No Analytical Crib

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No Biochemistry Crib

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Answers

INORGANIC CHEMISTRY

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(a) Derive rate expression if Cr(IV) is a steady-state species:

\[
\frac{d[Cr(IV)]}{dt} = k_1 [Cr(IV)][Fe(phen)_2^{2+}] - k_{-1} [Cr(IV)][Fe(phen)_3^{3+}]
- k_2 [Cr(IV)][Fe(phen)_2^{2+}] = 0
\]

So

\[
[Cr(IV)] = \frac{k_1 [Cr(IV)][Fe(phen)_2^{2+}]}{k_{-1} [Fe(phen)_3^{3+}] + k_2 [Fe(phen)_3^{3+}]}
\]

\[
\frac{d[Fe(phen)_3^{3+}]}{dt} = 3k_2 [Cr(IV)][Fe(phen)_2^{2+}]
\]

\[
\frac{d[Fe(phen)_2^{2+}]}{dt} = \frac{3k_2 k_1 [Cr(IV)][Fe(phen)_2^{2+}]^2}{k_{-1} [Fe(phen)_3^{3+}] + k_2 [Fe(phen)_3^{3+}]}
\]

(b) The steady-state approximation means that the concentration of Cr(IV) is negligible during the reaction so that the approximation \(\frac{d[Cr(IV)]}{dt} = 0\) is valid.

Note that the [Cr(IV)] also is negligible because it's fast and it is rapidly consumed to Cr(III).

(c) The overall reaction is:

\[
Cr(III) + 3Fe(phen)_3^{2+} \rightarrow Cr(III) + 3Fe(phen)_3^{3+}
\]

Hence, the factor of 3 in the rate expression.
(40 µs) 2. (c) Reactions of $H_3O^+$ with acac.

\[
\text{Acac} + H_3O^+ \xrightarrow{k_1} \text{Acyl form} \quad \text{and form}
\]

\[
\text{Acyl form} \xrightarrow{k_2} \text{Lactone form}
\]

(1) Two possible products are the enol and lactone forms of acetylacetone as shown.
(2) The reaction to give the enol form is faster, because hydrogen bonding to the enolic oxygen from water and $H_3O^+$ provides an excellent path for proton transfer. The electron pairs on the oxygen can $H$-bond to water and to $H_3O^+$ to give a facile path for $H^+$ transfer.

\[
\text{Lactone form}
\]

(3) The lactone form is the more stable product with two hydrogen atoms bound to the middle carbon. The only reaction pathway from the enol to the lactone form is via the reverse of $k_2$ path followed by the $k_2$ path.
In the reaction

\[ \text{H}_2\text{O}^+ + \text{acac}^- + \text{H}_2\text{O} \rightarrow \text{acac}^- + \text{H}_2\text{O} + \text{H}_3\text{O}^+ \]

One \text{H}_2\text{O}^+ converts \text{acac}^- to the \text{H}_2\text{O} form, only three levels of \text{acac}^- are left (so it is a steady-state species) and

\[ \frac{d[\text{H}_2\text{O}]}{dt} = k_2 [\text{H}_3\text{O}^+][\text{acac}^-] \]

as it \[ [\text{acac}^-] \]

\[ \frac{d[\text{H}_2\text{O}]}{dt} = k_2 [\text{H}^+][\text{acac}^-], \quad [\text{acac}^-] \approx \frac{k_{-1} [\text{emol}]}{(k_{-1} + k_2) [\text{H}^+]} \]

\[ \frac{d[\text{H}_2\text{O}]}{dt} = k_2 [\text{H}^+][\text{acac}^-], \quad [\text{acac}^-] = \frac{k_2 k_{-1} [\text{emol}]}{k_{-1} + k_2} \]

2.b) In general-acid-assisted reactions, the stronger the acid the faster the proton-transfer reaction.

Expected correlation for acids HA with various Ka values is the Brønsted relationship

\[ k_{HA} = G\alpha K_a, \quad \text{or} \quad \log k_{HA} = \log G\alpha + \alpha \log K_a \]

Expected correlation

The greater the acidity the faster the proton transfer is.

\[ \log k_{HA} = \alpha \log K_a \]

negative log K_a more positive
Alkene (H₂C = CHR) hydrogenation with Wilkinson's catalyst, (Ph₃P)₃RhCl.

