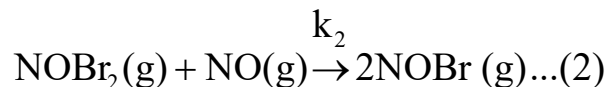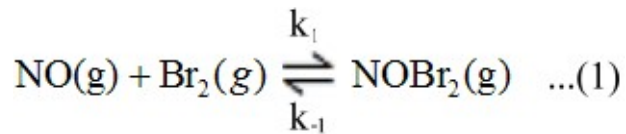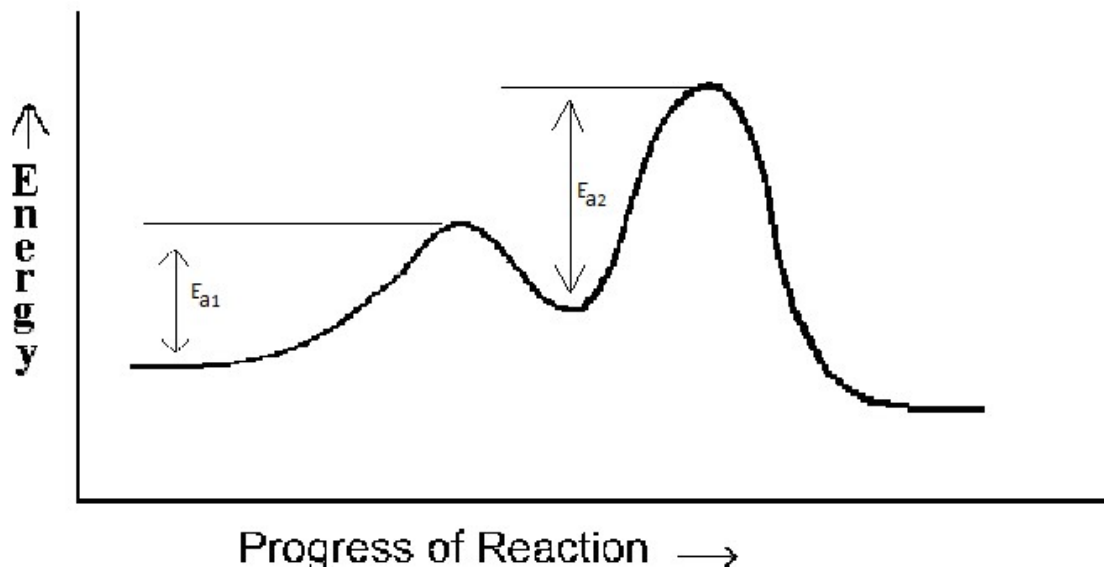# Chemistry 225 Semester 04-2016
Homework #4a – Answer Key

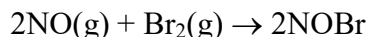1) The following mechanism has been proposed for the reaction of NO with Br_2 in the gaseous state:

$$NO(g) + Br_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOBr_2(g) \quad ...(1)$$

$$NOBr_2(g) + NO(g) \overset{k_2}{\rightarrow} 2NOBr(g) ...(2)$$

The potential energy profile for this reaction is given below:

a) Write the equation for the overall reaction. (1)

$$2NO(g) + Br_2(g) \rightarrow 2NOBr$$

b) Which step in the mechanism is the rate determining step? Give a reason for your answer. (2)

The second step must be the rate-determining step because it has the higher activation energy. ($E_{a1} < E_{a2}$ as shown on the diagram.)

c) Identify an intermediate in the mechanism. (1)

$NOBr_2$ is an intermediate.

d) Derive the rate law for the reaction from the mechanism. (4)

Rate of overall reaction, R_o = rate of rate-determining step, R_2

Since this is an elementary step, the rate equation follows the stoichiometry:

$$\therefore R_o = R_2 = k_2[NOBr_2][NO]$$

But $NOBr_2$ is an intermediate, and its concentration is unknown and uncontrollable. Its concentration must be related to the controllable concentrations of reactants: Since step 1 is fast, it is approximately an equilibrium, and so:

$$K_1 = [NOBr_2]/([NO][Br_2])$$

$$\therefore [NOBr_2] = K_1[NO][Br_2]$$

and substituting for $[NOBr_2]$ in the expression for R_2, we have:

$$R_o = k_2(K_1[NO][Br_2])[NO]$$

$$\therefore R_o = k_2K[NO]^2[Br_2]$$

and replacing k_2K with k_o we have:

$$\underline{R_o = k_o[NO]^2[Br_2]}$$

where k_o is the rate constant for the overall reaction.

