

# Spectrophotometric Study of Equilibrium

## A. Reaction



2. *Equilibrium*:  $K = \frac{[M \cdot I_2]}{[M][I_2]} \equiv \frac{x}{([M]_0 - x)([I_2]_0 - x)}$

3. *Conditions*:  $K \approx 1 \text{ M}^{-1}$ , so all species present at equilibrium.  
(Note that  $K[M] = [M \cdot I_2]/[I_2]$ , so  $I_2$  is 50:50 complexed when l.h.s. = 1.)

## B. Spectrophotometry

1.  $I/I_0 = 10^{-A} \equiv \text{transmittance}$ ;  $A$  (*absorbance*) =  $\epsilon c \ell$   
(molar absorptivity  $\times$  concentration  $\times$  path length)

2. *Additivity*:  $A = A_M + A_{I_2} + A_x + A_{\text{solv}}$

3. Choose  $\epsilon$  where only  $A_x$  significant:  $A \approx A_x = \epsilon_x x \ell$

4. *Analysis:* Use  $[M]_0 \gg [I_2]_0$ , so  $[M] \approx [M]_0$

$$\square \quad \frac{[I_2]_0^\ell}{A_x} = \frac{1}{\square_x K [M]_0} + \frac{1}{\square_x} \quad [y = bx + a, \text{ i.e.,}$$

straight line with intercept  $\square_x^{-1}$  and slope  $(\square_x K)^{-1}$ ; define fit parameters as  $\square_x$  and  $K$   $\square$  get uncertainties directly.]

### C. Thermodynamics

1.  $\square G^\circ = -RT \ln K^\circ$  [*conventional Gibbs energy change*]

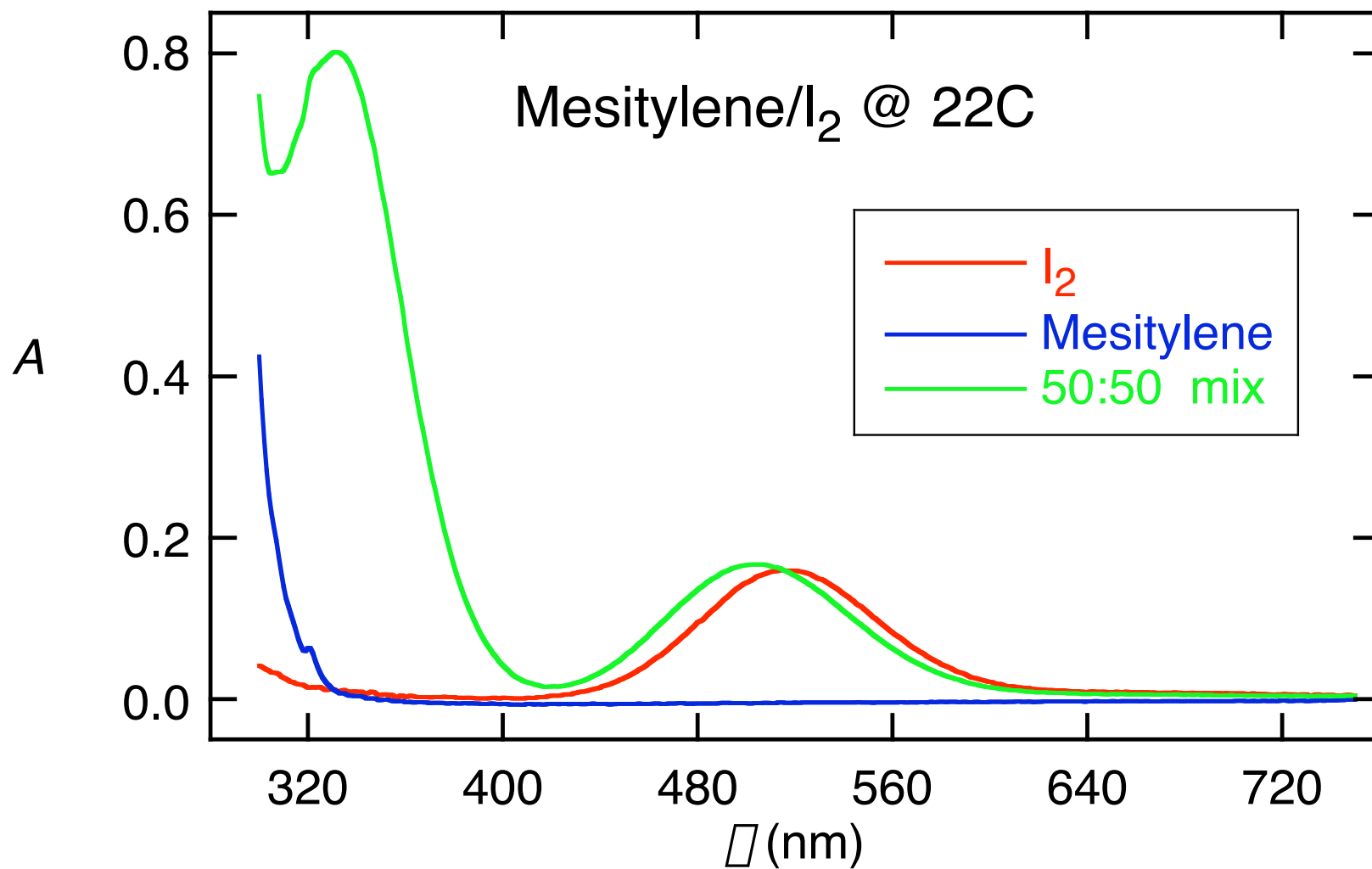
2. *van't Hoff:*  $\frac{\partial \ln K^\circ}{\partial (1/T)} = \frac{\square \square H^\circ}{R}$   $\square \quad \ln(K_2/K_1) = (\square H^\circ/R)(1/T_1 - 1/T_2)$