Overall reaction:

H₂C = CHR + H₂ → H₃C - CH₂R

(Ph₃P)₃RhCl is a square-planar complex, L = Ph₃P
S = solvent

L - Rh - L + S ⇄ L - Rh - L + L

↓ H₂
Oxidative addition

L - Rh - L + H₂C = CHR

↓ Solvent loss

L - Rh - L + S

Hydrogenation

↓ reds

Cl - Rh - L

+ S

Cl - Rh - L

↓ solvent addition

L - Rh - L + S

Cl - H

↓ Reductive elimination

w/ H⁻ migration

L - Rh - L + Cl₂CH₂R
No Organic Crib

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Written by Professor Chmielewski
Physical Cumulative Exam
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Solutions

a. Raoult’s Law says

\[ P_{B(c)} (80.1^\circ C) = P^0_{B(c)} (80.1^\circ C) x_B(c) \]  \hspace{1cm} (1)

where \( P_{B(c)} \) is the vapor pressure of \( B(c) \) is the vapor pressure above a \( B + C \) solution with mol fractions \( x_B \) and \( x_C \) and \( P^0_{B(c)} \) is the vapor pressure above pure liquid \( B(c) \) with \( x_B = 1 \)(\( x_C = 1 \)) at the same temperature.

Since benzene boils at 80.1°C and since camphor may be assumed to be nonvolatile at 80.1°C, it follows from Eq. (1) that

\[ P_B (80.1^\circ C) = 1 \text{ atm} \hspace{0.5cm} \text{and} \hspace{0.5cm} P^0_B (80.1^\circ C) = 0 \hspace{0.5cm} \text{atm} \]  \hspace{1cm} (2)

Also \( x_B + x_C = 1 \) or \( x_B = 1 - x_C = 1 - 0.27 = 0.73 \). Thus

\[ P_B (80.1^\circ C) = (1 \text{ atm})(0.73) = 0.73 \text{ atm} \]  \hspace{1cm} (3)

But the vapor pressure \( P = P_B + P_C \) or using Eqs. (2) and (3)

\[ P (80.1^\circ C) \text{ for solution} = 0.73 \text{ atm} \]  \hspace{1cm} (4)

b. For benzene-camphor solution

\[ C = 2, \ B \text{ and } C \]

\[ P = \beta \hspace{1cm} \text{lig.} \hspace{2cm} \text{vap} \hspace{2cm} \text{soln} \]

\[ \beta = \frac{C - P + \beta}{2 - 3 + 2} = 1 \]  \hspace{1cm} (5)

c.(i) Recall

\[ \mu_{\text{Bore, vectors}} = \left[ \frac{\partial G}{\partial n_{\text{Bore, vectors}}} \right]_{T, P} \]  \hspace{1cm} (6)

Also for equilibrium

\[ \partial G_{T, P} = 0 \]  \hspace{1cm} (7)
Combining Eqs. (6) and (7) gives
\[ \frac{dG}{\partial n_{v}} \frac{dn_{v}}{ \partial n_{v}} + \frac{dG}{\partial n_{e}} \frac{dn_{e}}{ \partial n_{e}} + \frac{dG}{\partial n_{s}} \frac{dn_{s}}{ \partial n_{s}} = 0, \]

Eq. (1.2) using the definitions of M's in Eq. (6) (8).

Also using Eq. (1.1) the forms of the M's may be simplified as follows:

\[ M_{v} = \left[ \frac{dG}{\partial n_{v}} \right]_{T,P} = \left[ \frac{dG_{v}}{\partial n_{v}} \right]_{T,P} \quad \text{and} \quad M_{e} = \left[ \frac{dG}{\partial n_{e}} \right]_{T,P} = \left[ \frac{dG_{e}}{\partial n_{e}} \right]_{T,P} \]  
(9a)

\[ M_{s} = \left[ \frac{dG}{\partial n_{s}} \right]_{T,P} = \left[ \frac{dG_{s}}{\partial n_{s}} \right]_{T,P} \quad \text{and} \quad M_{s} = \left[ \frac{dG}{\partial n_{s}} \right]_{T,P} = \left[ \frac{dG_{s}}{\partial n_{s}} \right]_{T,P} \]  
(9b)

and

\[ M_{e} = \left[ \frac{dG}{\partial n_{e}} \right]_{T,P} = \left[ \frac{dG_{e}}{\partial n_{e}} \right]_{T,P} \quad \text{and} \quad M_{s} = \left[ \frac{dG}{\partial n_{s}} \right]_{T,P} = \left[ \frac{dG_{s}}{\partial n_{s}} \right]_{T,P} \]  
(9c)

(9d) Since the total number of moles is given by

\[ n_{B} = n_{v} + n_{e} + n_{s} \]

is conserved during phase transitions during transitions \( dn_{B} = 0 \) or

\[ dn_{B} = dn_{v} + dn_{e} + dn_{s} = 0. \]  
(10a)

Similarly

\[ dn_{A} = dn_{v} + dn_{e} + dn_{s} = 0. \]  
(10b)

Eq. (10) are the same as Eq. (1.3) thus proving Eq. (2.3).

