


### Lecture 14 CH131 Summer 1

Thursday, June 13, 2019

- Complete: Reaction quotient, spontaneity, and equilibrium
- Effect of temperature on equilibrium


**Next lecture:** Complete ch14: Predicting direction of change.  $Q$  algebra; disturbing equilibrium. Begin ch15: Acid-base equilibria



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## Exam 2, Monday, June 17

Chapters 10, 11, 12, and 13  
Lecture 6 through 13

 2

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### Practice: Problem 14.41

$K = \frac{1}{P_{\text{NH}_3} P_{\text{HCl}}} = 4.0$

**ICE**

$\text{NH}_3$	$\text{HCl}$	$\text{NH}_4\text{Cl}$	$Q$
0.80	0	0	$Q > K$
+x	+x	-x	
0.80+x	x	0	4.0

$K = \frac{1}{(0.80+x)(x)} = 4.0$   
 $x = 0.24$

41. The equilibrium constant for the reaction

$$\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightleftharpoons \text{NH}_4\text{Cl}(\text{s})$$

at 340°C is  $K = 4.0$ .

(a) If the partial pressure of ammonia is  $P_{\text{NH}_3} = 0.80$  atm and solid ammonium chloride is present, what is the equilibrium partial pressure of hydrogen chloride at 340°C?


(b) An excess of solid  $\text{NH}_4\text{Cl}$  is added to a container filled with ammonia at 340°C and a pressure of 1.50 atm. Calculate the pressures of  $\text{NH}_3(\text{g})$  and  $\text{HCl}(\text{g})$  reached at equilibrium.

**ICE**

1.50	0	0
+x	x	-x
1.50+x	x	0

$K = \frac{1}{(1.50+x)(x)} = 4.0, x = 0.15$   
 $P_{\text{NH}_3} = 1.65, P_{\text{HCl}} = 0.15$

3



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### Q versus K is the key to spontaneity

If  $Q < K$ , product must form to get to equilibrium, so **spontaneous**  $\text{left} \rightarrow \text{right}, \Delta G < 0$


If  $Q > K$ , reactants must form to get to equilibrium, so **nonspontaneous**  $\text{left} \leftarrow \text{right}, \Delta G > 0$

This means  $\Delta G$  is proportional to  $\ln(Q/K)$ .  $Q < K, \frac{Q}{K} < 1, \ln(\frac{Q}{K}) < 0$

The constant of proportionality turns out to be  $RT$ .  $Q > K, \frac{Q}{K} > 1, \ln(\frac{Q}{K}) > 0$

$\Delta G = RT \ln(Q/K) = \Delta H - T\Delta S$

$\Delta G \propto \ln(Q/K)$

 4


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$N_2(g) + H_2(g) \rightarrow NH_3(g)$   $340^\circ C, K=4.0, V=1L$

I	1.50	0.30	0
C	-x	-x	+2x
E	1.50-x	0.30-x	2x

$K=4.0 = \frac{(2x)^3}{(1.50-x)(0.30-x)}$   $x = \{1.68, 0.17\}$   
 unphysical, since  $1.50-x = 1.50-1.68 < 0$

$m = \frac{PV}{RT} = \frac{0.12 \text{ atm} \cdot 1L}{0.0821 \text{ L atm / mol K} \cdot 340K}$

weird (in a great way) 

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### Effect of T on K

$\Delta G = RT \ln(Q/K) = \Delta H - T\Delta S$

13. Calculate  $\Delta G^\circ$  and the equilibrium constant K at  $25^\circ C$  for the reaction

$2 NH_3(g) + \frac{7}{2} O_2(g) \rightleftharpoons 2 NO_2(g) + 3 H_2O(g)$

using data in Appendix D.

What is the expression for  $\Delta G^\circ$  in terms of Q and K?

