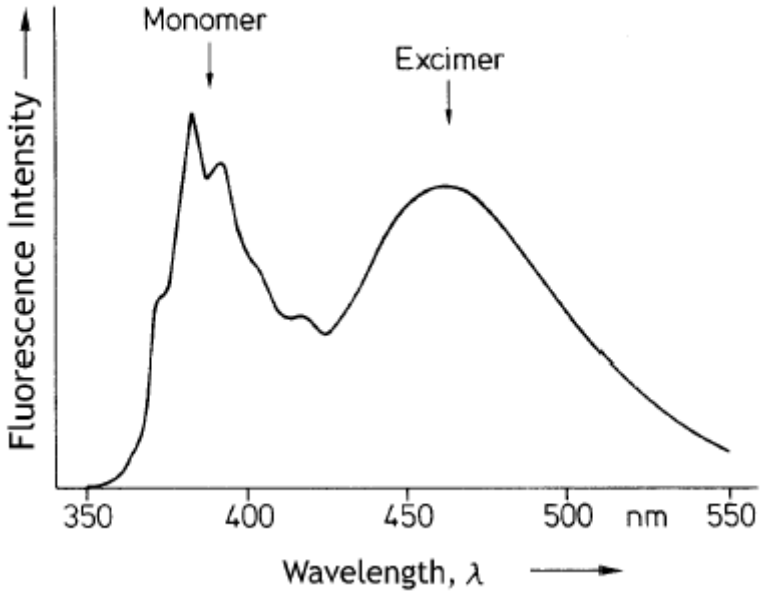
Physical Chemistry
Advanced laboratory course

Excimer formation

02-2010



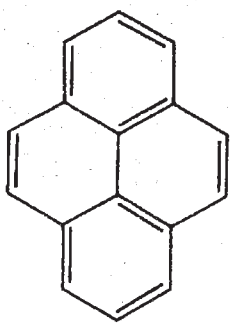
Experiment 36

The Enthalpy and Entropy of Excimer Formation

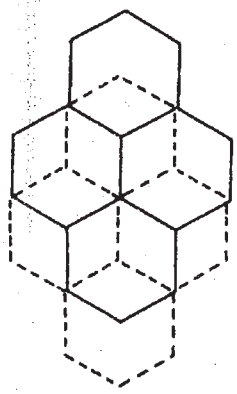
Objective To determine the enthalpy and entropy of formation of the dimer between ground state and electronically excited pyrene molecules in solution.

Introduction We know that the physical and chemical properties of a molecule are dictated by the nature of its electronic structure. It is not surprising, therefore, that such properties as acidity, dipole moment, and chemical reactivity may change considerably upon electronic excitation, in which there may be an abrupt change in the electronic wavefunction. In this experiment, you will investigate the pairwise interaction between pyrene molecules. The characteristics that we consider here relate to the *difference* in the properties of the interaction potential between two *ground state* molecules and also between a ground state and an electronically excited molecule.

Consider, then, the approach of two pyrene molecules along an axis perpendicular to their molecular planes. If both molecules are in the ground electronic state, there will be a very weak van der Waals attraction at moderate distances. At much closer approach, of course, significant intermolecular repulsion occurs. If, however, one of the molecules is in its *electronically excited* state (as a result of light absorption), and it is allowed to approach a ground state species with the appropriate orientation, a *stable dimer* will form. This dimer, whose structure is proposed to have a "sandwich" configuration (see below), is formed reversibly; that is, it can thermally dissociate back into an electronically *excited* pyrene molecule (excited monomer) and a ground state species.[1] This unusual dimeric species is stable *as long as it possesses electronic excitation* but dissociates as soon as this electronic excitation is dissipated and the system returns to the ground state. Such a species is called an *excimer* (from *exci*ted di*mer*).



Pyrene



Pyrene crystal dimer

A bound state that arises from the interaction between two dissimilar species when one is electronically excited is sometimes called an *exciplex* (excited complex) or heteroexcimer. Like

an excimer, an exciplex is dissociative in the electronic ground state. Because the excimer forms only when an electronically excited molecule and a ground state molecule come into specific and close contact with each other, excimer fluorescence is often used as a probe of molecular interactions. For example, pyrene-end-capped polymers are used to study the conformational structure and dynamics of linear chains. Excimer (or exciplex) emission is also used as a probe of the intercalation or binding of aromatic molecules into the crevices of certain macromolecules.