The left hand side of (ii) If the conditions of Eq. (1.4) are true then Eq. (2.3) may be written as
\[ M_B \left( d\eta_v + d\eta_e + d\eta_s \right) + M_C \left( d\eta_v + d\eta_e + d\eta_s \right) = 0 \]

where \( M_B = M_{\theta v} = M_{\theta e} = M_{\theta s} \) and \( M_C = M_{\nu v} + M_{\nu e} + M_{\nu s} \).

However, comparing Eq. (10) and (11) shows \( \eta = 0 \), proving that Eq. (11) is equivalent to the equilibrium condition of Eq. (1.2), thus showing that the condition of Eq. (1.4) is sufficient for three-phase equilibrium.

\[ \alpha \text{ (1) The general three phase (\nu, \ell, and s) condition for equilibrium for } C \text{ is from Eq. (1.4)} \]

\[ M_{\nu v} = M_{\nu e} = M_{\nu s}. \quad (10) \]

However, since \(\ell\) is non-volatile there is no equilibrium between \(\nu\) and \(\ell\) forms of \(C\). Thus Eq. (10) simplifies to the condition

\[ M_{\ell e} = M_{\ell s} \quad (10') \]

Next, note that since \(G_{\ell}\) is extensive from Eq. (1.1)

\[ G_{\ell} = G_{\ell} \left(T, P, \eta_{\ell e}, \eta_{\ell s} \right) = n G_{\ell} \left(T, P, x_{\theta e}, x_{\theta s} \right) \quad (13) \]

where \( n = \eta_{\ell e} + \eta_{\ell s} \) and \( x_{\theta e}(\eta) = \frac{\eta_{\theta e}(\eta)}{n} \) = mol fraction.

Thus, from the definition of \( M_{\ell e} \) in Eq. (1.4), since \( x_{\ell s} = 1 - x_{\ell e} \)

\[ M_{\ell e} = M_{\ell e} \left(T, P, x_{\theta e}, x_{\theta s} \right) \quad (14a) \]

Similarly

\[ M_{\ell s} = M_{\ell s} \left(T, P, x_{\theta s}, x_{\theta e} \right) = M_{\ell s} \left(T, P, x_{\theta s} \right) \quad (14b) \]
Thus Eqs. (12') and (14) give the equal equilibrium condition

\[ \mu_{c2}(T, P, X_{c2}) = \mu_{c2}^*(T, P) \]

where \( c \) in accord with the assumption that the \( c \) phase is pure \( c \), we have taken \( \mu_{c2}(T, P, X_{c2}) = \mu(T, P, X_{c2} = 1) = \mu_{c2}^*(T, P) \), the chemical potential of pure solid \( c \).

Solving Eq. (1-5) for \( X_{c2} \) allows the mole fraction in the \( c \) phase to be determined and eventually the solubility with a bit more information.

(i) Since \( B \) is not present in the solid, the general condition of equilibrium for \( B \)

\[ \mu_{B2} = \mu_{B2}^* = \mu_{B2}^* \]

simplifies to

\[ \mu_{B2}(T, P, X_{B2}) = \mu_{B2}^*(T, P, X_{B2}) \]

where we have followed steps similar to those leading from Eqs. (14) and (15). Also since the vapor is pure \( B \) we may write

\[ \mu_{B2}(T, P, X_{B2}) = \mu_{B2}(T, P, X_{B2} = 1) = \mu_{B2}^*(T, P) = \text{chemical potential of pure vapor } B. \]

Thus Eq. (1-6) reduces to the following equation

\[ \mu_{B2}(T, P, X_{B2}) = \mu_{B2}^*(T, P). \]

Assuming \( P \) and \( X_{B2} \) are specified, the above reduces to an equation for the boiling temperature \( T = T(X_{B2}, P) \). The boiling point elevation is

\[ \Delta T = T(X_{B2}, P) - T^*_B(P) \]

where \( T^*_B(P) \) is the boiling point for pure \( B \) at temperature \( T \).
Eqs. (4.5) involve the variables \( T, P, X_8, X_{8e}, X_{8g}, X_{8e}, X_{8g} \). However, the conditions provided by Eqs. (4.5) and also the additional conditions \( x_0 = 1 - x_8 \) for \( s, e, \) and \( v \) render only one of these variables independent. This is in accord with \( F = 1 \) from part b.