Study Guide for Test 4: Equilibrium

Answers

Review Material –

1) Study Guide
2) Review Problems
3) Chapter 17
4) Class Notes
5) Equilibrium I - IV

On the test, you will be expected to:

- Understand the relationship between equilibrium and
  - The rate of the forward and reverse directions of a reaction
  - The concentrations of reactants and products
  - The free energy of a reaction (ΔG_{rxn})
- Write equilibrium constants for homogeneous and heterogeneous reactions
- Understand the relationship between the equilibrium constant (K_{eq}) for a reaction and
  - The relative amounts of products and reactants at equilibrium
  - The activation energies for the forward and reverse directions of a reaction
  - The rate constants for the forward and reverse directions of a reaction
  - The standard-state free energy of a reaction (ΔG_{rxn}°)
- Distinguish ΔG_{rxn} and ΔG_{rxn}°
- Understand the relationship between the reaction quotient (Q) for a reaction and
  - The direction in which a reaction is spontaneous
  - The relative amounts of products and reactants, compared to equilibrium
  - The rates of the forward and reverse directions of a reaction as the system equilibrates
  - L'Chatlier's Principle (including effect of changing volume and temperature)
- Write equilibrium constants for combined reactions (Hess's Law)
- Identify equilibrium in graphs of concentration vs time and rate vs time
- Compare Q and Keq in graphs of concentration vs time and rate vs time
- Compare the rates of the forward and reverse reactions in graphs of concentration vs time
- Calculate equilibrium quantities using the RICE table technique

Important Equations:

For the reaction $aA + bB \underset{k_f}{\overset{k_r}{\leftrightharpoons}} cC + dD$ $\qquad K_{eq} = \frac{[C]_{eq}^c[D]_{eq}^d}{[A]_{eq}^a[B]_{eq}^b}$ $\qquad Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$

$K_{eq} = \frac{k_f}{k_r}$ $\qquad \Delta G_{rxn}^o = -RT\ln K_{eq}$ $\qquad \Delta G_{rxn} = \Delta G_{rxn}^o + RT\ln Q = RT\ln\frac{Q}{K_{eq}}$ $\qquad k_f = Ce^{\frac{-E_a^f}{RT}}$

At equilibrium ...

... the rate of the forward direction and the rate of the forward direction of a reaction are equal

... the concentrations of all products and reactants are constant

... Q = K_{eq}

... $\Delta G_{rxn} = 0$

... static macroscopic observations are the result of dynamic microscopic changes

Review Problems

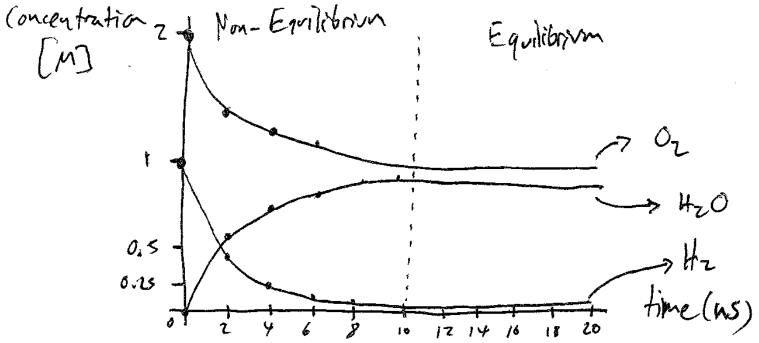
Consider the equilibrium $H_{2(g)} + 0.5\ O_{2(g)} \leftrightharpoons H_2O_{(g)}$ $\Delta H^o_{rxn} = -242\ kJ/mol$ (Reaction A)
Assume that the rates of the forward and reverse directions of the reaction are given by

$$r_f = k_f[H_2][O_2]^{0.5}$$
$$r_r = k_r[H_2O]$$

Using an ultrafast spectrophotometer, a chemist recorded the following experimental data for the reaction at 25 C.