Figure 1 illustrates the potential energy diagram for electronic transitions and excimer formation. At large intermolecular separation (which occurs at low concentration), electronic transitions involving the excited monomer (absorption and fluorescence) are shown. The involvement of molecular vibrations in these transitions is also indicated. Although the monomer absorption and fluorescence spectra show vibrational structure (usually involving a skeletal mode), excimer emission is structureless. This is characteristic of electronic transitions (absorption or emission) between bound and unbound states.

The maximum in the excimer emission spectrum corrresponds to transitions between the minimum of the excimer potential well (which exists at the equilibrium separation between the excimer components) and the unbound, ground state dimer having the *same* intermolecular separation as the excimer. Hence, excimer formation involves the creation of a bound species subsequent to photon absorption. Conceptually, this is the reverse of photo*dissociation*, in which light absorption results in bond breakage. Moreover, photon emission in the excimer (fluorescence) brings about molecular dissociation, since the repulsive ground state pair rapidly dissociates.

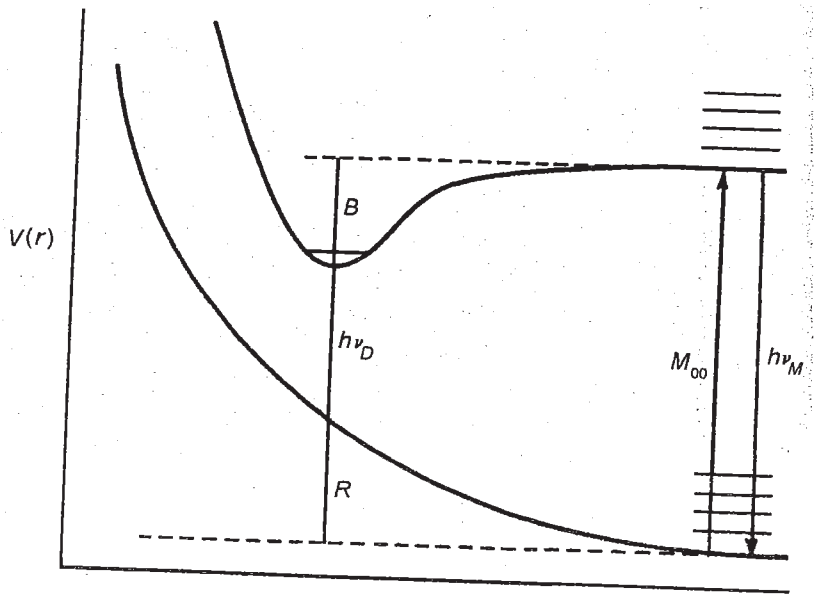


Figure 1. Potential energy of two pyrene molecules as a function of intermolecular separation. The coordinate r describes the approach of the molecules having the equilibrium orientation of the excimer. The right-hand transitions represent the isolated monomer (M).

The potential energy diagram in Figure 1 can also be used to compare the emission energies of monomer and excimer in terms of the excimer binding energy, B, and the ground state repulsion energy, R. Thus,

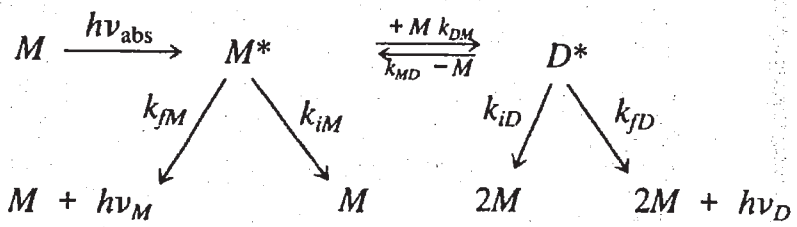
$$h\nu_M = h\nu_D + B + R\,, \tag{1}$$

where $h\nu_M$ represents the *monomer* fluorescence energy (called the 0-0 energy because the transition takes place between excited and ground state monomers possessing zero quanta of vibrational energy), and $h\nu_D$ is the energy of the *excimer* fluorescence maximum. The binding energy of the excimer is just the negative of its enthalpy of formation, i.e., $B = -\Delta H$ (the system is studied at constant pressure).

