

Show all work with units and correct significant figures. Leave pure solids and liquids out of every Q and K expression. When you explain a shift, compare Q to K.

Equations	$K_c = [C]^c[D]^d / ([A]^a[B]^b)$	$K_p = (P_C)^c(P_D)^d / ((P_A)^a(P_B)^b)$	Q < K: net forward Q > K: net reverse	$K_{sp} = [M^{y+}]^x[X^{x-}]^y$ for $M_xX_y(s)$
	Reverse a reaction: $K_{new} = 1/K$	Multiply coefficients by n: $K_{new} = K^n$	Add reactions: $K_{overall} = K_1 \times K_2$	Only temperature changes the value of K

Part 1. Reversible Reactions and Dynamic Equilibrium (Topics 7.1 to 7.2)

1. A sealed flask starts with 0.100 M $N_2O_4(g)$ and no $NO_2(g)$. The reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is followed over time. Curves X and Y are shown.

- (a) Which curve, X or Y, represents NO_2 ? Justify your answer with the change in each concentration.

Curve X is NO_2 . Curve Y falls by 0.040 M while curve X rises by 0.080 M. The coefficients show that 2 NO_2 form for every 1 N_2O_4 used, so the species that changes twice as much is NO_2 .

- (b) At what time is equilibrium first reached? Describe the forward and reverse rates at 40 s.

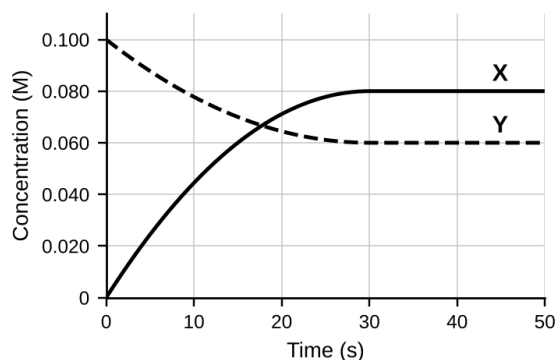
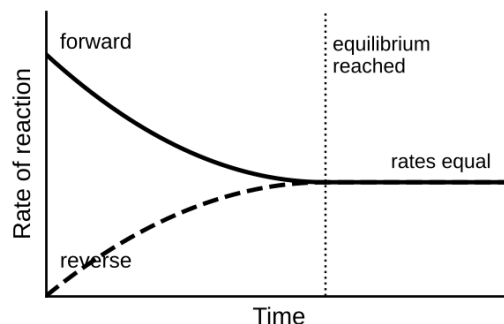
Equilibrium is reached at **30 s**, when both curves become flat. At 40 s the forward and reverse reactions are still happening, but at **equal rates**, so there is no net change.

- (c) Calculate K_c for this reaction.

$$K_c = [NO_2]^2 / [N_2O_4] = (0.080)^2 / 0.060 = \mathbf{0.11}$$

2. On the axes, sketch the rate of the forward reaction and the rate of the reverse reaction for the flask in Question 1, from the moment N_2O_4 is added until after equilibrium. Label each curve.

The forward rate starts high and decreases as N_2O_4 is used up. The reverse rate starts at zero because no NO_2 is present, then increases. The two curves meet at equilibrium and stay equal and constant after that.



3. At one moment during the reaction $A(g) \rightleftharpoons B(g)$, the forward rate is 3.2×10^{-3} M/s and the reverse rate is 1.1×10^{-3} M/s. Is the system at equilibrium? In which direction is there a net change, and is Q greater than or less than K? Explain.

No. The forward rate is greater than the reverse rate, so there is a **net conversion of A to B** (net forward). A net forward reaction means Q is still **less than K**, so Q increases until it equals K.

4. Decide whether each statement is true or false. Rewrite each false statement so it is true.

Statement	T or F	Correction (if false)
At equilibrium, the concentrations of reactants and products are equal.	F	The concentrations are constant , not necessarily equal.
At equilibrium, the forward and reverse reactions stop.	F	Both reactions continue at equal rates . Equilibrium is dynamic.
In a sealed bottle of water at constant temperature, evaporation stops once the vapor pressure stays constant.	F	Evaporation and condensation both continue at equal rates.
Equilibrium can be reached starting from only reactants or from only products.	T	

The key idea: equilibrium means constant amounts and equal rates, not equal amounts and stopped reactions.

