in the lab in your study of the complexation reaction, I$_2$ + M $\leftrightarrow$ I$_2$•M, stock solutions of mesitylene (M) and I$_2$ having concentrations of 2.322 mol/L and 3.34×10$^{-4}$ M, respectively, are available. The absorbance is measured at 330 nm (the complex's peak) for two mixtures of these stock solutions: (1) 5.00 mL of M and 2.00 mL of I$_2$; and (2) 1.00 mL of M and 10.0 mL of I$_2$. The measured absorbances $A$ are 0.577 for (1) and 0.401 for (2), for cuvettes having a path length of 1.00 cm.

1. Assuming that volumes are additive, calculate the concentrations of the two reagents in each of these two mixtures prior to complexation. [These are the [M]$_0$ and [I$_2$]$_0$ values.]

2. Express the equilibrium constant $K$ in terms of the concentrations of all three reagents at equilibrium. Then re-express $K$ in terms of [I$_2$•M] (= $x$), [I$_2$]$_0$, and [M]$_0$. What useful simplification results from having [M]$_0$ $\gg$ [I$_2$]$_0$?

3. Give (derive if necessary) the linear relation we used to analyze the data. What important property about the absorption at 330 nm do we use to advantage in this derivation?

4. Use this relation and your two $A$ values to solve for $K$ and the molar absorptivity $\varepsilon_x$ of the complex at 330 nm.
B. Thermal Expansivity. [Hint: Precision is very important in all these calculations.]

1. The data given here concern a dilatometer like that you used in the lab. It has a capillary extension of diameter 0.900 mm. Neglect buoyancy corrections and the thermal expansivity of Pyrex glass in your calculations. [Show work clearly for full credit.]

The empty, dry dilatometer weighs 106.863 g. Filled with water at 20.0°C ($\rho = 0.998207$ g/mL) to the low mark on the capillary extension, it weighs 134.144 g. Later, containing a sample of an alcohol, the capillary reading is $h = 9.3$ mm at 22.3°C and rises to $h = 97.2$ mm at 25.6°C. Calculate $V_b$ for the dilatometer and estimate the thermal expansivity $\alpha$ for the alcohol over this $T$ range.

2. Assuming that the $h$ measurements just given are uncertain by 0.3 mm, and the $T$ measurements by 0.15°C, calculate the uncertainties in $\Delta h$, $\Delta T$, and $\alpha$. Then use the 10% rule to properly state $\alpha$ and its uncertainty.

3. The density of ethanol in the range 20-90°C can be represented as

$$\rho = 0.76302 \exp(bx + cx^2 + dx^3),$$

where $\rho$ is in g/mL and $x = t(°C) - 50°C$.

(a) What is $\rho$ at 50°C?

(b) Obtain an expression for $\alpha(t)$ for ethanol in this $T$ range.

(c) The coefficients $b$, $c$, and $d$, are $-0.00118$, $-2.262 \times 10^{-6}$, and $-1.3639 \times 10^{-8}$, respectively. Calculate $\rho$ and $\alpha$ at $t = 30.0°C$.

(d) If $\rho$ were reexpressed as a function of $z = t(°C) - 30°C$, would the just-calculated quantities change?
C. Physical Adsorption. 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. \([R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} = 0.082058 \text{ L atm mol}^{-1} \text{ K}^{-1}; 1 \text{ atm} = 1.0133 \times 10^5 \text{ Pa}; V_{\text{STP}} = 22414 \text{ cm}^3]\)

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 \( \text{N}_2 \) to \( P = 203 \text{ torr} \). Then the valve to the cell is opened. What is the new \( P \)?

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

3. The system is charged with \( \text{N}_2 \) to a pressure exceeding 800 Torr. When the cell is then cooled in liquid \( \text{N}_2 \), the pressure drops and levels out at 765 Torr. If the atmospheric \( P \) is 745 Torr, what does this result tell us?

4. A different cell (same \( V_{\text{cell}} \)) is charged with a sample of silica gel and carefully evacuated and degassed. Then the manifold is charged with \( \text{N}_2 \) to \( P = 465 \text{ torr} \). With the silica gel sample immersed in liquid \( \text{N}_2 \), the valve to the cell is opened, whereupon the \( \text{N}_2 \) pressure drops and settles at 36.5 torr. The "cold volume" of this cell has previously been determined to be 8.2 cm\(^3\). Calculate the amounts (in STP cm\(^3\)) of \( \text{N}_2 \) (a) at the outset, in the manifold; (b) remaining in the gas phase at equilibrium, and (c) adsorbed on the silica gel.

5. Adsorption data for the adsorbed amount \( v \) (STP cm\(^3\)) can be analyzed by fitting to two different relationships, one of which gives a straight-line presentation.

(a) The fitted quantity "\( y \)" is \( \propto v^n \) in both cases (different \( n \)). What are the values of \( n \)?

(b) Assuming the measured \( v \)s have constant uncertainty, how should the data in each of these two fits be weighted?

(c) If these data have proportional uncertainty (\( \sigma_v \propto v \)), how should the data be weighted in each case?
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 18. If you leave this space blank, your points will be distributed 12:12. (Members of teams of two receive 24 each.)

II. (21) Review.

A. (6) 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.

2.

B. (5) 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?

   2. Estimate the precision \( s_T \) of these \( T \) measurements.

   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 remain unchanged?

C. (10) J. Walker studies the temperature dependence of a certain first-order reaction and obtains \( k = 3.48(15) \times 10^{-4} \text{ s}^{-1} \) \( [\text{i.e.}, (3.48 \pm 0.15) \times 10^{-4} \text{ s}^{-1} ] \) at 21.0°C and \( 13.19(21) \times 10^{-4} \text{ s}^{-1} \) at 38.0°C. Calculate the activation energy \( E_a \) and its uncertainty for this reaction in kJ/mol, and report your answer with the correct number of significant figures. \( \left( R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}; \right. \) neglect uncertainties in \( T \).