1B Review for Final — part 2

Answers Part 2

1. Rate = rate of slow step Rate = $k_2[C][D][A]$ but C and D are intermediates. Step 1 is eq. $Rate_f = k_1[A][B] = rate_r = k_{-1}[C][D][E]$

so $[C][D] = \frac{k_1[A][B]}{k_{-1}[E]}$

so $Rate = k_2\left(\frac{k_1}{k_{-1}}\frac{[A][B]}{[E]}\right)[A]$ $Rate = \frac{k_2 k_1}{k_{-1}}\frac{[A]^2[B]}{[E]}$ experimental rate constant $k = \frac{k_2 k_1}{k_{-1}}$

2. Rate = rate of slow step $Rate = k_1[A][B]^2$
3. 1st order ln [A] vs t
   2nd order 1/[A] vs t
   Zero [A] vs t
4. Like we did in lab 5. ① Determine rate law for rxn (by the method of initial rates) ② Do rxn at different temperatures, and determine k at each temp. ③ graph ln k vs 1/T Slope = $-E_a/R$ calc E_a.
5. ① Complex will form. Find $[Zn^{2+}]$, $[OH^-]$ after mixing $M_1V_1 = M_2V_2$

	Zn^{2+} +	$4\ OH^-$ →	$Zn(OH)_4^{2-}$
	0.0500 M	2.5 M	0
	−0.0500	−4(0.0500)	+0.0500 M
	0	2.3 M	0.0500 M

goes to completion $K_f = 2.8 \times 10^{15}$ huge

Then comes to equilibrium

	$Zn(OH)_4^{2-}$ ⇌	Zn^{2+} +	$4OH^-$
	0.0500 M	0	2.3 M
	−x	+x	+4x
	0.0500 − x	x	2.3 + 4x

$K_d = \frac{1}{K_f} = 3.\overline{57} \times 10^{-16}$ small neglect x's!

$$K_d = \frac{(x)(2.3+4x)^4}{(0.0500-x)} = \frac{x(2.3)^4}{0.0500}$$

neglect

$$x = \frac{K_d(0.0500)}{(2.3)^4} = 6.4 \times 10^{-19} M$$

6. At the halfway point, pH = pKa (of conj. acid) [Base] = [acid] (conjugates)

K_b of trimethylamine = 7.4×10^{-5} $pK_b = 4.13$ pK_a of CA. = 9.87

1/2 way pt 9.87

At the 3/4 point: $(CH_3)_3N + H_3O^+ \rightarrow (CH_3)_3NH^+ + H_2O$

1/4 original base left
3/4 is conj. acid

	$(CH_3)_3N$	H_3O^+	$(CH_3)_3NH^+$
	all	3/4	0
	−3/4	−3/4	+3/4
	1/4	0	3/4

6. $K_a = \frac{[H_3O^+][A^-]}{[HA]}$ buffer $[H_3O^+] = K_a\left(\frac{\text{mol HA}}{\text{mol } A^-}\right) = 1.35\times10^{-10}\left(\frac{3/4}{1/4}\right) = K_a(3)$

$[H_3O^+] = 4.05\times10^{-10}$ M pH = 9.39

7. $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$

a) N_2 added: shift → Rt [Reactants]↘, [Prod]↗

b) NH_3 added: shift ← Lf [R]↗, [P]↘

c) T↗ favors endothermic direction. Forward is endo. will shift → Rt [R]↘, [P↗]

d) V↘ so shifts toward less moles gas: forward [R]↘ [P]↗

e) no shift. Will just get to equilibrium faster.

8. $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$ 1.0 L flask so moles = M

a) $K_c = \frac{[NO_2]}{[NO][O_2]^{1/2}} = \frac{(1.4\times10^{-3})}{(6.5\times10^{-4})(0.25)^{1/2}} = 4.3$

b) Totals: 10.5×10^{-4} mol NO
0.35 mol O_2
2.4×10^{-3} mol NO_2

$Q = \frac{(2.4\times10^{-3})}{(10.5\times10^{-4})(0.35)^{1/2}} = 3.9$

Q < K. Rxn must go forward to reach eq. (Q must get larger)

9. Find initial M mol/L

Rxn must go reverse. Reverse Rxn has a large K_c, so goes to completion in the reverse first.