Part 2. Writing Q and K Expressions (Topic 7.3)

5. Write the equilibrium expression asked for in each row. Then explain why $\text{CaCO}_3(\text{s})$ and $\text{CaO}(\text{s})$ do not appear in the second expression, even though both must be present for the system to be at equilibrium.

Reaction	Write	Expression
$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$	K_p	$(P_{\text{SO}_3})^2 / ((P_{\text{SO}_2})^2 P_{\text{O}_2})$
$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	K_p	P_{CO_2}
$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$	K_c	$[\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3]$
$\text{Ag}_2\text{CrO}_4(\text{s}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$	K_{sp}	$[\text{Ag}^+]^2[\text{CrO}_4^{2-}]$

Solids (CaCO_3 , CaO , Ag_2CrO_4) and the pure liquid H_2O are left out. In K_p , write the products' pressures on top, each raised to its coefficient.

The concentration of a pure solid depends only on its density, not on how much is present. Adding more CaCO_3 or CaO does not change Q, so solids are left out of the expression.

Part 3. Calculating K and Q (Topics 7.4, 7.5, and 7.7)

6. For $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ at 430°C , an equilibrium mixture contains $[\text{H}_2] = 0.0110\text{ M}$, $[\text{I}_2] = 0.0110\text{ M}$, and $[\text{HI}] = 0.0786\text{ M}$. Calculate K_c .

$$K_c = [\text{HI}]^2 / ([\text{H}_2][\text{I}_2]) = (0.0786)^2 / ((0.0110)(0.0110)) = \mathbf{51.1}$$

7. For $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, the equilibrium partial pressures are $P_{\text{PCl}_5} = 0.875\text{ atm}$, $P_{\text{PCl}_3} = 0.463\text{ atm}$, and $P_{\text{Cl}_2} = 0.463\text{ atm}$. Calculate K_p .

$$K_p = (P_{\text{PCl}_3})(P_{\text{Cl}_2}) / P_{\text{PCl}_5} = (0.463)(0.463) / 0.875 = \mathbf{0.245}$$

8. Use $K_c = 51.1$ for $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ from Question 6. A flask at the same temperature contains $[\text{H}_2] = 0.020\text{ M}$, $[\text{I}_2] = 0.020\text{ M}$, and $[\text{HI}] = 0.200\text{ M}$. Calculate Q, then state which direction the reaction proceeds and whether $[\text{HI}]$ increases or decreases.

$$Q = (0.200)^2 / ((0.020)(0.020)) = \mathbf{1.0 \times 10^2}$$

$Q > K$ ($100 > 51.1$), so the reaction proceeds in the **reverse** direction. HI is consumed, so **[HI] decreases** until $Q = K$.

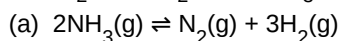
9. For each reaction, describe what the equilibrium mixture mostly contains.

Reaction	K	Mostly reactants, mostly products, or large amounts of both?
$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$	3×10^{81}	Mostly products (essentially goes to completion)
$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ at 25°C	4×10^{-31}	Mostly reactants (barely proceeds)
$\text{CH}_3\text{COOH}(\text{aq}) + \text{CH}_3\text{OH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COOCH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	4	Large amounts of both

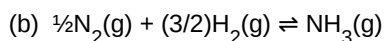
When K is much greater than 1, products dominate. When K is much less than 1, reactants dominate. When K is near 1, both are present in significant amounts.

Part 4. Manipulating K (Topic 7.6)

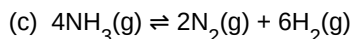
10. For $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, $K_c = 0.50$ at a certain temperature. Find K_c for each reaction at the same temperature.