[NOTE: This is our **third** encounter with this relation.]

3.  $\square G^\circ = \square H^\circ - T \square S^\circ$  [The previous equation assumes that  $\square H^\circ$  and  $\square S^\circ$  are independent of  $T$ ; with that assumption this equation yields identical  $\square H^\circ$  (hence  $\square S^\circ$ ) from  $K$  at two  $T$ s.]

In all such thermodynamic applications,  $T$  is in K.

## D. Spectral Results

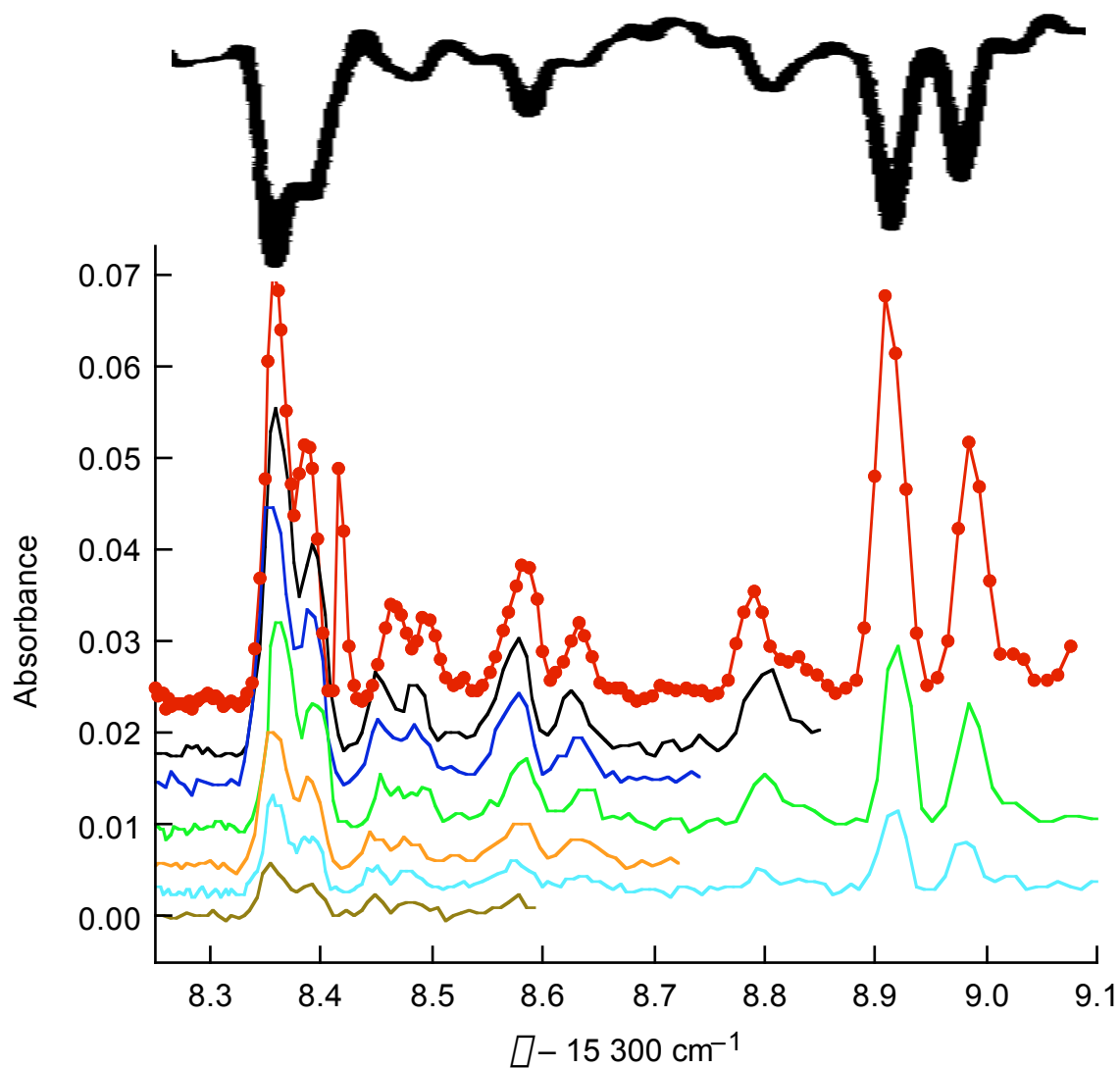


# Figures, Tables, and Captions

- A. In lab text (GNS) see pp. 12, 13; examples p. 150 (figure) and p. 515 (tables).
- B. Work to make captions to figures self-contained, complete descriptions of the figure contents.
- C. Likewise with tables. Here footnotes can also be used.

