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[TP] For the reaction  $2A + B \rightarrow 2C$ , at a certain time the value of its **reaction quotient** is  $Q = 7$ . This means the value of the **equilibrium constant** for the reaction is ...

16% 1.  $< 7$   
 40% 2. 7  
 23% 3.  $> 7$   
 21% 4. Further information needed

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Lecture 21 CH131 Fall 2020  
 Tuesday, December 18, 2020

- Predicting direction of change
- Calculate equilibration using an ICE table
- Equilibrium calculation examples
- Effect of temperature on equilibrium:  $\Delta G = RT \ln(Q/K) = \Delta H - T\Delta S$

Final lecture: Complete: Effect of temperature on equilibrium; Course evaluation; Ch15: Acid-base equilibria

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Predicting direction of change

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[TP] For the reaction  $2A + B \rightarrow 2C$ , at a certain time the value of its **reaction quotient** is  $Q = 7$ . This means the value of the **equilibrium constant** for the reaction is ...

✓ 13% 1.  $< 7$   
 ✓ 40% 2. 7  
 ✓ 27% 3.  $> 7$   
 19% 4. Further information needed

$\frac{[C]^2}{[A]^2[B]} = 7$

$Q < K$   
 $Q = K$   
 $Q > K$

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[TP] The value of the **equilibrium constant** for the gas-phase reaction  
 $2A + B \rightarrow C$  is  $K = 10$ .

At a certain time, the partial pressures are A, B and C are, respectively, 1 bar, 1 bar and 2 bar. The value of the **reaction quotient** is  $Q = \dots$

65% 1. 2  
 29% 2. 10  
 6% 3. Further information needed

$$\frac{[C]_e}{[A]_e^2 [B]_e} = 10$$

$$\frac{2}{(1)^2 (1)} = 2$$

$Q < K$

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[TP] The value of the **equilibrium constant** for the gas-phase reaction  
 $2A + B \rightarrow C$  is  $K = 10$ .

At a certain time, the partial pressures are A, B and C are, respectively, 0.2 bar, 1 bar and 4 bar. The value of the reaction quotient is  $Q = \dots$

3% 1. 0.04  
 15% 2. 4  
 16% 3. 10  
 63% 4. 100  
 2% 5. None of these

$$Q = \frac{4}{(0.2)^2 (1)} = \frac{4}{0.04} = 100$$

$Q > K$  too much product, too little reactant

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[TP] The value of the **equilibrium constant** for the gas-phase reaction  
 $2A + B \rightarrow C$  is  $K = 10$ .

At a certain time, the partial pressures are A, B and C are such that the value of the reaction quotient is  $Q = 100$ . As time passes, the value of  $Q$  will ...

17% 1. increase  
 26% 2. stay the same  
 57% 3. decrease

$Q > K$

$Q = \frac{\text{products}}{\text{reactants}}$

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[TP] The value of the **equilibrium constant** for the gas-phase reaction  
 $2A + B \rightarrow C$  is  $K = 10$ .

At a certain time, the partial pressures are A, B and C are such that the value of the reaction quotient is  $Q = 6$ . As time passes, the value of  $Q$  will ...

80% 1. increase  
 17% 2. stay the same  
 3% 3. decrease

$Q$  vs  $K$  tells what change is necessary to get to equilibrium.

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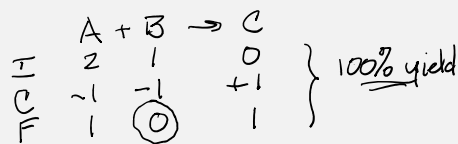
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## Calculate equilibration using an ICE table

When the equilibrium constant is neither very big or very small, the calculation of equilibrium amounts must be done exactly.

$$K = 3 = \frac{[C]}{[A][B]}$$



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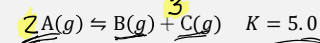
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## Calculate equilibration using an ICE table



	A(g)/M	B(g)/M	C(g)/M
Initial	3.0	2.0	1.0
Change	-2x	+x	+3x
Equilibrium	3.0-2x	2+x	1.0+3x

$$Q = \frac{(2.0)(1.0)}{(3.0)^2} = \frac{2.0}{9.0} < K$$

$$K = 5.0 = \frac{(2+x)(1.0+3x)^3}{(3.0-2x)^2}$$

*Solve numerically*

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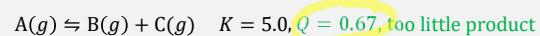
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## Calculate equilibration using an ICE table