Alternatively we may note, that since step 1 is an elementary step, the rate of the forward reaction is given by:

$$R_1 = k_1[NO][Br_2]$$

and the rate of the reverse reaction is:

$$R_{-1} = k_{-1}[NOBr_2]$$

Since the step is fast, both in the forward and reverse directions:

$$R_1 \simeq R_{-1}$$

and so:

$$k_1[NO][Br_2] = k_{-1}[NOBr_2]$$

$$\therefore [NOBr_2] = (k_1/k_{-1})[NO][Br_2]$$

and substituting as before:

$$R_o = k_2 (k_1/k_{-1})[NO]^2[Br_2]$$

e) What can you conclude about the proposed mechanism if the experimentally determined rate law is found to be the same as that determined from the mechanism. (1)

This tells us that the mechanism *may be* correct, but does not tells us that it *definitely* is, since other mechanisms may lead to the same rate equation.

f) If the rate constant is found to be $1.00 \times^{-3} s^{-1}$, what is the order of the reaction? (1)

The reaction is first order. (Since the units are s^{-1}.)

i) Determine the half-life of the reaction. (2)

$$t_{\frac{1}{2}} = \ln(2)/k = \ln(2)/1.00 \times 10^{-3} = 693.1471806 \text{ s} = \underline{693 \text{ s}} \text{ to 3 s.f.}$$

ii) Determine the time required for the concentration of NO to fall from 0.100M to 0.0750M. (3)
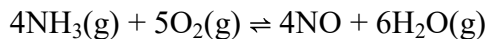
For a first order reaction: $\ln([A]_t) = \ln([A]_0 - k t$ or

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

$$\therefore \ln\left(\frac{0.100}{0.0750}\right) = 1.00 \times 10^{-3} \times t$$

$$\therefore t = \left(\frac{\ln\left(\frac{0.1}{0.075}\right)}{1 \times 10^{-3}}\right) = 287.6820725 = \underline{\underline{288 \text{ s}}} \text{ to 3 s.f.}$$

2) The reaction
$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO + 6H_2O(g)$$
has $\Delta H° = $ -906.2 kJ mol^{-1} and Kp is 3.97×10^{167} at 25°C. (If your calculator can't handle the large numbers involved, use a spread sheet to do the calculations.)

a) Calculate $\Delta G°$, making sure to include units. What does the sign of this value tell you? (3)
$$\Delta G° = -RT\ln(K) = -8.31 \times 298 \times \ln(3.97 \times 10^{167}) = -9.55660986 \times 10^5 \text{ J mol}^{-1}$$
$$= \underline{-9.56 \times 10^2 \text{ kJ mol}^{-1}} \text{ to 3 s.f.}$$
The negative value shows that the reaction is spontaneous in the forward direction.

b) Calculate ΔG when the partial pressures of NO, H_2O, NH_3, and O_2 are 2.00, 2.50, 1.00×10^{-25} and 1.00×10^{-30} atm respectively and determine the direction of reaction under these conditions. (4)
$$\Delta G = \Delta G° + RT\ln(Q)$$
$$\text{But } Q = \frac{(p_{NO})^4 (p_{H_2O})^6}{(p_{NH_3})^4 (p_{O_2})^5} = \frac{2.00^4 \times 2.50^6}{(1.00 \times 10^{-25})^4 \times (1.00 \times 10^{-30})^5} = 3.9063 \times 10^{253}$$
$$= 3.9063 \times 10^{253}$$
$$\therefore \Delta G = -9.55660986 \times 10^5 + 8.31 \times 298 \times \ln(3.9063 \times 10^{253}) = 490338.451 \text{ J mol}^{-1}$$
$$= \underline{+490 \text{ kJ mol}^{-1}} \text{ to 3 s.f.}$$
The positive sign indicates that the reaction is spontaneous in the reverse direction.
(Alternatively, Q>>K gives the same conclusion.)

c) Estimate K_p at 1000°C. Why is this estimate liable to be very inaccurate? Is its magnitude relative to K_p at 25°C to be expected on the basis of Le Chatelier's principle? (8)

Van t'Hoff's equation may be stated as:
$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
$$\therefore \ln\left(\frac{K_2}{K_1}\right) = -\frac{-906.2 \times 10^3}{8.31}\left(\frac{1}{1000+273} - \frac{1}{25+273}\right)$$
$$= 1.0905 \times 10^5 \times (0.000785546 - 0.003355705) = -2.802741 \times 10^2$$
$$\therefore \frac{K_2}{K_1} = e^{-2.802741 \times 10^2} = 1.8989 \times 10^{-122}$$
$$\therefore K_2 = K_1 \times 1.8989 \times 10^{-122} = 3.97 \times 10^{167} \times 1.8989 \times 10^{-122} = 7.5356 \times 10^{45}$$
$$= \underline{\underline{7.54 \times 10^{45}}} \text{ to 3 s.f.}$$
The value is liable to be very inaccurate because Van t'Hoff's equation includes the implicit assumption that $\Delta H°$ does not change with temperature. This is approximately true over small ranges of temperature, but 975°C is hardly a small

range of temperature.

