Solutions Manual

BIOPHYSICAL CHEMISTRY: Principles, Techniques and Applications

Alan G. Marshall
University of British Columbia

Solutions Manual

BIOPHYSICAL CHEMISTRY: Principles, Techniques and Applications

Alan G. Marshall
University of British Columbia

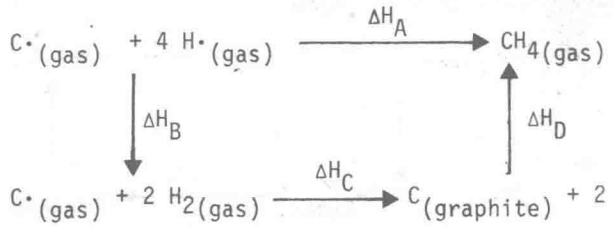
John Wiley & Sons, Inc.
New York · Chichester · Brisbane · Toronto

ISBN 0 471 03674 9
Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

CHAPTER 1

1.

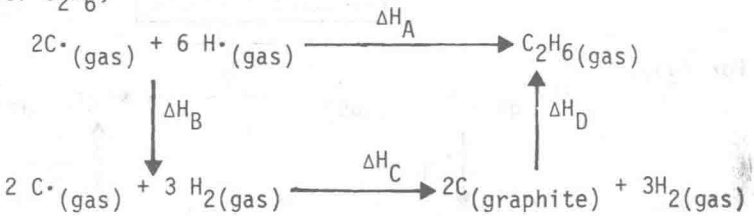


Average C-H bond enthalpy $\equiv \frac{1}{4}(\Delta H_A) = \frac{1}{4}(\Delta H_B + \Delta H_C + \Delta H_D)$

$= \frac{1}{4}(2(-104{,}200) - 171{,}700 - 17{,}865)$ cal/mole

$= \boxed{-99{,}491 \text{ cal/mole}}$

Similarly for C_2H_6,



Thus, $\Delta H_A = \Delta H_B + \Delta H_C + \Delta H_D$

$= 3(-104{,}200) + 2(-171{,}700) + (-20{,}190)$

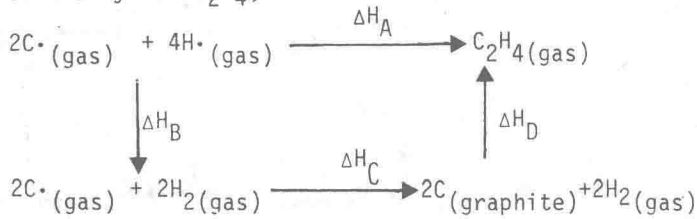
$= -676{,}190$ cal/mole

= 6 C-H bond enthalpy + 1 C-C single bond enthalpy

Therefore, 1 C-C bond enthalpy = $-676{,}190 - 6(-99{,}491)$

$= \boxed{-79{,}244 \text{ cal/mole}}$

1., continued. Similarly for C_2H_4,

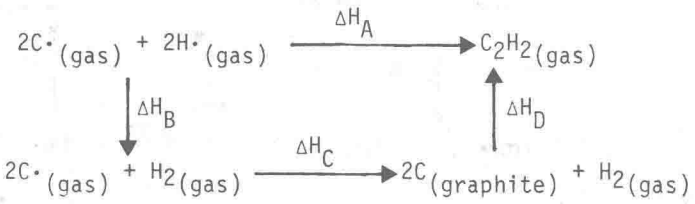


$$\Delta H_A = \Delta H_B + \Delta H_C + \Delta H_D$$
$$= 2(-104,200) + 2(-171,700) + 12,555$$
$$= -539,245 \text{ cal/mole} = 4 \text{ C-H bond enthalpy} + 1 \text{ C=C bond enthalpy}$$

Thus, 1 C=C bond enthalpy = -539,245 -4(-99,491)

$$= \boxed{-141,281 \text{ cal/mole}}$$

For C_2H_2,



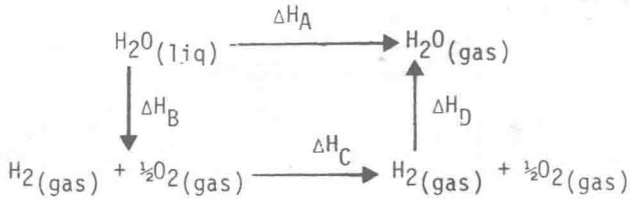
$$\Delta H_A = \Delta H_B + \Delta H_C + \Delta H_D$$
$$= -104,200 + 2(-171,700) + 54,230$$
$$= -393,370 \text{ cal/mole} = 2 \text{ C-H bond enthalpy} + 1 \text{ C}\equiv\text{C bond enthalpy}$$