$\Delta G^\circ = RT \ln(1/K) = \Delta H^\circ - T\Delta S^\circ$   $\Delta G^\circ = 2 \Delta G_f^\circ(NO_2) + 3 \Delta G_f^\circ(H_2O) - 2 \Delta G_f^\circ(NH_3) - \frac{7}{2} \Delta G_f^\circ(O_2)$

Example: 14.13  $\ln(K) = \frac{\Delta G^\circ}{-RT}$

$\Delta G_f^\circ = -RT \ln(K)$

$\ln(K) = \frac{\Delta G^\circ}{-RT} = \frac{550.23 \text{ kJ/mol}}{-8.314 \text{ J/mol K} \cdot 298K} = 22.2$

$K = e^{22.2} = 2.7 \times 10^9$

$\Delta G_f^\circ$  values:  
 $NO_2 = 51.29 \text{ kJ/mol}$   
 $H_2O = -228.59 \text{ kJ/mol}$   
 $NH_3 = -16.48 \text{ kJ/mol}$   
 $O_2 = 0$

$\Delta G^\circ = -550.23 \text{ kJ/mol}$

2 mole of  $NH_3$   
 8 mole of  $O_2$   
 How much  $NH_3$  at equilibrium?

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$2NH_3 + \frac{7}{2} O_2 \rightleftharpoons 2NO_2 + 3H_2O$   $K = 2.59 \times 10^9$

I	2	3.5	0	0
C	-2x	-3.5x	+2x	+3x
E	2x	3.5x	2x	3x

$K = \frac{P_{NO_2}^2 P_{H_2O}^3}{P_{NH_3}^2 P_{O_2}^{3.5}} = \frac{(2x)^2 (3x)^3}{(2x)^2 (4.5)^{3.5}} = K$

$4x^2 = (2x)^2 = \frac{K (4.5)^{3.5}}{27}$

$x = \sqrt{\frac{K (4.5)^{3.5}}{27}} = 2.32 \times 10^{-4}$

$2 - 2y = 2 \times (2.32 \times 10^{-4})$   
 $1 - y \Rightarrow y = 1 - 2.32 \times 10^{-4}$

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### Effect of T on K

$\Delta G^\circ = RT \ln(1/K) = \Delta H^\circ - T\Delta S^\circ$

For values of T near 298 K,  $\Delta H^\circ$  and  $\Delta S^\circ$  are nearly constant.

This means the graph of  $\ln(K)$  versus  $1/T$  is nearly a straight line,

with slope  $m = -\Delta H^\circ/R$

and intercept  $b = \Delta S^\circ/R$  at  $1/T = 0$  ( $T = \infty$ )

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**Practice: Problem 14.61**  $K = \frac{P_{NO_2}}{(P_{NO_2})^2} = \frac{k_f}{k_r} \left( \frac{[NO_2]}{[NO]^2} \right)$

$\ln(K) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$

$\Delta S^\circ = R \ln(K) + \frac{\Delta H^\circ}{T}$   
 $= R \ln(K) + \frac{\Delta H^\circ}{T}$

$\Delta G^\circ = RT \ln(K) = \Delta H^\circ - T\Delta S^\circ$

61. The equilibrium constant at 25°C for the reaction  $2 NO_2(g) \rightleftharpoons N_2O_4(g)$  is 6.8. At 200°C the equilibrium constant is  $1.21 \times 10^{-3}$ . Calculate the enthalpy change ( $\Delta H$ ) for this reaction, assuming that  $\Delta H$  and  $\Delta S$  of the reaction are constant over the temperature range from 25°C to 200°C.

$T_1 = 298 K, K_1 = 6.8$   
 $T_2 = 473 K, K_2 = 1.21 \times 10^{-3}$   
 $\text{slope} = \frac{\ln(K_2) - \ln(K_1)}{\frac{1}{T_2} - \frac{1}{T_1}} = -\frac{\Delta H^\circ}{R}$

$\Delta H^\circ = \frac{R(\ln(K_1) - \ln(K_2))}{\frac{1}{T_2} - \frac{1}{T_1}}$

$\Delta H^\circ = \frac{8.314 \text{ J/mol K} (\ln(6.8) - \ln(1.21 \times 10^{-3}))}{\frac{1}{473} - \frac{1}{298}}$