Since $\Delta H°<0$, Le Chatelier's principle suggests that equilibrium should shift to the left as temperature increases. The smaller value of K at the higher temperature shows that it has, so, yes, it is consistent with Le Chatelier's principle.

3) Determine the pH of each of the following solutions:

a) 0.0200 M formic acid solution, $K_a(HCO_2H) = 1.77\times10^{-4}$ @ 25°C (5)

The equation is $HCO_2H(aq) + H_2O(l) \rightleftharpoons HCO_2^-(aq) + H_3O^+(aq)$ giving the ICE table:

	HCO_2H	H_2O	HCO_2^-	H_3O^+
I /M	0.0200	--	0	0^1
C /M	-x	--	+x	+x
E /M	0.02-x	--	x	x

[1] Assuming the contribution from water is negligible – see end of this work.

$$K_a = 1.77 \times 10^{-4} = \frac{[HCO_2^-][H_3O^+]}{[HCO_2H]} = \frac{x.x}{0.02 - x}$$

Assume x< 5% of 0.02 so that $0.02 - x \approx 0.02$

$$\therefore K_a \approx \frac{x^2}{0.02}$$

$$\therefore x = \sqrt{0.02K_a} = \sqrt{0.02 \times 1.77 \times 10^{-4}} = 1.88149 \times 10^{-3}$$
$$\therefore [H_3O^+] = 1.88149\times10^{-3}$$
$$\therefore pH = -Log([H_3O^+]) = = -Log(1.88149\times10^{-3}) = 2.725498369 = 2.73 \text{ to 2 d.p.}$$
Check assumption:

$x/0.02 = 1.88\times10^{-3}/0.02 = 0.094 \approx 9.4\%$ - assumption not valid: we must solve the quadratic.

$$K_a \approx \frac{x^2}{0.02 - x}$$
$$\therefore x^2 + K_a x - 0.02 \times K_a = 0$$
$$\therefore x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-K_a \pm \sqrt{(-0.02)^2 + 4 \times 0.02 K_a}}{2}$$
$$= \frac{-0.000177 + \sqrt{(0.000177)^2 + 4 * 0.02 * 0.000177}}{2} = 1.7950 \times 10^{-3}$$

(Only the positive sign gives x>0.)
$$\therefore [H_3O^+] = 1.7950\times10^{-3}$$
$$\therefore pH = -Log([H_3O^+]) = = -Log(1.7950\times10^{-3}) = 2.7459 = \underline{2.75} \text{ to 2 d.p.}$$
(Not a very significant difference!)

a) _____

b) 0.0600 M sodium hydroxide solution. (3)
For a strong base such as NaOH, [OH⁻] = conc. of base = 0.0600 M

$$\therefore pOH = -Log[OH^-] = -Log(0.06) = 1.2218\ldots$$
$$\therefore pH = pK_w - pOH = 14.00 - 1.2218\ldots = \underline{12.78} \text{ to 2 d.p.}$$

c) A mixture formed by adding 60.0 cm³ of solution (a) to 20.0 cm³ of solution (b).(5)
(See sample exercise Sample Exercise 17.9 in your textbook.)

We first consider the reaction that occurs between HCO_2H and NaOH by considering the # of moles of each.

Solution (a) contains $\dfrac{60}{1000} \times 0.02 = 1.2 \times 10^{-3} \ mol$ and solution (b) contains

$\dfrac{20}{1000} \times 0.06 = 1.2 \times 10^{-3} \ mol$ so the NaOH completely neutralises the HCO_2H,

according to $HCO_2H(aq) + Na^+OH^-(aq) \rightarrow HCO_2^-Na^+(aq) + H_2O(l)$
and produces 1.2×10^{-3} mol of HCO_2^- in solution.
(Acid plus base gives salt plus water.)