Thus, 1 C≡C bond enthalpy = -393,270 -2(-99,491)

$$= \boxed{-194,388 \text{ cal/mole}}$$

Note that carbon-carbon bond strengths (from bond enthalpy) follow the order, C≡C > C=C > C-C, but the double bond is less than twice as strong as a single bond, and the C≡C bond is less than 1.5 times as strong as the C=C bond. In other words, multiple-bond strengths are not additive. This is because the double and single bonds are derived from different-shaped "orbitals" (see Chapter 18).

2.



$$\Delta H_A = \Delta H_B + \Delta H_C + \Delta H_D$$
$$= 68{,}320 + 0 - 57{,}800 = 10{,}520 \text{ cal/mole of } H_2O$$
$$= \frac{10{,}520 \text{ cal/mole}}{18 \text{ gram/mole}} = \boxed{584 \text{ cal/gram of } H_2O}$$

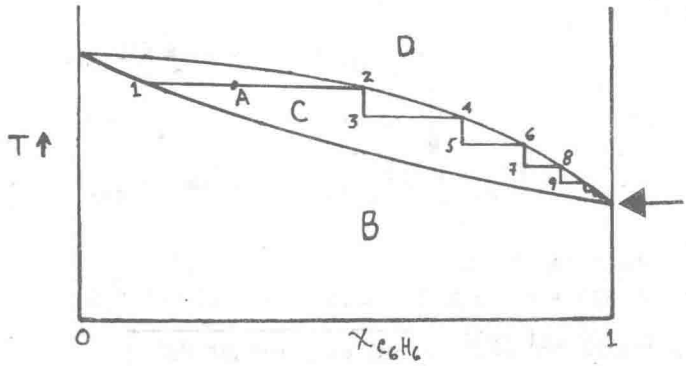
Now, if 1 calorie heats 1 gram of H_2O by 1 K,
then 2.5 kcal will heat 70 kg of H_2O by $\frac{2{,}500{,}000}{70{,}000} = 35.7$ K ,
or to a body temperature of 37 + 35.7 = $\boxed{72.7^oC \simeq 163^oF\ !}$

If evaporation of 1 gram of $H_2O_{(liq)}$ requires 584 cal (see above), then the amount of $H_2O_{(liq)}$ which would be vaporized to dissipate 2.5 kcal would be $\frac{2{,}500{,}000}{584} = 4{,}280$ gram

$= 4.28$ kg H_2O .

Obviously, there must be other means than sweating to get rid of the heat: principally radiation from the skin and convection of heat from warming of inspired air in the lungs.

1.



(a) Number of components = c = 2.

Region B: p = 1 (liquid); f = c-p+2 = 3 = T,P, and $x_{C_6H_6}$
Region C: p = 2 (liq and vap); f = c-p+2 = 2 = P, T or $x_{C_6H_6}$
Region D: p = 1 (vapor); f = c-p+2 = 3 = T,P, and $x_{C_6H_6}$

For f = 3, can fix pressure and still vary temperature and composition without changing the number of phases.
For f = 2, can fix pressure and vary either temperature or composition, but not both independently.

(b) At point A, vapor is benzene-rich (2) and liquid is benzene-poor (1). Collect vapor at this temperature (2); then cool vapor to (3). Again discard benzene-poor liquid and keep benzene-rich vapor (4). Continue along path, 4→5→6→7→8→9→etc., and the vapor will continue to become richer in benzene until it approaches pure benzene (arrow at right of diagram).

(c) Same procedure in this case will produce the limiting composition labeled as "azeotrope" for the limiting liquid, or pure acetone for the limiting vapor composition (depending on whether liquid or vapor is collected at each step).