Kinetic Scheme

Excimer formation (called photoassociation) and reversible dissociation can be represented by the following set of elementary processes, or mechanism:

Process	Equation	Rate Constant
1. Electronic excitation	$M + h\nu_{abs} \rightarrow M^*$	(rate $= I_{abs}$)
2. Photoassociation	$M^* + M \rightarrow D^*$	k_{DM}
3. Excimer dissociation	$D^* \rightarrow M + M^*$	k_{MD}
4. Excited monomer decay	$M^* \rightarrow M + h\nu_M$	k_{fM}
	$M^* \rightarrow M + \cdots$	k_{iM}
5. Excimer decay	$D^* \rightarrow (M_2)' + h\nu_D$	k_{fD}
	$D^* \rightarrow 2M + \cdots$	k_{iD}



In the above scheme, I_{abs} is the number of moles of photons (einsteins) absorbed by ground state monomer per cubic decimeter per second. For convenience, k_M and k_D are defined as the total *intrinsic* (i.e., intramolecular) decay rate constants of monomer and excimer, respectively, *independent* of photoassociation or dissociation, i.e.,

$$k_M = k_{fM} + k_{iM} \quad \text{and} \quad k_D = k_{fD} + k_{iD}\,. \tag{2}$$

k_{DM} is the second-order rate constant for excimer formation from M and M^* (DM denotes "dimer from monomer"), and k_{MD} refers to the first-order rate constant for the dissociation of the excimer into M^* and M (MD denotes "monomer from dimer"). The formation rate of excited monomer (in mol dm^{-3} s^{-1}) is

$$\frac{d[M^*]}{dt} = I_{abs} - \left(k_M + k_{DM}[M]\right)[M^*] + k_{MD}[D^*] , \tag{3}$$

while that for the excimer is

$$\frac{d[D^*]}{dt} = k_{DM}[M][M^*] - \left(k_D + k_{MD}\right)[D^*] . \tag{4}$$

Note that $k_{DM}[M]$ is the pseudo-first-order rate of formation of excimer from excited and ground state monomers. Also, it is implied that $[M^*] << [M]$; i.e., a very small fraction of monomer is electronically excited. In experiments using conventional light sources (arc lamps, not focused lasers) this is indeed the case.

Under conditions of steady-state illumination, the rates in both equations (3) and (4) are equal to zero (photostationary conditions). The ratio of $[D^*]$ to $[M^*]$ can be thus obtained

$$\frac{[D^*]}{[M^*]} = \frac{k_{DM}[M]}{k_D + k_{MD}} . \tag{5}$$

It stands to reason that since the objective of this experiment is the determination of thermodynamic quantities, we must determine the temperature dependence of the excimer formation equilibrium constant. Therefore, the first thing we need to do is to obtain the *equilibrium concentrations* of M, M^*, and D^*. First, we will assume that the equilibrium ground state concentration $[M]$ is equal to the bulk pyrene concentration. This is consistent with the inequality $[M^*] << [M]$ discussed above. The second crucial, and fundamental, assumption is that the fluor (i.e., fluorescent species) concentration (i.e., $[M^*]$ or $[D^*]$) is proportional to its respective *fluorescence intensity*. This is a basic tenet of spectrofluorimetry and is perhaps analogous to Beer's law in absorption spectrophotometry.

This experiment is based on the fact that it is possible to obtain the ratio of excimer to excited monomer concentrations from the measured fluorescence intensities, each measured at the appropriate wavelength. Both of the fluor concentrations are assumed to be proportional to the respective *integrated fluorescence intensities* (areas under the monomer and excimer fluorescence spectra),

$$I_{fM} = k_{fM}[M^*] \quad \text{and} \quad I_{fD} = k_{FD}[D^*] , \tag{6}$$

where the proportionality constants are the *radiative rate constants*. The dimensions of I_f are einsteins $dm^{-3}\ s^{-1}$ (an einstein is 1 mol of photons). Combining equations (5) and (6), we have

$$\frac{I_{fD}}{I_{fM}} = \frac{k_{fD}k_{DM}[M]}{k_{fM}(k_D + k_{MD})} . \tag{7}$$

Equation (7) is central to the application of photostationary techniques to the study of photoassociation. (The distinction between the integrated and "instantaneous" fluorescence intensities will be discussed below.)