N_2	+ $3\,H_2$	⇌ $2\,NH_3$	$K_c = 1.5\times10^{-6}$ small
0	1.0 M	2.0 M	
+x	+3x	−2x	
		−2.0 M	
x	1.0+3x	0	2.0 − 2x = 0
1.0 M	4.0 M		so x = 1.0 M

Then it comes to equilibrium

N_2	+ $3H_2$	⇌ $2NH_3$
1.0	4.0	0
−x	−3x	+2x
1.0−x	4.0−3x	2x M

$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2x)^2}{(1.0)(4.0)^3} = 1.5\times10^{-6}$ $4x^2 = \frac{1.5\times10^{-6}(1.0)(4.0)^3}{4}$

K_c is small. Neglect x! x = 0.0049

$[NH_3] = 2x = 0.0098$ $[N_2] = 1.0$ M $[H_2] = 4.0$ M

10. $2NO_2 \rightleftharpoons N_2 + 2O_2$

① find K_c · find [ ]

$K_c = \frac{[N_2][O_2]^2}{[NO_2]^2} = \frac{(0.40M)(1.2M)^2}{(1.6)^2}$

$K_c = 0.225$

	$2NO_2$	$\rightleftharpoons$ N_2	$+ 2O_2$
i	1.6 M	0.40M	1.2 M
Δ	−2x	−A +x	+2x
eq	1.6−2x	0.40−A+x	1.2+2x
	1.4 M	0.50 − A	1.4 M

If N_2 is removed, eq will shift to Rt to repace some N_2

A = M N_2 removed

NO_2 at eq = 0.70 moles ÷ 0.50 L = 1.4 M so $1.6-2x = 1.4$

$-2x = -0.2$

$x = 0.10$ M

$K_c = \frac{(0.50-A)(1.4)^2}{(1.4)^2}$ $K_c = 0.50 - A$

$A = 0.50 - K_c = 0.50 - 0.225 = 0.275$ = M N_2 removed

$\left(0.275 \frac{mol}{L}\right)(0.50L) = 0.1375$ moles N_2 to be removed : 0.14 mol N_2

11. normal bp - bp at 1.00 atm pressure, $CCl_{4(l)} \rightleftharpoons CCl_{4(g)}$

Temp at which $P_{CCl_4} = 1.00$ atm $K = P_{CCl_4}$

Temp at which $K = 1$

$\Delta G^\circ = -RT\ln K$ if $K=1$, $\ln K = 0$, and $\Delta G^\circ = 0$

so it's also the temp at which $\Delta G^\circ = 0$.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ calc ΔH°, ΔS°

ΔH° = prod - react = gas - liquid = $(-106.7) - (-139.3) = +32.6$ kJ/mol

$\Delta S^\circ = (309.4 - 214.4) = +95.0$ J/K·mol $= 0.0950$ kJ/K·mol

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$0 = \Delta H^\circ - T\Delta S^\circ$ $\Delta H^\circ = T\Delta S^\circ$

$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{32.6 \text{ kJ/mol}}{0.0950 \text{ kJ/K·mol}} = 343$ K ⇒ 70.°C

12. vp at 50°C $CCl_{4(l)} \rightleftharpoons CCl_{4(g)}$ $K = P_{CCl_4}$

vp = P_{CCl_4} = K ! ① find ΔG° @ 50°C ② find K at 50°C

use ΔH°, ΔS° from above problem.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ = 32600 J/mol − (323K)(95.0 J/K·mol)

32600 − 30685

= 1915 J/mol

12 continued

$\Delta G^\circ = -RT\ln K$ $\quad \ln K = \frac{-\Delta G^\circ}{RT} = \frac{-1915\ J/mol}{(8.314\ J/K\,mol)(323\ K)} = -0.7131$