---

2. (a)
$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

$$= \frac{\frac{2.5\times10^{-3}}{20{,}000}\,20{,}000 + \frac{1.5\times10^{-3}}{50{,}000}\,50{,}000 + \frac{1\times10^{-3}}{100{,}000}\,100{,}000}{\frac{2.5\times10^{-3}}{20{,}000} + \frac{1.5\times10^{-3}}{50{,}000} + \frac{1.0\times10^{-3}}{100{,}000}}$$

M_n = 30,303 = Number-average molec wt from osmotic press.

2. (b) $$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

$$= \frac{\frac{2.5\times10^{-3}}{20,000}(20,000)^2 + \frac{1.5\times10^{-3}}{50,000}(50,000)^2 + \frac{1\times10^{-3}}{100,000}(100,000)^2}{\frac{2.5\times10^{-3}}{20,000}\,20,000 + \frac{1.5\times10^{-3}}{50,000}50,000 + \frac{1.0\times10^{-3}}{100,000}\,100,000}$$

M_w = 45,000 = Weight-average molec wt from diffusion expts.

2. (c) $$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2}$$

$$= \frac{2.5\times10^{-3}}{20,000}(20,000)^3 + \frac{1.5\times10^{-3}}{50,000}(50,000)^3 + \frac{1\times10^{-3}}{100,000}(100,000)^3$$

M_z = 65,556 = z-average molec wt from sedimentation equilibrium.

Note that $M_z > M_w > M_n$.

---

3. (a) $$m = \frac{\Pi}{RT} = \frac{7.7 \text{ atm}}{(0.08206 \text{ l atm mol}^{-1} \text{ K}^{-1})(273.16 + 40)\text{K}}$$

$$= 0.300 \text{ moles/liter}$$

(b) $$\frac{\Pi_1}{\Pi_2} = \frac{mRT_1}{mRT_2} \quad ; \qquad \Pi_2 = \Pi_1 \frac{T_2}{T_1}$$

$$= 7.7 \frac{(273.16 + 4)}{(273.16 + 40)}$$

$$\Pi_2 = 6.81 \text{ atm at } 4^{\circ}\text{C}$$

---

4. First, expand the (given) van der Waals equation:

$$(P + \frac{a}{V^2})(V - b) = RT \quad ,$$

$$PV + \frac{a}{V} - bP - \frac{ab}{V^2} = RT$$

This term is smaller than the others, since it is the product of two small numbers, a and b, divided by the square of a large number, V.

Thus, $PV \simeq bP - \frac{a}{V} + RT$

but since this is a correction term, we may approximate $P \simeq (RT/V)$ in this term,

to give, $PV = \frac{bRT}{V} - \frac{a}{V} + RT$.

Now, to switch to the osmotic pressure case, we need only identify

$P \rightarrow \pi$, where π is osmotic pressure

and $V \rightarrow (M/c)$, where M is solute molecular weight and c is grams solute per liter solvent

to give, $\frac{\pi M}{c} = \frac{bcRT}{M} - \frac{ac}{M} + RT$; Multiply through by (1/MRT):

$$\frac{\pi}{cRT} = \frac{c}{M^2}(b - \frac{a}{RT}) \qquad \text{Q.E.D.}$$

Equivalently, we may rearrange to obtain,

$$\frac{\pi}{c} = \frac{RT}{M^2}(b - \frac{a}{RT})c + \frac{RT}{M} \quad , \text{ which is clearly of the form,}$$

$$y = m \cdot x + b \quad .$$

Therefore, a plot of (π/c) versus c (Figure 2-11) should give a straight line of positive or negative slope (depending on whether the "size" term, $(bcRT/M^2)$, is bigger or smaller than the "aggregation" term, $-(ac/M^2)$), and the plot approaches ideal behavior (zero slope, $\pi = (cRT/M)$) as $c \rightarrow 0$. Finally, since rod-shaped macromolecules have larger effective size than a sphere of the same molecular weight (see Chapter 7.C.2.), the plot for fibrous (elongated) proteins will have more positive slope than for globular (spherical) proteins.

5.(a) $$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{\frac{40}{100{,}000}\,100{,}000 + \frac{0.04}{100}\,100}{\frac{40}{100{,}000} + \frac{0.04}{100}}$$

M_n = 50,050 = Number-average molecular weight.