Because we seek thermodynamic data, we will examine the temperature dependence of equation (7). First, we make the general observation that both the formation and dissociation rate constants are temperature-dependent and can be expressed in Arrhenius form:

$$k_{DM} = A_{DM} \exp\left(\frac{-E_{DM}}{RT}\right) \quad \text{and} \quad k_{MD} = A_{MD} \exp\left(\frac{-E_{MD}}{RT}\right), \tag{8}$$

where the A's and E's are the preexponential factors and activation energies, respectively. Because intermolecular excimer formation is restricted only by molecular transport, or diffusion, the activation energy, E_{DM}, is related to the activation to viscous flow of the solvent medium. E_{MD}, however, reflects the intrinsic strength of the "excimer bond" as well as the energetics of molecular diffusion. This is because E_{MD} represents the activation energy for the *dissociation* of the bound excimer into *separated* and individually solvated excited and ground state constituents.

If we assume that the temperature dependence of k_{MD}, the rate constant for thermally activated excimer dissociation, is much larger than that for k_D, the intrinsic decay rate of excimer (indeed, for many systems, k_D is nearly temperature-independent), we have $k_{MD} \gg k_D$ in the limit of high temperature. Applying this result to equation (7), we have

$$\frac{I_{fD}}{I_{fM}} \simeq \frac{k_{fD} k_{DM} [M]}{k_{fM} k_{MD}} \qquad \text{(high temperature).} \tag{9}$$

If we furthermore make the general assumption (which has been confirmed by measurements of several monomer/excimer systems) that both radiative rate constants (k_{fM} and k_{fD}) are temperature-independent, an Arrhenius plot of I_{fD}/I_{fM} yields, in the limit of high temperature, a slope

$$\frac{d \ln\left(\frac{I_{fD}}{I_{fM}}\right)}{d\left(\frac{1}{T}\right)} = \frac{-\left(E_{DM} - E_{MD}\right)}{R} \qquad \text{(high temperature).} \tag{10}$$

See equations (7) and (8). Because $E_{MD} > E_{DM}$, the desired binding energy (the negative of the enthalpy of formation) of the excimer can be determined as the slope of such a plot.

At low temperatures, where excimer dissociation is slow compared with its intrinsic decay rate (i.e., $k_{MD} \ll k_D$), we can write equation (7) as

$$\frac{I_{fD}}{I_{fM}} \simeq \frac{k_{fD} k_{DM} [M]}{k_f M k_D} \qquad \text{(low temperature).} \tag{11}$$

An Arrhenius plot of the left-hand side of (7) will have a slope approaching

$$\frac{d \ln\left(\frac{I_{fD}}{I_{fM}}\right)}{d\left(\frac{1}{T}\right)} = \frac{-E_{DM}}{R} \qquad \text{(low temperature).} \tag{12}$$

E_{DM} has been found to be closely related to the activation energy associated with molecular diffusion (hence bulk viscous flow) in the solvent medium. This is one of the reasons that excimer formation is interpreted as a diffusion-controlled process.

An Arrhenius plot of equation (7) illustrates the behavior of the monomer and excimer fluorescence spectra over a wide temperature range (Figure 2). At low temperature, the ratio of excimer to monomer emission is small because excimer formation is impeded by the high viscosity of the solvent; indeed, in a glass or rigid medium, excimer formation does not take place because of the inability of excited monomer and ground state species to diffuse. (It is possible, however, that weak van der Waals dimers may be stable at low temperatures and that emission from these directly photoexcited dimers may be observed. Strictly speaking, this is not excimer emission.) At very high temperature, excimer emission is also suppressed because of the high dissociation rate of the excimer. Thus there is an intermediate temperature at which there is a maximum excimer emission intensity relative to the excited monomer. This temperature depends not only on the nature of the excimer system (its binding energy and entropy of formation) but also on the solvent characteristics such as its viscosity and activation to viscous flow.

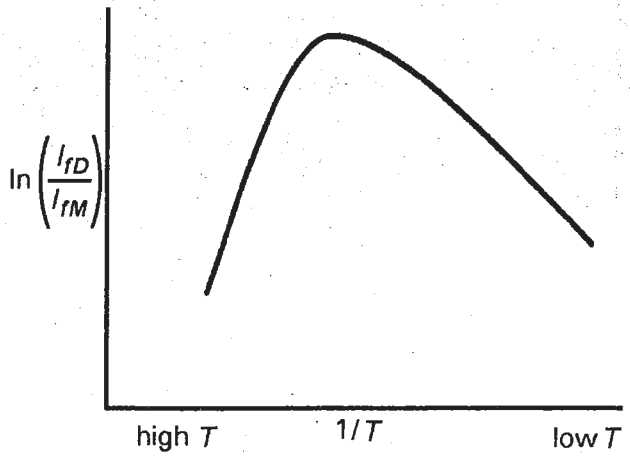


Figure 2. Arrhenius plot of the ratio of excimer to monomer fluorescence intensities. The low-temperature regime (right) reflects the activation energy of excimer formation, whereas the high-temperature regime (left) indicates the "equilibrium" enthalpy of excimer formation.