Time (ns)	0	2	4	6	8	10	12	14	16	18
$[H_2]$ (M)	1	0.45	0.25	0.16	0.12	0.10	0.09	0.09	0.09	0.09
$[O_2]$ (M)	2	1.45	1.25	1.16	1.12	1.10	1.09	1.09	1.09	1.09
$[H_2O]$ (M)	0	0.55	0.75	0.84	0.88	0.90	0.91	0.91	0.91	0.91

1. Make a plot of concentration vs. time below. Draw curves for H_2, O_2, and H_2O.



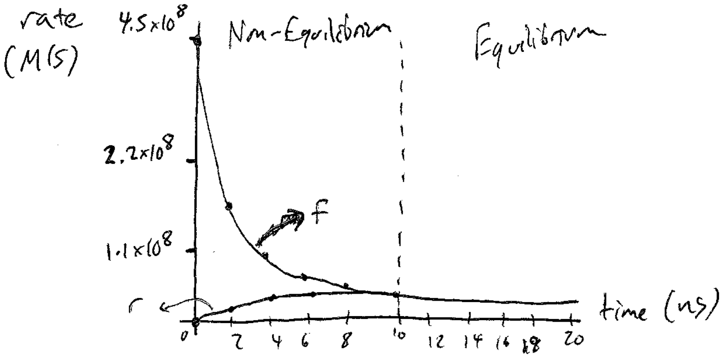
2. On your graph above, draw a vertical dotted line separating the 'equilibrium' and 'non-equilibrium' stages of Reaction A. Clearly label each stage.

3. In the equilibrium stage, the concentrations of reactants and products are constant.

4. Complete the table below by calculating the rates of the forward and backward reactions at each time. Use C = 10^{12}. Use scientific notation!

Time (ns)	0	2	4	6	8	10	12	14	16	18
r_f (M/s)	4.4×10^8	1.7×10^8	8.7×10^7	5.4×10^7	4.0×10^7	3.3×10^7	2.9×10^7	2.9×10^7	2.9×10^7	2.9×10^7
r_r (M/s)	0	1.7×10^7	2.3×10^7	2.6×10^7	2.7×10^7	2.8×10^7	2.9×10^7	2.9×10^7	2.9×10^7	2.9×10^7

5. Make a plot of rate vs time below. Draw curves for both the forward and reverse rates.



6. On your graph above, draw a vertical dotted line separating the 'equilibrium' and 'non-equilibrium' stages of Reaction A. Clearly label each stage.

7. In the equilibrium stage, the rates of the forward and reverse reactions are equal.

8. Write an expression for the equilibrium constant, K_c, of Reaction A.

$$K_c = \frac{[H_2O]_{eq}}{[H_2]_{eq}[O_2]_{eq}^{1/2}}$$

9. Determine the value of K_c from your graph in question 1.

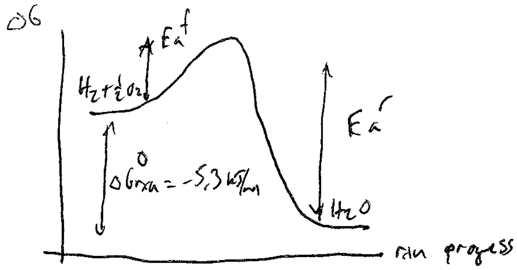
$$K_c = \frac{(0.91)}{(.09)(1.09)^{1/2}} = 9.68$$

10. Determine the value of ΔG^{o}_{rxn} for Reaction A. (R = 8.314 x 10^{-3})

$$\Delta G^{o}_{rxn} = -RT\ln K_c = -(8.314\times10^{-3})(298\,K)\ln(8.51)$$

$$\Delta G^{o}_{rxn} = -5.3\ kJ/mol$$

11. Draw a reaction profile for Reaction A below. Be sure to label the reactants, products, and the transition state.



12. Label the activation energies for the forward and reverse reactions on your graph above. Label ΔG^{o}_{rxn}.

13. ΔG^{o}_{rxn} for reaction A is (circle one): [✓ < 0] = 0 > 0

14. Reaction A is (circle one): spontaneous non-spontaneous [✓ not enough information]

15. Explain your answer to #14.

The spontaneity of a chemical reaction depends on ΔG_{rxn}, not only on ΔG^{o}_{rxn}. To determine the spontaneity, you must know Q or specify the time of the reaction:

$$\Delta G_{rxn} = \Delta G^{o}_{rxn} + RT\ln Q = RT\ln\frac{Q}{K_{eq}}$$

where Q depends on time.