(b) Note that M_n is almost 50% less than the molecular weight of the (polymer) component that comprises 99.9% by weight of the mixture! Obviously, it is important to exclude even trace amounts of low molecular weight impurities in determination of (average) molecular weights of macromolecules in solution. Finally, this calculation shows why Donnan effects on osmotic pressure can be important, since even small amounts of salt added to the macromolecular compartment can markedly decrease M_n.

6.(a) Since we must move a positive ion across the membrane for each negative ion (in order to preserve electrical neutrality), we begin by considering each possible salt, and then set $\bar{G}_{salt}(\text{left}) = \bar{G}_{salt}(\text{right})$.

For NaCl, we have already shown that $\dfrac{(Na^+)_L}{(Na^+)_R} = \dfrac{(Cl^-)_R}{(Cl^-)_L}$.

Similarly for KCl, $\dfrac{(K^+)_L}{(K^+)_R} = \dfrac{(Cl^-)_R}{(Cl^-)_L}$.

And for $NaNO_3$, $\dfrac{(Na^+)_L}{(Na^+)_R} = \dfrac{(NO_3^-)_R}{(NO_3^-)_L}$.

Combining these results, we obtain,

$$\frac{(Na^+)_L}{(Na^+)_R} = \frac{(K^+)_L}{(K^+)_R} = \frac{(Cl^-)_R}{(Cl^-)_L} = \frac{(NO_3^-)_R}{(NO_3^-)_L}$$

Extension to any other possible monovalent ions should be obvious.

6.(b). For $(La^{+3})_2(SO_4^{-2})_3$, begin as before from

$$\overline{G}_{La_2(SO_4)_3}(\text{left}) = \overline{G}_{La_2(SO_4)_3}(\text{right})$$

But $(La_2(SO_4)_3)_{aq} = 2La^{+3} + 3(SO_4^{-2})$, so the above eq'n becomes $2\overline{G}_{La^{+3}}(L) + 3\overline{G}_{(SO_4^{-2})}(L) = 2\overline{G}_{La^{+3}}(R) + 3\overline{G}_{(SO_4^{-2})}(R)$.

Then since $\overline{G} = \overline{G}^\circ + RT\ \ln(m)$ for dilute solutes, we have

$$2\overline{G}^\circ_{La^{+3}} + 2RT\ \ln(m_{La^{+3}})_L + 3\overline{G}^\circ_{SO_4^{-2}} + 3RT\ \ln(m_{SO_4^{-2}})_L$$
$$= 2\overline{G}^\circ_{La^{+3}} + 2RT\ \ln(m_{La^{+3}})_R + 3\overline{G}^\circ_{SO_4^{-2}} + 3RT\ \ln(m_{SO_4^{-2}})_R ,$$

or, $$\ln(m_{La^{+3}})_L^2 + \ln(m_{SO_4^{-2}})_L^3 = \ln(m_{La^{+3}})_R^2 + \ln(m_{SO_4^{-2}})_R^3 \quad ;$$

$$\ln[(m_{La^{+3}})_L^2(m_{SO_4^{-2}})_L^3] = \ln[(m_{La^{+3}})_R^2(m_{SO_4^{-2}})_R^3] \quad ;$$

$$(m_{La^{+3}})_L^2(m_{SO_4^{-2}})_L^3 = (m_{La^{+3}})_R^2(m_{SO_4^{-2}})_R^3 \quad .$$

Extension to the general M_rX_s case should now be obvious.

7.(a) We know that at equilibrium,

$$\frac{[Mg^{++}]_L}{[Mg^{++}]_R} = \frac{[Cl^-]_R^2}{[Cl^-]_L^2} \quad .$$

Therefore, since $[Cl^-]_R = 0$ initially, some $MgCl_2$ must move from left to right to achieve equilibrium.

Since the two compartments have the same volume, we need not carry the volume through the calculation and may simply consider

$x \equiv$ the increase in $[Mg^{++}]$ on the right

$=$ the decrease in $[Mg^{++}]$ on the left, so that

$2x =$ the increase (decrease) in $[Cl^-]$ on the right (left).