Another very important condition, which is pertinent to the high-temperature limit and is crucial to this experiment, concerns the fact that if interconversion between photoexcited monomer and excimer is rapid relative to the intrinsic decay rates of M^* and D^*, these species are in *dynamic equilibrium*. Thus with

$$k_{DM}[M] \gg k_M \qquad \text{and} \qquad k_{MD} \gg k_D ,$$

$K_{eq} = [D^*]_{eq}/[M^*]_{eq}[M]_{eq}$, we can express the true *equilibrium constant* (we assume unit activity coefficients) for photoassociation as the ratio of the formation and dissociation rate constants. Using this result and rearranging equation (9), we have

$$K_{eq} = \frac{k_{DM}}{k_{DM}} = \frac{k_{fM} I_{fD}}{k_{fD} I_{fM}[M]} . \tag{13}$$

The high-temperature or dynamic equilibrium regime can be depicted by an analogy to two leaky containers connected to each other by two tubes, each containing a pump. Refer to Figure 3. The containers are filled with a liquid. If the leak rate in container A is small compared with the rate of transport of liquid from container A to container B, *and*, likewise, the leak rate of container B is small relative to the flow rate from B to A, the amounts of liquid present in each container depend only on the $A \rightarrow B$ and $B \rightarrow A$ flow rates. This situation thus represents the dynamic equilibrium state; the volumes of liquid in A and B are intrinsic to the plumbing between them. On the other hand, if one of the leak rates is too large, the volume of liquid in that container will be depleted and will not reflect the "equilibrium" condition.

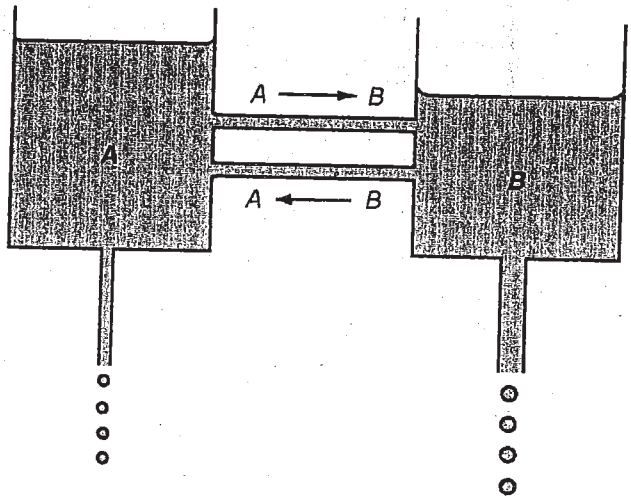


Figure 3. Hydrodynamic model of reversible reactions between two metastable (electronically excited) species.

The link between K_{eq} and the enthalpy and entropy of excimer formation is

$$-RT \ln K_{eq} = \Delta G^\circ - T\Delta S^\circ , \tag{14}$$

and if we combine the expressions in equations (13) and (14), we can represent the temperature dependence of I_{fD} and I_{fM} as

$$\ln\left(\frac{I_{fD}}{I_{fM}}\right) = -\ln\left(\frac{k_{fM}}{k_{fD}[M]}\right) + \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} . \tag{15}$$

Assuming that k_{fM} and k_{fD} are temperature-independent, a plot of $\ln (I_{fD}/I_{fM})$ vs. $1/T$ should be linear, having a slope equal to $-\Delta H^\circ/R$. The intercept can also provide a value of ΔS° if we know the ratio of the radiative rate constants of the excimer and monomer. While this information can be obtained from fluorescence lifetime and efficiency studies, Stevens and Ban have described a photostationary fluorimetric technique for obtaining ΔS° and ΔH°;[2] we will discuss this below.