	A(g)/M	B(g)/M	C(g)/M
Initial	3.0	2.0	1.0
Change	-x	+x	+x
Equilibrium			

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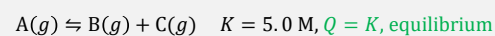
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## Calculate equilibration using an ICE table



	A(g)/M	B(g)/M	C(g)/M
Initial	3.0	2.0	1.0
Change	-x	+x	+x
Equilibrium	3.0-x	2.0+x	1.0+x

$$K = \frac{[B][C]}{[A]} = \frac{(2.0+x)(1.0+x)}{(3.0-x)}$$

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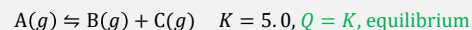
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## Calculate equilibration using an ICE table



	A(g)/M	B(g)/M	C(g)/M
Initial	3.0	2.0	1.0
Change	-x	+x	+x
Equilibrium	1.6	3.4	2.4

$$K = \frac{[B][C]}{[A]} = \frac{(2.0+x)(1.0+x)}{(3.0-x)} \rightarrow x = 1.4$$

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## Practice: Problem 14.25

	SO <sub>2</sub> Cl <sub>2</sub> (g)	SO <sub>2</sub> (g)	Cl <sub>2</sub> (g)	Q
I	0.720	0	0	0
C	-x	+x	+x	
E	0.720-x	x	x	

$$\text{Total pressure} = 0.720 - x + x + x = 0.720 + x = 1.30 \text{ atm}$$

$$x = 1.30 - 0.720 = 0.58 \text{ atm}$$

$$K = \frac{x^2}{0.720 - x} = \frac{(0.58)^2}{0.720 - 0.58}$$

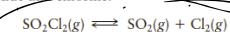
$$3.17 \text{ g} \times \frac{1 \text{ mole}}{M_{\text{SO}_2\text{Cl}_2}} = m$$

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$$Q = \frac{P_{\text{SO}_2} P_{\text{Cl}_2}}{P_{\text{SO}_2\text{Cl}_2}} = \frac{0}{0.720} = 0$$

25. Sulfur chloride (SO<sub>2</sub>Cl<sub>2</sub>) is a colorless liquid that boils at 69°C. Above this temperature, the vapors dissociate into sulfur dioxide and chlorine:



This reaction is slow at 100°C, but it is accelerated by the presence of some FeCl<sub>3</sub> (which does not affect the final position of the equilibrium). In an experiment, 3.174 g of SO<sub>2</sub>Cl<sub>2</sub> and a small amount of solid FeCl<sub>3</sub> are put into an evacuated 1.000-L flask, which is then sealed and heated to 100°C. The total pressure in the flask at that temperature is found to be 1.30 atm.

- (a) Calculate the partial pressure of each of the three gases present.  
(b) Calculate the equilibrium constant at this temperature.

$$P_{\text{SO}_2\text{Cl}_2} = \frac{nRT}{V} = \frac{mR}{M_{\text{SO}_2\text{Cl}_2} V} = \frac{3.174 \text{ g} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 373.15 \text{ K}}{1.000 \text{ L} \times 169.07 \text{ g mol}^{-1}} = 0.720 \text{ atm}$$

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## Practice: Problem 14.33

	N <sub>2</sub>	O <sub>2</sub>	NO	Q
I	0.41	0.59	0.22	>>K
C	+x	+x	-2x	
E	0.41+x	0.59+x	0.22-2x	

$$K = 4.2 \times 10^{-3} = \frac{(0.22-2x)^2}{(0.41+x)(0.59+x)}$$

$$K = \frac{4x^2}{0.52 \times 0.70} = 4.2 \times 10^{-3}$$

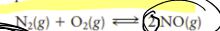
$$x = \sqrt{\frac{4.2 \times 10^{-3} \times 0.52 \times 0.70}{4}} = 2 \times 10^{-2}$$

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33. At 25°C, the equilibrium constant for the reaction



is  $4.2 \times 10^{-3}$ . Suppose a container is filled with nitrogen (at an initial partial pressure of 0.41 atm), oxygen (at an initial partial pressure of 0.59 atm), and nitrogen oxide (at an initial partial pressure of 0.22 atm). Calculate the partial pressures of all three gases after equilibrium is reached at this temperature.