With these definitions, the equilibrium Donnan condition becomes,

7.(a) $$\frac{[Mg^{++}]^{\circ}_L - x}{[Mg^{++}]^{\circ}_R + x} = \frac{([Cl^-]^{\circ}_R + 2x)^2}{([Cl^-]^{\circ}_L - 2x)^2}$$ Substituting,

$$\frac{0.003 - x}{0.001 + x} = \left(\frac{2x}{0.006 - 2x}\right)^2$$. Clearing fractions,

$8x^3 - 0.032x^2 + 1.08\times10^{-4}x - 1.08\times10^{-7} = 0$. Solving by trial and error (it should take about 4 tries to reach 3-place accuracy), one quickly finds that

$x = 1.37\times10^{-3}$ moles/liter, so that at equilibrium,

$[Mg^{++}]_L = 0.00163$ M, $[Cl^-]_L = 0.00326$ M
$[Mg^{++}]_R = 0.00237$ M, $[Cl^-]_R = 0.00274$ M

7.(b) For a neutral protein (0.002M) with no salt present, the osmotic pressure at 25°C, measured against distilled water, is

$$\pi = m_{protein}RT$$
$$= (0.002)(0.08205 \text{ l atm mol}^{-1}\,^{\circ}\text{-}^{1})(298^{\circ}K)$$
$$= 0.04890 \text{ atm.}$$

For the charged protein of part 7.(a), the concentration of salt in the protein compartment = 0.00237 + 0.00274 M, and in the other compartment = 0.00163 + 0.00326 M.

There is thus an additional salt concentration on the right-hand (protein) compartment of 0.00511 - 0.00489 M, or 0.00022M salt. Thus, the osmotic pressure of the protein solution, measured against the solution on the other side of the membrane, will be larger by (0.00022)(0.08205)(298) = 0.0054 atm than would be the case for the same concentration of a neutral protein.

7.(c) Finally, since the apparent number of protein molecules for the charged-protein case is 0.002+0.00022 = 0.00222M rather than the assumed 0.002 M for a neutral protein, the calculated (from osmotic pressure) protein molecular weight will be too small by a factor of

$$\frac{0.002}{0.00222} = 0.901,$$ or about 10% too small.

This example illustrates how the charge of a protein can have unexpectedly large effects on its properties: in this case osmotic pressure, and in future cases electrophoresis, sedimentation, chromatography, and the like.

8. This is just like the ordinary equilibrium dialysis described in the text, except that $[I^-]_{in} \neq [I^-]_{out}$ because of the Donnan condition. One might proceed as follows:
   (a) Determine $[I^-]_{outside}$ by radioactive counting.
   (b) Measure $pH = -\log[H^+]$ inside and outside to obtain $[H^+]_{inside}$ and $[H^+]_{outside}$.
   (c) Now use the Donnan condition,

$$\frac{[H^+]_{out}}{[H^+]_{in}} = \frac{[I^-]_{in}}{[I^-]_{out}}$$

   to obtain $[I^-]_{in}$ from the other three (known) concentrations.

   (d) Obtain $[I]_{total,inside}$ from radioactivity counts; then use

$$[I]_{in,total} = [I^-]_{in} + [Albumin{:}I]$$

(known; known; calculate)

   (e) Then use (for example) optical absorbance to determine the total albumin concentration inside the bag, and

$$[Albumin]_{in,total} = [Albumin]_{in,free} + [Albumin{:}I]_{in}$$

(known; calculate; known)

   (f) Finally, one can now construct the binding constant from the above calculated concentrations of each species:

$$K_{binding} = \frac{[Albumin{:}I]_{inside}}{[Albumin]_{in,free} \cdot [I^-]_{in}}$$