Reversed, so K is inverted: $K = 1/0.50 = 2.0$

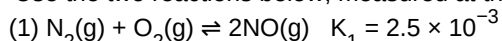
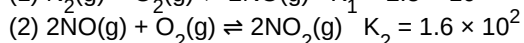
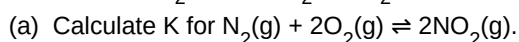


Coefficients multiplied by $\frac{1}{2}$, so $K = (0.50)^{1/2} = 0.71$

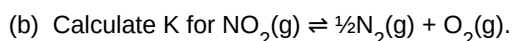


Reversed and doubled: $K = (1/0.50)^2 = 4.0$

11. Use the two reactions below, measured at the same high temperature.



Adding (1) and (2) cancels 2NO, so $K = K_1 \times K_2 = (2.5 \times 10^{-3})(1.6 \times 10^2) = 0.40$



This reverses the reaction in (a) and multiplies it by $\frac{1}{2}$: $K = (1/0.40)^{1/2} = 1.6$

Part 5. Finding Equilibrium Concentrations (Topic 7.7)

12. For $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$, $K_c = 4.00$ at a certain temperature. A flask starts with 0.200 M CO and 0.200 M H_2O and no products. Complete the ICE table and find every equilibrium concentration.

	CO	H_2O	CO_2	H_2
Initial (M)	0.200	0.200	0	0
Change (M)	-x	-x	+x	+x
Equilibrium (M)	$0.200 - x$	$0.200 - x$	x	x

$4.00 = x^2 / (0.200 - x)^2$. Take the square root of both sides: $2.00 = x / (0.200 - x)$.

$x = 0.400 - 2.00x$, so $3.00x = 0.400$ and $x = 0.133$

$[\text{CO}_2] = [\text{H}_2] = 0.133 \text{ M}$ and $[\text{CO}] = [\text{H}_2\text{O}] = 0.200 - 0.133 = 0.067 \text{ M}$

13. At 1500 K, $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ has $K_c = 1.0 \times 10^{-5}$. A flask starts with 0.80 M N_2 and 0.20 M O_2 . Calculate [NO] at equilibrium. Explain why you can treat x as small.

Equilibrium: $[\text{N}_2] = 0.80 - x$, $[\text{O}_2] = 0.20 - x$, $[\text{NO}] = 2x$. K is very small, so x is tiny compared with 0.80 and 0.20, and $0.80 - x \approx 0.80$ and $0.20 - x \approx 0.20$.

$1.0 \times 10^{-5} = (2x)^2 / ((0.80)(0.20))$, so $4x^2 = 1.6 \times 10^{-6}$ and $x = 6.3 \times 10^{-4} \text{ M}$

$[\text{NO}] = 2x = 1.3 \times 10^{-3} \text{ M}$. Check: x is only 0.3% of 0.20 M, so the approximation is valid.

14. A rigid container at constant temperature is filled with NOCl(g) at 1.00 atm. When $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$ reaches equilibrium, $P_{\text{Cl}_2} = 0.120$ atm. Find the other equilibrium pressures and calculate K_p .

Cl_2 increased by 0.120 atm, so NO increased by $2(0.120) = 0.240$ atm and NOCl decreased by 0.240 atm.

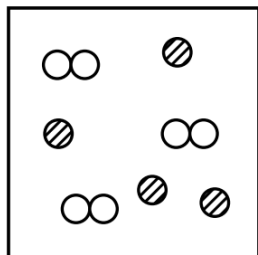
$P_{\text{NO}} = 0.240$ atm, $P_{\text{NOCl}} = 1.00 - 0.240 = 0.760$ atm

$K_p = (P_{\text{NO}})^2 P_{\text{Cl}_2} / (P_{\text{NOCl}})^2 = (0.240)^2(0.120) / (0.760)^2 = \mathbf{0.0120}$

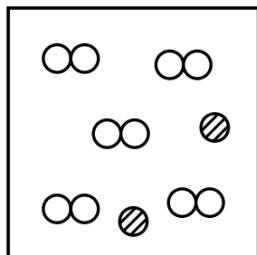
Part 6. Particle Representations of Equilibrium (Topic 7.8)

15. The diagrams show the reaction $\text{X}_2\text{(g)} \rightleftharpoons 2\text{X(g)}$ at one temperature.

Box 1 (at equilibrium)



Box 2 (another mixture)



$\text{O} = \text{X}_2$ $\text{O} = \text{X}$ Each particle = 0.10 mol. Each box = 1.0 L.

