E19 SOLUBILITY, COMPLEX FORMATION AND COMPETING EQUILIBRIA
Involving species containing silver(I)

Complex Stability Constant
A complex is usually a metal cation (M) surrounded by ligands (L) that are coordinated to the ion. An important property of any complex is that in a solution, it is in equilibrium with its constituents:

$$M(aq) + nL(aq) \rightleftharpoons ML_n(aq)$$

Here a metal cation is acting as a Lewis acid or electron-pair acceptor towards a ligand, such as water, or other Lewis bases, *eg* NH_3, present in solution.

For any complex, the concentrations of complex and constituents are related by the expression:

$$K_{stab} = \frac{[ML_n]}{[M][L]^n}$$

This equilibrium-constant is the stability-constant, *K*stab.

For example, for the complexes $[Ni(NH_3)_6]^{2+}$, $[NiCl_4]^{2-}$ and $[Ni(H_2O)_6]^{2+}$, the form of K_{stab} is given in the table below.

Complex	***K*stab**
$[Ni(NH_3)_6]^{2+}$	$K_{stab} = \frac{[[Ni(NH_3)_6]^{2+}]}{[Ni^{2+}][NH_3]^6}$
$[NiCl_4]^{2-}$	$K_{stab} = \frac{[[NiCl4]^{2-}]}{[Ni^{2+}][Cl^-]^4}$
$[Ni(H_2O)_6]^{2+}$	$K_{stab} = \frac{[[Ni(H_2O)_6]^{2+}]}{[Ni^{2+}][H_2O]^6}$

A meaningful comparison of stability-constants can only be made if the constants are of the same form. As $[Ni(NH_3)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$ both involve six ligands binding to the metal ion, the stability constants can be directly compared. As $[NiCl_4]^{2-}$ has only four ligands, its stability constant has a different form and its value cannot be compared to that of the other complexes.

The complex that has the *larger* K_{stab} is more stable so has the *lower* concentration of free $Ni^{2+}(aq)$ ions.

Solubility Product Constant
When a solid salt $M_aX_b(s)$ of low solubility is at equilibrium with its ions in solution,

$$M_aX_b(s) \rightleftharpoons aM(aq) + bX(aq)$$

the *product* of the concentrations of the ions in the solution is found to be constant:

$$K_{sp} = [M]^a[X]^b$$

The constant is known as the solubility product constant, *K*sp or simply the solubility product..

When the solution is unsaturated or supersaturated, there is no equilibrium and the product is known as the ionic product and is not a constant.

A meaningful comparison of solubility product-constants can only be made if the constants are of the same form. A large value of the solubility constant corresponds to a high concentrations of ions in solution and so a high solubility.

Common Ion Effect

As the solubility product is a constant, its value must be maintained whenever the ions are present in solution. Consider the dissolution of the sparingly soluble silver(I) salt, AgCl:

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

The solubility product constant is

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

If NaCl(s) is added, it will completely dissolve leading to an increase in the chloride ion concentration. As the product of the silver and chloride ion concentrations is a constant, the concentration of silver ions must decrease to compensate. Thus, addition of the *common ion* Cl^{-}, leads to the precipitation of metallic silver.