	N <sub>2</sub>	O <sub>2</sub>	NO
I	0.41	0.59	0.22
R I	0.41+0.11	0.59+0.11	0
C	-x	-x	+2x
E	0.52-x	0.70-x	2x
	0.52	0.70	2x

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## Practice: Problem 14.41

	NH <sub>3</sub>	HCl	NH <sub>4</sub> Cl(s)	Q
I	0.80	0	some	>>K
C	+x	+x	-x	
E	0.80+x	x	some	

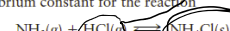
	NH <sub>3</sub>	HCl	NH <sub>4</sub> Cl(s)
I	1.50	0	some
C	+x	+x	-x
E	1.50+x	x	some

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

41. The equilibrium constant for the reaction



at 340°C is  $K = 4.0$ .

- (a) If the partial pressure of ammonia is  $P_{\text{NH}_3} = 0.80 \text{ atm}$  and solid ammonium chloride is present, what is the equilibrium partial pressure of hydrogen chloride at 340°C?  
(b) An excess of solid NH<sub>4</sub>Cl is added to a container filled with ammonia at 340°C and a pressure of 1.50 atm. Calculate the pressures of NH<sub>3</sub>(g) and HCl(g) reached at equilibrium.

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

$$\text{Solve for } x: x = 0.24$$

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### Q versus K is the key to spontaneity

If  $Q < K$ , product must form to get to equilibrium, so **spontaneous**,  $\frac{Q}{K} < 1, \ln(<1) < 0 \rightarrow \Delta G < 0$

If  $Q > K$ , reactants must form to get to equilibrium, so **nonspontaneous**,  $\frac{Q}{K} > 1, \ln(>1) > 0 \rightarrow \Delta G > 0$

This means  $\Delta G$  is proportional to  $\ln(Q/K)$ .

The constant of proportionality turns out to be  $RT$ :

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

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### Effect of T on K

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

$$2 \text{NH}_3(\text{g}) + \frac{5}{2} \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$$

using data in Appendix D.

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

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

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

Example: 14.13

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

$$K = \exp\left[-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}\right]$$

$\ln(Q/K) = \ln(Q) - \ln(K)$   
 $\ln(K) = -\ln(K)$

$\Delta H^\circ$   
 $\Delta S^\circ$

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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  $1/T = 0$  ( $T = \infty$ )

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

$$y = mx + b$$

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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,  $\Delta_r G$ , at room temperature is ...

44% 1.  $< 0$   
 20% 2.  $= 0$   
 36% 3.  $> 0$   
 1% 4. More information is required

$K(T)$

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

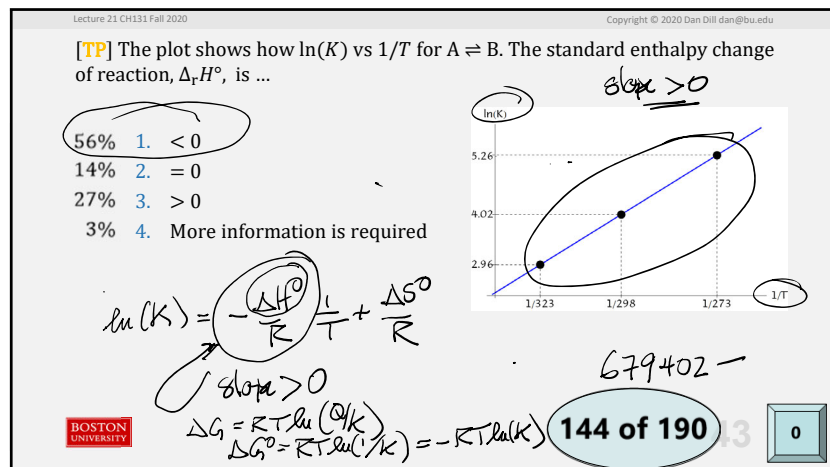
$\Delta G^\circ = RT \ln(1/K)$   
 $= -RT \ln K$   
 $\ln K = -\frac{\Delta G^\circ}{RT} = \boxed{+4.02}$

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