- (a) Use Box 1 to calculate K_c .

Box 1 has 3 X_2 and 4 X . $[\text{X}_2] = 3(0.10 \text{ mol})/1.0 \text{ L} = 0.30 \text{ M}$ and $[\text{X}] = 0.40 \text{ M}$. $K_c = [\text{X}]^2 / [\text{X}_2] = (0.40)^2 / 0.30 = \mathbf{0.53}$

- (b) Is Box 2 at equilibrium? If not, which way will it shift? Support your answer with Q .

Box 2 has 5 X_2 and 2 X : $Q = (0.20)^2 / 0.50 = 0.080$. $Q < K$, so Box 2 is **not at equilibrium**. It shifts **forward**: some X_2 breaks apart into X until $Q = K$.

Part 7. Le Châtelier's Principle (Topics 7.9 to 7.10)

16. Consider $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$, $\Delta H^\circ = +57 \text{ kJ/mol}_{\text{rxn}}$. Complete the table for each change made to a mixture at equilibrium.

Change	Shift (left, right, or none)	Value of K (increases, decreases, or no change)
Add more N_2O_4	Right	No change
Remove some NO_2	Right	No change
Raise the temperature	Right	Increases
Decrease the volume at constant temperature	Left	No change
Add argon gas at constant volume	None	No change

The forward reaction is endothermic, so heating shifts right and increases K . Only temperature changes K .

Smaller volume favors the side with fewer gas particles (1 N_2O_4 versus 2 NO_2), so it shifts left. Argon at constant volume does not change any partial pressure, so Q still equals K .

17. For the same mixture, the volume is suddenly cut in half at constant temperature, so every concentration doubles. Show what happens to Q_c , and use it to explain the direction of the shift.

$Q_c = (2[\text{NO}_2])^2 / (2[\text{N}_2\text{O}_4]) = 4[\text{NO}_2]^2 / (2[\text{N}_2\text{O}_4]) = 2K_c$. Now $Q > K$, so the reaction shifts **left**, converting NO_2 into N_2O_4 until Q equals K again.

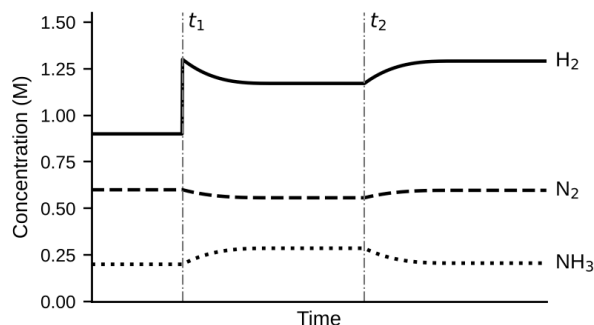
18. The graph shows $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ($\Delta H^\circ < 0$) as two different changes are made at t_1 and t_2 .

(a) What change was made at t_1 ? Explain why $[\text{N}_2]$ decreases after t_1 .

H₂ was added (its concentration jumps instantly). Q becomes less than K , so the reaction shifts right, which uses up N_2 as well as some of the added H_2 .

(b) At t_2 the temperature was changed. Was it raised or lowered? Justify your answer.

Raised. No concentration jumps at t_2 , which fits a temperature change. $[\text{NH}_3]$ decreases, so the reaction shifted left. For an exothermic reaction, heating shifts left and decreases K .



19. A solution contains the equilibrium $\text{CoCl}_4^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq})$. CoCl_4^{2-} is blue and $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is pink. Circle the color change for each action, then answer the question.

(a) Concentrated HCl is added (more Cl^-). more blue / more pink

More blue. Adding Cl^- (a product) makes $Q > K$, so the reaction shifts left.

(b) AgNO_3 is added, which removes Cl^- as $\text{AgCl}(\text{s})$. more blue / more pink

More pink. Removing Cl^- makes $Q < K$, so the reaction shifts right.