$K = e^{-0.7131} = 0.49$

vp = 0.49 atm at 50°C

13. $Ag_2S_{(s)} \rightleftharpoons 2Ag^+_{(aq)} + S^{2-}_{(aq)}$ $\quad K_{sp} = [Ag^+]^2[S^{2-}]$

① calc $\Delta H^\circ, \Delta S^\circ$ ② calc ΔG° @ 45°C ③ calc K_{sp} @ 45°C ④ calc solubility

$\Delta H^\circ = [2(105.9) + (41.8)] - [-31.8] = 285.4\ kJ/mol$

$\Delta S^\circ = [2(73.93) + (22)] - [146] = 23.86\ J/K\cdot mol$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = (285400\ J/mol) - (318\ K)(23.86\ J/K\cdot mol)$

$= 285400 - 7587.48 = 277812.52\ J/mol$

$\Delta G^\circ = -RT\ln K$

$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-277812.52\ J/mol}{(8.314\ J/K\,mol)(318\ K)} = -105.08$

$K = e^{-105.08} = 2.3\times10^{-46}$ (no sf)

$Ag_2S_{(s)}$	$\rightleftharpoons 2Ag^+$	$+ S^{2-}$
some	0	0
$-x$	$+2x$	$+x$
some $-x$	$2x$	x

$K_{sp} = (2x)^2(x = 4x^3$

$x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{2.3\times10^{-46}}{4}} = 3.9\times10^{-16}\ M$

$\left(\frac{3.9\times10^{-16}\ mol}{L}\right)\left(\frac{247.87\ g}{1\ mol}\right) = 9.7\times10^{-14}\ g/L$ so close to 1×10^{-13} g/L solubility @ 45°C

At room temp (25°C), will it be more or less soluble?

Look @ signs of ΔS° and ΔH°

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ at first sight, it looks like we can just answer this on the basis of the sign of ΔS°

if ΔS° is ⊕, The $T\Delta S$ term is larger at higher temps, so it gives us a larger ⊖ term ... more favorable @ higher temps. But, if we look more closely ...

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K$ $\quad$ ΔG° and K both depend on T.

$$\frac{\Delta H^\circ - T\Delta S^\circ}{-RT} = \frac{-RT \ln K}{-RT}$$

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

The value of K_{sp} at a particular temperature is directly related to solubility.

according to this, it's really the sign of ΔH° that matters.
if ΔH° is ⊕ and ΔS° is ⊕, as is the case here,

$$\ln K = \underbrace{\frac{-(+)}{RT}}_{\text{negative term}} + \underbrace{(+)}_{\text{positive term}}$$

if T is <u>lower</u>, the $\frac{\Delta H^\circ}{RT}$ term will have a higher magnitude.
Since this term is ⊖, it will <u>lower</u> ln K and <u>lower</u> K.
* If ΔH° is ⊕, higher T ⇒ higher K (more favorable)
If ΔH° is ⊖

$$\ln K = \frac{-(-)}{RT} + \underset{(+)\text{or}(-)}{\text{constant}}$$

lower T, larger magnitude of $\frac{\Delta H^\circ}{RT}$ term. Term is ⊕ overall.
This means ln K is larger, so K is larger.
* If ΔH° is ⊖, higher T ⇒ lower K (less favorable)

14. $2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$ gases are <u>much</u> more disordered than solids. ~~Even though we have 3 sub~~
Since a gas is being consumed, products have more order. ΔS⊖

15. a. larger molecules have <u>more entropy</u> – more bending + vibration motions are possible. $CH_3CH_2CH_3$
b. 2 mol NO_2 has more degrees of freedom than 1 mol N_2O_4.
the molecules are separate and can move around independently.
c. $H_2O_{(l)}$ liquids are more disordered than solids.

16. see sheet for answers. Think of exo/endo and increase/decrease in disorder.