1. We are given that, $n_A \, d\ln(a_A) + n_B \, d\ln(a_B) = 0$.

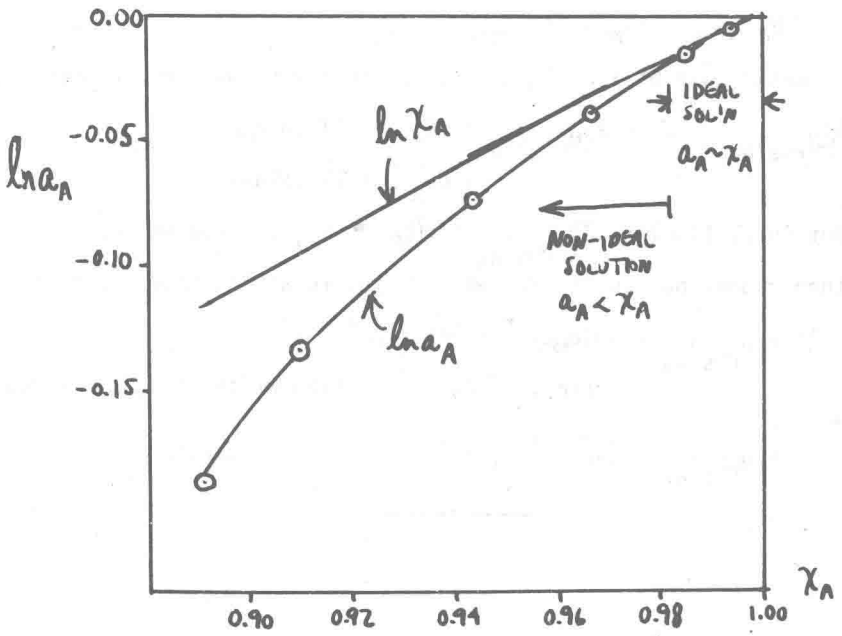
Thus, in particular, $n_A \dfrac{d\ln(a_A)}{dx_A} + n_B \dfrac{d\ln(a_B)}{dx_A} = 0$, or

$$\frac{n_A}{n_B} \frac{d\ln(a_A)}{dx_A} = - \frac{d\ln(a_B)}{dx_B} .$$

But $x_A = 1 - x_B$, so that $dx_A = -dx_B$,

and $\dfrac{n_A}{n_B} \underbrace{\dfrac{d\ln(a_A)}{dx_A}} = \dfrac{d\ln(a_B)}{dx_B}$.

slope of a plot of $\ln(a_A)$ versus x_A (see graph below):



1. (cont.). Procedure is as follows. First, plot $\ln(a_A)$ versus x_A (see above graph from Table 3-1), and calculate the slope at each tabulated x_A-value. Then multiply by (n_A/n_B) to obtain $(n_A/n_B)(d\ln(a_A)/dx_A)$ which gives $(d\ln(a_B)/dx_B)$.

[Note: $x_A = \dfrac{n_A}{n_A + n_B}$, or equivalently, $\dfrac{1}{x_A} = 1 + \dfrac{n_B}{n_a}$;

Rearranging gives, $\dfrac{n_A}{n_B} = \dfrac{x_A}{1 - x_A}$, where x_A is known.]

At this stage, we know $(d\ln(a_B)/dx_B)$ as a function of x_B. Now we simply use a digital computer to integrate $d\ln(a_B)/dx_B$ numerically from $x_B = 0$ to the x_B-value of interest. This then gives a table of $\ln(a_B)$ as a function of x_B, from which we can easily take antilogarithms to obtain a_B at any tabulated x_B.

This procedure shows why digital computers are so useful and necessary, even for problems that can be stated in a relatively simple way.

---

2. $\overline{G}_{(M_rX_s)_{aq}} = r\overline{G}_{M+s} + s\overline{G}_{X-r}$.

But $\overline{G} = \overline{G}^\circ + RT\ln(a)$, so the first equation becomes,

$$\overline{G}^\circ_{(M_rX_s)_{aq}} + RT\ln a_{(M_rX_s)_{aq}} = r\overline{G}^\circ_{M+s} + RT\ln(a_{M+s})^r + s\overline{G}^\circ_{X-r} + RT\ln(a_{X-r})^s .$$

But in particular, $\overline{G}^\circ_{(M_rX_s)_{aq}} = r\overline{G}^\circ_{M+s} + s\overline{G}^\circ_{X-r}$, and we may then cancel out an RT from each of the remaining terms to give,

$$\ln a_{(M_rX_s)_{aq}} = \ln(a_{M+s})^r + \ln(a_{X-r})^s$$
$$= \ln[(a_{M+s})^r(a_{X-r})^s] \text{ , from which it is clear that}$$

$$a_{(M_rX_s)_{aq}} = (a_{M+s})^r(a_{X-r})^s \qquad \text{Q.E.D.}$$

---

3. We have $E + I \rightleftarrows EI$ for each of n sites per macromolec.

with $K_I = \dfrac{[E][I]}{[EI]}$ as the dissociation equilibrium constant for each site.