**NEVER** submit printouts of long data files collected by the computer: We will **NOT** be impressed! Instead, select samples (where relevant to make particular points) or just specify file names and information permitting us to look them up if we choose to do so.

**Figure 1.** Absorption spectra of  $I_2$  recorded using as source an RLP operating near 653 nm. The  $I_2$  cell (silica, 9.93 cm) was maintained at a temperature of  $60^\circ\text{C}$ , with the pressure controlled by a cooler side tube, giving  $I_2$  pressures from 1.5 Torr at top, decreasing to 0.17 Torr at bottom. The ordinate scale is quantitative, but with a zero offset. The actual recorded points are shown in the top spectrum, as logged at intervals of 0.2 s. The sharp peak near  $15\,308.4\text{ cm}^{-1}$  in this spectrum is spurious, attributed to a laser "burp." The spectrum at top is from the  $I_2$  atlas of Gerstenkorn and Luc.<sup>1</sup>



**Table 1** Standard errors for  $a$  and  $b$  in linear calibration model, for both constant data error and proportional error, as obtained by analysis with correct weighting (from  $V_{\text{prior}}$ ) and incorrect weighting (from  $V_{\text{act}}$  and  $V_{\text{post}}$ )

	Correct weighting From $V_{\text{prior}}$	Incorrect weighting	
		Actual ( $V_{\text{act}}$ ) <sup>a</sup>	Apparent ( $V_{\text{post}}$ ) <sup>a</sup>
Homoscedastic data, $\sigma = 1$ , evenly spaced model.			
$\sigma_a$	0.7237	0.9990 (9970)	0.0304
$\sigma_b$	0.1195	0.2527 (2517)	0.1394
Geometric spacing			
$\sigma_a$	0.5503	0.9002 (8991)	0.425
$\sigma_b$	0.1181	0.5382 (5361)	0.667
Heteroscedastic data, $\sigma = 0.02 y$ , evenly spaced model.			
$\sigma_a$	0.01999	0.4810 (4820)	0.867
$\sigma_b$	0.09157	0.1625 (1627)	0.1432
Geometric spacing			
$\sigma_a$	0.07603	0.3043 (3056)	0.363
$\sigma_b$	0.1194	0.1958 (1961)	0.0779

<sup>a</sup> Last column and quantities in parentheses under “actual” from MC computations for  $10^5$  data sets.

## Today's Practice Quiz !

A quantity  $z$  can be expressed as a ratio of two intermediate quantities,  $x$  and  $y$ . Suppose that  $x$  and  $y$  are in turn obtained from measured quantities  $t$ ,  $u$ , and  $v$ , according to  $x = t u^2/v$  and  $y = t u v$ . Further, say that  $t$ ,  $u$ , and  $v$  have percent uncertainties of 3.0%, 5.0%, and 2.0%, respectively.

1. Calculate the % uncertainty in  $x$ .  $[3.0^2 + 4(5.0)^2 + 2.0^2]^{1/2} \% = 10.6\%$
2. Calculate the % uncertainty in  $y$ .  $6.2\%$
3. Calculate the % uncertainty in  $z$ .

$$z = x/y = u/v^2 \quad \square \quad [5.0^2 + 4(2.0)^2]^{1/2} \% = 6.4\%$$

4. The density of steel is about  $7.85 \text{ g/cm}^3$ . Calculate the density and its uncertainty for a spherical steel ball of mass  $10.000(5) \text{ g}$  and radius  $0.6725(15) \text{ cm}$ . ( $V = \frac{4}{3} \pi r^3$ .) Report your answer with the correct number of significant figures.

$$\text{Rel Err} = ? \quad [(0.005/10)^2 + 9 (0.0015/0.6725)^2]^{1/2} = 0.00671$$

$$\square \quad 7.85(5) \text{ g cm}^{-3}.$$

Some data follow the relationship  $y = a/x^2 + bx^2$ .

5. How would you define  $Y$  and  $X$  so that you could fit these data to a straight line,  $Y = a + bX$ ?

$$Y_i = x_i^2 y_i; \quad X_i = x_i^4.$$

6. If you do such a fit, how should you weight the  $Y$  values, if  $\sigma_y = \text{constant}$ ?

$$s_{Y_i}^2 = x_i^4 \quad \square \quad w_{Y_i} = x_i^{-4}$$