(c) Water is added until the volume doubles. more blue / more pink

More pink. H_2O is a pure liquid, so it is not in Q . Halving every ion concentration multiplies Q by $(\frac{1}{2})(\frac{1}{2})^4 / (\frac{1}{2}) = 1/16$, so $Q = K/16$. $Q < K$, so the reaction shifts right.

(d) The solution turns blue when it is heated. Is the forward reaction endothermic or exothermic? Explain.

Exothermic. Heating shifts the reaction left (toward blue CoCl_4^{2-}), which happens when heat is a product of the forward reaction.

Part 8. Solubility Equilibria and the Common-Ion Effect (Topics 7.11 to 7.12)

20. The molar solubility of PbI_2 in pure water is 1.3×10^{-3} M. Calculate K_{sp} for PbI_2 .

$\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq})$. $[\text{Pb}^{2+}] = s$ and $[\text{I}^-] = 2s$. $K_{\text{sp}} = s(2s)^2 = 4s^3 = 4(1.3 \times 10^{-3})^3 = 8.8 \times 10^{-9}$

21. AgCl has $K_{\text{sp}} = 1.8 \times 10^{-10}$ and Ag_2CrO_4 has $K_{\text{sp}} = 1.1 \times 10^{-12}$.

(a) Calculate the molar solubility of each salt in pure water.

AgCl : $K_{\text{sp}} = s^2$, so $s = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5}$ M. Ag_2CrO_4 : $K_{\text{sp}} = (2s)^2(s) = 4s^3$, so $s = (1.1 \times 10^{-12} / 4)^{1/3} = 6.5 \times 10^{-5}$ M

(b) A student says AgCl is more soluble because its K_{sp} is larger. Do you agree? Explain.

Disagree. Ag_2CrO_4 has the larger molar solubility. K_{sp} values can only be compared directly for salts that produce the same number of ions per formula unit.

22. Equal volumes of 2.0×10^{-4} M AgNO_3 and 2.0×10^{-4} M NaCl are mixed. Will AgCl precipitate? ($K_{\text{sp}} = 1.8 \times 10^{-10}$) Show your reasoning with Q .

Mixing equal volumes halves each concentration: $[\text{Ag}^+] = [\text{Cl}^-] = 1.0 \times 10^{-4}$ M. $Q = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8}$. $Q > K_{\text{sp}}$, so **yes, AgCl precipitates.**

23. Calculate the molar solubility of AgCl in 0.10 M NaCl. How does it compare with its solubility in pure water? Explain the difference using Le Châtelier's principle.

$[\text{Cl}^-] = 0.10 + s \approx 0.10 \text{ M}$. $K_{\text{sp}} = (s)(0.10)$, so $s = 1.8 \times 10^{-10} / 0.10 = \mathbf{1.8 \times 10^{-9} \text{ M}}$.

That is about 7000 times less than $1.3 \times 10^{-5} \text{ M}$ in pure water. The Cl^- already present shifts $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ to the left, so less solid dissolves.

24. The molar solubility of CaF_2 in 0.020 M NaF is measured as $9.8 \times 10^{-8} \text{ M}$. Calculate K_{sp} for CaF_2 .

$[\text{Ca}^{2+}] = s = 9.8 \times 10^{-8} \text{ M}$ and $[\text{F}^-] = 0.020 + 2s \approx 0.020 \text{ M}$. $K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2 = (9.8 \times 10^{-8})(0.020)^2 = \mathbf{3.9 \times 10^{-11}}$

25. A student finds K_{sp} for $\text{Ca}(\text{OH})_2$ by titrating the OH^- in a saturated solution, then sets $s = [\text{OH}^-]/2$ and uses $K_{\text{sp}} = 4s^3$. By mistake, the student made the saturated solution with 0.010 M CaCl_2 instead of pure water. Will the calculated K_{sp} be too high, too low, or correct? Explain.

Too low. The Ca^{2+} from CaCl_2 is a common ion, so less $\text{Ca}(\text{OH})_2$ dissolves and the measured $[\text{OH}^-]$ is smaller. The student's s and calculated K_{sp} are therefore smaller than the true value. (The true K_{sp} does not change; only the measured solubility does.)