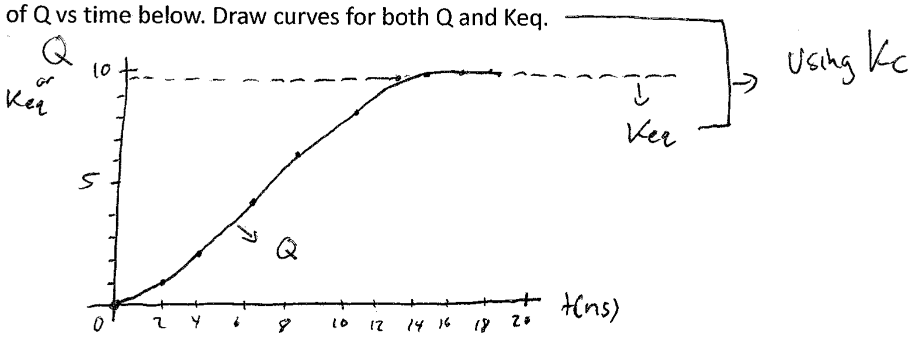
16. Complete the following table comparing K_{eq}, ΔG^o_{rxn}, and activation energies for ANY equilibrium.

	>, =, < (choose one)	>, =, < (choose one)
$K_{eq} >> 1$	ΔG^o_{rxn} $<$ 0	E^f_a $<$ E^r_a
$K_{eq} \sim 1$	ΔG^o_{rxn} $\approx$ 0	E^f_a $\approx$ E^r_a
$K_{eq} << 1$	ΔG^o_{rxn} $>$ 0	E^f_a $>$ E^r_a

17. Complete the table below by calculating Q for Reaction A at each time.

Time (ns)	0	2	4	6	8	10	12	14	16	18
Q	0	1.01	2.68	4.87	6.93	8.58	9.68	9.68	9.68	9.68

18. Make a plot of Q vs time below. Draw curves for both Q and Keq.



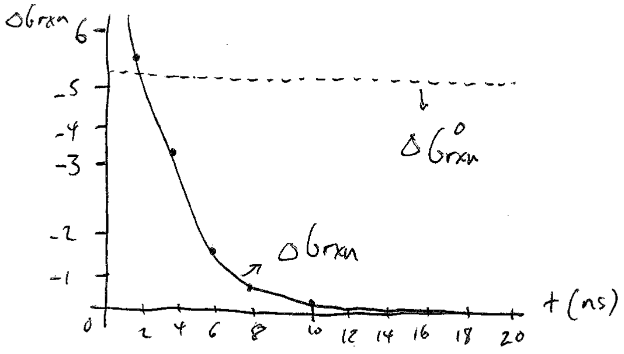
19. What happens to the value of Q over time?

Over time, Q approaches Keq. In otherwords, the reaction proceeds spontaneously toward equilibrium.

20. Complete the table below by calculating ΔG_{rxn} at each time.

Time (ns)	0	2	4	6	8	10	12	14	16	18
ΔG_{rxn}	undefined $-\infty$	-5.59	-3.18	-1.70	-0.83	-0.30	0	0	0	0

21. Make a plot of ΔG_{rxn} vs time below. Draw curves for both ΔG_{rxn} and ΔG^o_{rxn}.



What happens to the value of ΔG_{rxn} over time?

Over time, ΔG_{rxn} approaches 0. In contrast, ΔG°_{rxn} stays constant.
In otherwords, the system
approaches equilibrium.

At the start of the experiment (time = 0s) ...