$\Delta H^\circ = \frac{8.314 \text{ J/mol K} (1.917 - (-6.72))}{\frac{1}{473} - \frac{1}{298}}$

$\Delta H^\circ = \frac{8.314 \text{ J/mol K} (-8.637)}{\frac{1}{473} - \frac{1}{298}}$

$\Delta H^\circ = \frac{-71.8 \text{ J/mol}}{\frac{1}{473} - \frac{1}{298}}$

$\Delta H^\circ = \frac{-71.8 \text{ J/mol}}{\frac{298 - 473}{298 \times 473}}$

$\Delta H^\circ = \frac{-71.8 \text{ J/mol} \times 298 \times 473}{-175}$

$\Delta H^\circ = \frac{-100000 \text{ J/mol}}{-175}$

$\Delta H^\circ = +571 \text{ J/mol}$

$\Delta S^\circ = \frac{\Delta H^\circ - T\Delta G^\circ}{T}$

$\Delta S^\circ = \frac{571 \text{ J/mol} - 298 \text{ K} \ln(6.8)}{298 \text{ K}}$

$\Delta S^\circ = \frac{571 \text{ J/mol} - 298 \text{ K} (1.917)}{298 \text{ K}}$

$\Delta S^\circ = \frac{571 \text{ J/mol} - 571 \text{ J/mol}}{298 \text{ K}}$

$\Delta S^\circ = 0 \text{ J/mol K}$

$\Delta S^\circ_{\text{sur}} = \frac{-\Delta H^\circ}{T} = \frac{-571 \text{ J/mol}}{298 \text{ K}} = -1.91 \text{ J/mol K}$

$\Delta S^\circ_{\text{tot}} = \Delta S^\circ + \Delta S^\circ_{\text{sur}} = 0 - 1.91 = -1.91 \text{ J/mol K}$

$\Delta S^\circ_{\text{tot}} = +1.94 \text{ J/mol K}$

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[TP] The plot shows how  $\ln(K)$  vs  $1/T$  for  $A \rightleftharpoons B$ . The standard free energy change of reaction,  $\Delta_r G^\circ$ , at room temperature is ...

75% 1.  $< 0$   
 13% 2.  $= 0$   
 13% 3.  $> 0$   
 0% 4. More information is required

$\ln(K) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$

$\Delta G^\circ = RT \ln(K)$   
 $= -RT \ln(K)$   
 $< 0$

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[TP] The plot shows how  $\ln(K)$  vs  $1/T$  for  $A \rightleftharpoons B$ . The standard enthalpy change of reaction,  $\Delta_r H^\circ$ , is ...

69% 1.  $< 0$   
 0% 2.  $= 0$   
 31% 3.  $> 0$   
 0% 4. More information is required

$\ln(K) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$

$\text{slope} = -\frac{\Delta H^\circ}{R} > 0$   
 $\Delta H^\circ < 0$

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[TP] The plot shows how  $\ln(K)$  vs  $1/T$  for  $A \rightleftharpoons B$ . The standard entropy change of reaction,  $\Delta_r S^\circ$ , is ...

69% 1.  $< 0$   
 0% 2.  $= 0$   
 31% 3.  $> 0$   
 0% 4. More information is required

$\ln(K) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$

at  $T \rightarrow \infty$   
 $\ln(K) = \frac{\Delta S^\circ}{R} < 0$

$\lim_{T \rightarrow \infty} \frac{1}{T} = 0$

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[TP] For the reaction  $2 \text{H}_2\text{O}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{O}_2(g)$ , what temperature range will result in the **greatest amount of products**? Hint: Sketch  $\ln(K)$  vs  $1/T$ .

27% 1. Very low  $T$

73% 2. Very high  $T$

0% 3. The amount will be the same at all  $T$

0% 4. More information needed

$\Delta H^\circ > 0$   
 $\Delta S^\circ > 0$ ,  $\ln(K)$  at  $1/T \rightarrow 0$  will be  $> 0$

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13