There is another interesting consequence of high-temperature conditions. Although the *distribution* between D^* and M^* changes with temperature in this regime, the *total* concentration of excited states ($D^* + M^*$) remains constant. In other words, M^* and D^* form a "closed system." Hence,

$$[M^*]_T + [D^*]_T = \text{constant} = [M^*]_0 , \tag{16}$$

where the temperature dependence of the excited monomer and excimer concentrations is explicit. The spectrometric significance is that there is a specific wavelength between the maxima of the monomer and excimer emission spectra at which the emission intensity is independent of temperature. This position, called the *isostilbic* (equal brightness) *point*, is analogous to the isosbestic point (equal extinction) seen in absorption spectra when there is linear relationship between the concentrations of two absorbing species.

In order to proceed with the fluorimetric analysis, we must consider the important distinction between the total molecular fluorescence intensity, I_{fM} (area under the spectrum), and the fluorescence intensity at a specific wavelength, f_M. The latter is a function of energy or wavenumbers [$f_M(\tilde{\nu})$ represents the monomer emission spectrum], whereas the former is a constant at a given temperature and monomer concentration. This distinction is important, because in this experiment, we measure fluorescence intensities of the monomer and excimer emission spectra at *specific* wavelengths (e.g., the respective maxima) rather than the total areas under the spectra. The relationships between the total intensity and the instantaneous intensity are

$$I_{fM} = C\int f_M(\tilde{\nu})\,d\tilde{\nu} \qquad \text{and} \qquad I_{fD} = C'\int f_D(\tilde{\nu})\,d\tilde{\nu} . \tag{17}$$

C and C' are instrumental constants that link the integrals of instantaneous intensities with the molecular fluorescence strengths.

One problem with the analysis presented thus far is that we need the ratio of the excimer and monomer radiative rate constants, k_{fD}/k_{fM} [see equations (7), (9), and (11)]. Although this information can be obtained independently from fluorescence lifetime and (absolute) quantum efficiency measurements, Stevens and Ban have described an approach that gets around this problem. Observe in equation (15) that the value of k_{fD}/k_{fM} is needed only to determine the *entropy* of photoassociation (i.e., an absolute intercept).

Although the method for obtaining this information from fluorimetric measurements is straightforward, the development of the result is presented in the appendix. The approach is as follows.

Let R_D^o and R_M^o be the recorded intensities of excimer and monomer at their respective maxima. In the high-temperature regime, a plot of R_{M}^{o} vs. $R_{M_D}^{o}$ (for different temperatures) is expected to be linear with a negative slope ($-a/b$). Thus, as the temperature increases, the excimer intensity decreases with a concomitant increase in the monomer intensity. The relation used to obtain the entropy and enthalpy of excimer formation is

$$\ln\left(\frac{R_D^o}{R_M^o}\right) = \ln\left\{[M]\left(\frac{b}{a}\right)\right\} + \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} . \qquad (18)$$

Safety Precautions

- Safety glasses that block ultraviolet light must be worn during this experiment.
- Wear gloves when handling pyrene.
- Make sure you are instructed in proper pipetting techniques. Never pipet by mouth.
- If solid pyrene or its solutions come in contact with the skin, immediately wash the affected area with soap and water.
- A cylinder containing N_2 at high pressure is used. Be sure it is securely attached to a firm foundation. A reducing valve is used to deliver the N_2 at a pressure slightly above ambient (< 5 psig). Do not change this pressure.
- The fluorimeter may produce ozone. Make sure the ultraviolet source is vented. If you notice a sharp, pungent odor, inform your instructor immediately.
- The experiment must be performed in an open, well-ventilated laboratory.

Procedure

Prepare 25 mL of a 5.0×10^{-3} M solution of pyrene in methylcyclohexane. The pyrene should be of high purity (and should be sublimed or recrystallized before use if necessary). The solvent must have a negligible fluorescence background and preferably should be of spectrometric quality.

Add sufficient solution to a fluorescence cell that is equipped with a gas-tight, PTFE (Teflon) stopper. Deaerate by bubbling a fine stream of pure dry N_2 through the solution for 4 to 6 min. Control the gas flow so that solution is not expelled from the cell. [Deaerating with N_2 is *essential* because it displaces dissolved oxygen, which significantly quenches the pyrene fluorescence. This procedure is an application of Henry's law; the air above the liquid is replaced

Experimental

Make a $1*10^{-2}$ M solution of pyrene ($C_{16}H_{10}$, molecular weight M = 202.25 g/mol) in methylcyclohexane. From this solution, make three dilutions with c = $5*10^{-3}$, $2.5*10^{-3}$ and $1*10^{-3}$ M. 20 ml of each solution is a sufficient amount for the measurements.