As before, $\dfrac{[I]}{[I] + K_I}$ = fraction of each site occupied, so that

[i] $\nu = \dfrac{n[I]}{K_I + [I]}$ = number of bound ligands per macromolec.

(a). Clearly a DIRECT PLOT of ν versus [I] is still a hyperbola, with a limiting height of

$$\lim_{[I]\to\infty} \nu = \lim_{[I]\to\infty} \frac{n[I]}{K_I + [I]} = \frac{n[I]}{[I]} = n \ .$$

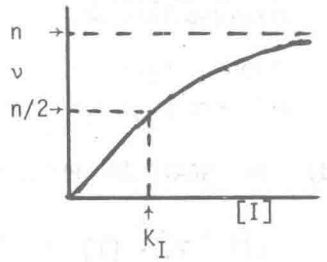
When half the sites per macromolecule are occupied,

$$\nu = \frac{n}{2} = \frac{n[I]}{K_I + [I]} \quad ; \text{ Cross-multiplying,}$$

$$K_I/2 + [I]/2 = [I] \ ,$$

$$K_I/2 = [I]/2 \ ,$$

$$\boxed{K_I = [I] \text{ at } \nu = n/2}$$



(b). For the TITRATION PLOT, begin by solving Eq. [i] for K_I:

$$\nu K_I + \nu[I] = n[I]$$

$$K_I = [I](n-\nu)/\nu \quad ; \quad \text{Take } \log_{10} \text{ of both sides:}$$

$$\log K_I = \log[I] + \log\left(\frac{n-\nu}{\nu}\right) \quad ; \quad \text{Rearranging,}$$

$$-\log[I] = -\log K_I + \log\left(\frac{n-\nu}{\nu}\right) \ , \text{ or,}$$

$$\boxed{pI = pK_I + \log\left(\frac{n-\nu}{\nu}\right)} \ , \text{ where } pI \equiv -\log[I] \text{ and } pK_I \equiv -\log K_I .$$

(b). (cont.) Finally, when $\nu = n/2$,

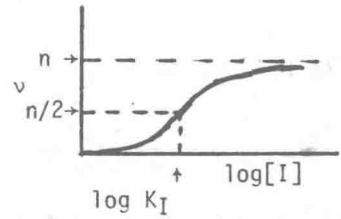
$$\log\left(\frac{n-\nu}{\nu}\right) = \log\left(\frac{n/2}{n/2}\right) = \log(1) = 0, \text{ so that}$$

$pI = pK_I$

for $\nu = n/2$

(midpoint of titration),

and $\lim_{\log[I]\to\infty} \nu = n$.



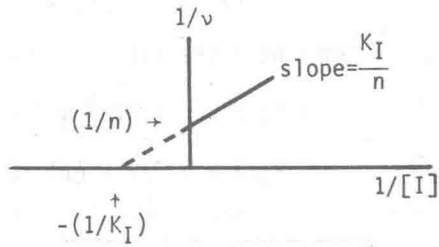
(c). For RECIPROCAL PLOT, begin by taking the reciprocal of both sides of Eq. [i] above:

$$\frac{1}{\nu} = \frac{K_I}{n}\,\frac{1}{[I]} + \frac{1}{n} \quad .$$

Clearly, a plot of $(1/\nu)$ versus $(1/[I])$ will give a straight line of

Slope = K_I/n ,

y-intercept = $1/n$.



(d). For SCATCHARD PLOT, begin by dividing Eq. [i] by [I]:

$$\frac{\nu}{[I]} = \frac{n}{K_I + [I]} \quad .$$ Now substitute again for ν in

$$\frac{n}{K_I} - \frac{\nu}{K_I} = \frac{n}{K_I} - \frac{n[I]}{K_I(K_I+[I]} = \frac{nK_I + n[I] - n[I]}{K_I(K_I + [I]} \quad , \text{ or}$$

$$\frac{n}{K_I} - \frac{\nu}{K_I} = \frac{n}{K_I + [I]} = \frac{\nu}{K_I}$$

from the first equation in part (d).

Thus, a plot of $\nu/[I]$ versus ν will be a straight line of slope = $-(1/K_I)$ and y-intercept = n/K_I, and x-intercept at $\nu = n$.