The HCO_2^- is dissolved in 60 + 20 = 80 cm³ of solution, and so the concentration is

$$\dfrac{1.2 \times 10^{-3}}{(80/1000)} = 1.50 \times 10^{-2} M \ .$$

HCO_2^- is the conjugate base of HCO_2H, and so its K_b is given by $K_aK_b = 10^{-14}$ or
$K_b = 10^{-14}/K_a = 10^{-14}/1.77 \times 10^{-4} = 5.64972 \times 10^{-11}$

The equilibrium equation is $HCO_2^-(aq) + H_2O(l) \rightleftharpoons HCO_2H(aq) + OH^-(aq)$ giving the
ICE table:

	HCO_2^-	H_2O	HCO_2H	OH^-
I /M	0.015	--	0	0¹
C /M	-x	--	+x	+x
E /M	0.015-x	--	x	x

¹ Assuming the contribution from water is negligible. See last page.

$$K_b = 5.64972 \times 10^{-11} = \frac{[HCO_2^-][H_3O^+]}{[HCO_2H]} = \frac{x.x}{0.015 - x}$$

Assume x<<0.015 so that $0.015 - x \simeq 0.015$

$$\therefore K_b \approx \frac{x^2}{0.015}$$

$$\therefore x = \sqrt{0.015 K_b} = \sqrt{0.015 \times 5.64972 \times 10^{-11}} = 9.20575 \times 10^{-7}$$
$$\therefore [OH^-] = 9.20575 \times 10^{-7}$$
$$\therefore pOH = -Log([OH^-]) = -Log(9.20575 \times 10^{-7}) = 6.0359$$
$$\therefore pH = pK_w - pOH = 14.00 - 6.0359 = \underline{7.96} \text{ to 2 d.p.}$$

Now we check the assumption:

$x/0.015 = 8.2 \times 10^{-7}/0.015 \simeq 5.5 \times 10^{-5} = 5.5 \times 10^{-3}\%$ <<5%- assumption valid.

Check if the contribution of H_3O^+ or OH^- from water is truly negligible.

For the dissociation of the acid as in 3(a), the ICE table, allowing for the H_3O^+ contributed by H_2O, becomes:

	HCO_2H	H_2O	HCO_2^-	H_3O^+
I /M	0.0200	--	0	y_1
C /M	-x	--	+x	+x
E /M	0.02-x	--	x	y + x

Where y_1 and y represent the concentration of H_3O^+ from water, and x is the contribution from the acid. Note that $y_1 \neq y$ since the presence of H_3O^+ from the dissociation of the acid suppresses the dissociation of water. Since water dissociates to form $1OH^-$ for every H_3O^+, at equilibrium $[OH^-] = y$. We may now construct two simultaneous equations:

$$K_w = [H_3O^+][OH^-] = (y+x)y = 1.00 \times 10^{-14}....(1)$$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{x(y+x)}{0.02-x} = 1.77 \times 10^{-4}........(2)$$

If we assume as a first approximation that y<<x, then $y+x \simeq x$, and equation (2) becomes the same as the one we solved earlier to give x = 1.7950×10^{-3}. Also, from equation (1) we see that:

$$y = \frac{1.00 \times 10^{-14}}{y+x}...(3)$$

and again assuming y<<x, (3) becomes:

$$y = \frac{1.00 \times 10^{-14}}{x}$$

Substituting for x = 1.7950×10^{-3} gives: $y = \frac{1.00 \times 10^{-14}}{1.795 \times 10^{-3}} = 5.57082 \times 10^{-12}$

Checking our assumption, y/x = $(5.57 \times 10^{-12})/(1.7950 \times 10^{-3}) = 3.1 \times 10^{-9}$ or $3.1 \times 10^{-7}\%$ which is much less than 5%, so the assumption is valid.
(Solving the equations exactly using the *solve* function at https://cloud.sagemath.com also gives x = 1.7950×10^{-3} and y = 5.5708×10^{-12})

For the dissociation of the base, as in 3(c), the ICE table becomes:

	HCO_2^-	H_2O	HCO_2H	OH^-
I /M	0.015	--	0	y_1
C /M	-x	--	+x	+x

E /M   0.0015-x   --   x   y + x

$$K_b = \frac{[OH^-][HCO_2H]}{[HCO_2^-]} = \frac{(y+x)x}{0.015-x}$$

and $K_w = (y+x)y$

The equations are the same except K_b replaces K_a, y is the [OH⁻] from water, and x is [HCO₂H].   Solving as above gives y/x ≃ 1.2%, i.e. less than 5%. Again the assumption is justified, though errors are greater than in the previous case.
Clearly the assumption would not work for a much weaker base, or a much more dilute solution.

(https://cloud.sagemath.com gives x =9.15×10^{-7}, y =1.08×10^{-8}, so y/x ≃ 1.17×10^{-2} or 1.2%.)