Measure the emission spectra for these four solutions at room temperature with the Varian Cary Eclipse spectrofluorometer. Use an excitation wavelength of 370 nm and measure the emission spectrum at the 375-500 nm range. Use the following settings: Excitation slit ”5 nm”, Emission slit ”2,5 nm”, Scan control ”medium”, Excitation filter ”Auto”, Emission filter ”open”. Set the PMT Detector voltage at first to the ”medium” value, but if necessary, change the voltage setting to ”manual” and a smaller value, so that the fluorescence of the most concentrated sample stays withing the measurement scale. Also, set the intensity values visible in the spectra (label peaks ”Y labels”, threshold ”30.0”).

Do the temperature-dependent measurements for the $5*10^{-3}$ M solution. In fluorescence measurements the oxygen dissolved in the solution will cause problems by quenching the fluorescence. The amount of dissolved oxygen is also temperature dependent, so in temperature-dependent measurements it may cause a significant error. This is why the oxygen should be removed from the solution by bubbling nitrogen through the solution. Use the pasteur-pipette attached to the nitrogen hose in the fume cupboard. Detach the cuvette holder from the spectrometer and set the cuvette in it. Fill the cuvette with the $5*10^{-3}$ M pyrene solution and put the tip of the pipette on the bottom of the cuvette. Adjust the nitrogen flow rate with the needle valve. Bubble nitrogen through the solution for 5-7 minutes and then close the cuvette with a stopper with a small hole for the thermometer probe.

Put the thermometer probe into the solution through the hole in the stopper and put the cuvette into the spectrometer. Warm the solution to about 30 °C and let the temperature stabilize for about 5 minutes. Measure the emission spectrum as before. Write down the temperature during the measurement and save the spectrum. Repeat the measurement for temperatures of 40, 50, 60, 65, 70, 75, 80, 85, 90 and 95 °C. **Note**: The sample in cuvette does not warm up exactly to the value shown in the temperature controller, so

use as the set value for example 31, 41, 52, 62, 68, 73, 79, 84, 90, 95 and 99, and make your calculations using the real values shown by the thermometer. After measurements, set the temperature controller value back to about room temperature so that it won't start heating immediately when the next measurer turns it on.

For the report

Compare the fluorescence spectra of the solutions with different concentrations. Concentrate especially on the relative changes in the excimer and monomer contribution to the spectra. Describe how and why the concentration affects the excimer formation.

Plot the fluorescence spectra in different temperatures in the same graph. Observe how the spectra change as a function of temperature and explain the changes. Tabulate the monomer and excimer emission intensities ($R_M°$ and $R_D°$) at the maximum intensity wavelenghts in different temperatures. The wavelengths of the maximum intensity may change a little as a function of temperature, but use the same wavelength for all measurements. Plot a graph of $R_M°$ vs. $R_D°$ at temperatures between 60 and 85 °C. From the slope of this plot determine the constant –a/b to get the constant b/a for equation (18).

Determine the enthalpy and entropy of formation, $\Delta H°$ and $\Delta S°$ from equation (18) using an appropriate linear fit. In the equation, use the pyrene concentration and the constant b/a determined earlier, and the measurements at temperatures between 60 and 85 °C. Then determine the excimer binding energy B and the ground state repulsion energy R.

Estimate the errors for $\Delta H°$, $\Delta S°$, B and R and compare your results to the literature values:

$\Delta H° = -7.8$ kcal mol^{-1} (in cyclohexane)

$\Delta S° = -18.5$ cal mol^{-1} K^{-1} (in ethanol)

R = 7.9 kcal/mol (in ethanol)

Questions for discussion

1. In excimer lasers, the lasing is based on the emission of an excimer formed of a rare gas atom and a halogen atom. Why is it easy to make a laser this way? Hint: Think about the population of the lasing states.
2. Does the following statement make sense: The ground state of an excimer is an excited state.
3. The probability that the ends of a linear polymer molecule come into close proximity can be probed by attaching pyrene probes to the ends of the molecule. How does such a technique work?
4. For some excimers, the fluorescence emission can be observed also at low temperatures. However, the excimer emission nearly vanishes when the solvent becomes glassy or crystalline, why?

References:

The English instructions: Halpern A.M., *Experimental Physical Chemistry 2nd Edition*, 1997, Prentice-Hall, Inc

Literature values: Stevens and Ban, *Trans. Faraday. Soc.* 60:1515 (1964)