22. ... r_f is (circle one): < rr = rr [✓ > rr]

23. ... Q is (circle one): [✓ $< K_c$] $= K_c$ $> K_c$

24. ... the concentration of products is relatively too (circle one): high [✓ low]

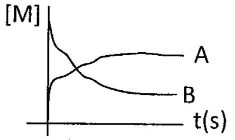
25. ...ΔG_{rxn} (circle one): [✓ < 0] = 0 > 0

26. ... the reaction is spontaneous to the (circle one): [✓ right (forward direction)] left (reverse direction)

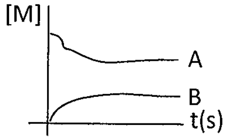
27. Complete the following table comparing Q, Keq, concentrations, rates of reaction, and spontaneity for ANY reaction:

	products, reactants, neither (choose one)	>, =, < (choose one)	right, left, equilibrium (choose one)
$Q > K_c$	Relatively too much products	r_f < r_r	Spontaneous to the left
$Q = K_c$	Relatively too much neither	r_f = r_r	Spontaneous to the equilibrium
$Q < K_c$	Relatively too much reactants	r_f > r_r	Spontaneous to the right

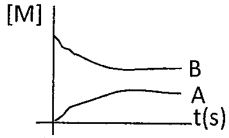
28. For each of the graphs below, circle the larger quantity at time = 0s for the equilibrium A ⇆ B.



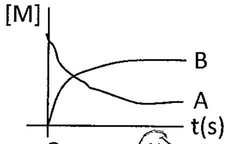
[✓ Q] vs. K_{eq}
r_f vs. [✓ r_r]



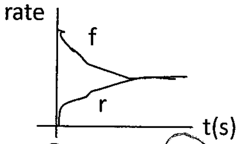
Q vs. [✓ K_{eq}]
[✓ r_f] vs. r_r



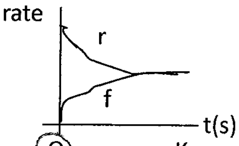
[✓ Q] vs. K_{eq}
r_f vs. [✓ r_r]



Q vs. [✓ K_{eq}]
[✓ r_f] vs. r_r



Q vs. [✓ K_{eq}]
[✓ r_f] vs. r_r



[✓ Q] vs. K_{eq}
r_f vs. [✓ r_r]

29. Assume that Reaction A has come to equilibrium. Complete the following table comparing the effects of imposing the following changes on the system. Indicate in which direction the equilibrium will shift to minimize the change. Indicate whether the concentrations of each of the products and reactants will have increased, decreased, or remained constant relative to before the change.

Change	Shift to the ...	$[H_2]$	$[O_2]$	$[H_2O]$
Add $[H_2]$	right	increased	decreased	increased
Remove $[O_2]$	left	increased	decreased	decreased
Remove $[H_2O]$	right	decreased	decreased	decreased
Increase volume	left	hard to say ...		decreased
Decrease temp.	right	decreased	decreased	increased
Add catalyst	no effect	constant	constant	constant

30. Another chemist fills a reaction vessel with 1 M H_2, 1 M O_2, and 2 M H_2O. What will be the concentrations of the gases after the system reaches equilibrium?

R	$H_2 + \frac{1}{2}O_2$		$\rightleftharpoons H_2O$
I	1	1	2
C	$-x$	$-\frac{1}{2}x$	$+x$
E	$1-x$	$1-\frac{1}{2}x$	$2+x$

$$K_c = \frac{(H_2O)}{(H_2)[O_2]^{1/2}} = \frac{(2+x)}{(1-x)(1-\frac{1}{2}x)^{1/2}} = 9.68$$

$x = 0.663$

$[H_2]_{eq} = 1-x = 1-0.663 = 0.337\ M$

$[O_2]_{eq} = 1-\frac{1}{2}x = 1-\frac{1}{2}(0.663) = 0.669\ M$

$[H_2O]_{eq} = 2+x = 2+(0.663) = 2.663\ M$

31. Draw a picture of the contents of the reaction vessel in question 30 just after it was filled, 10 nanoseconds after it was filled, and at equilibrium. Does the reaction ever fully 'stop'?