



The Stubborn Equilibrium

*Chemical equilibrium and Le Chatelier's principle:
why nature always pushes back*

INSTITUTE Prodigy Educlasses	CLASS XI (Class 11)	BOARD CBSE / ISC / WBCHSE
TOPIC Chemical Equilibrium (Le Chatelier's Principle)	CHAPTER / UNIT Equilibrium	FACULTY Surajit Sir (Chemistry)

Twist the cap of a fizzy drink and listen. Hiss! Bubbles rush up. Why?

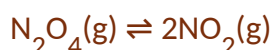
Before you opened it, the bottle was at peace. Dissolved carbon dioxide and gaseous carbon dioxide were swapping places at equal rates, so nothing seemed to change. Opening the cap suddenly dropped the pressure, and the system did the only thing it could: it pushed back by releasing more gas. In 1884, a French chemist named Henry Louis Le Chatelier realised that **every system at equilibrium behaves this way**. Poke it, and it pokes back. That one idea helps chemists squeeze ammonia out of thin air, decide how much acid to make in a factory, and explain why mountaineers feel breathless. Let us see how.

The Mystery Box: 4 questions to keep in your head

- If a reaction never 'finishes', how do we know when it is done?
- Why does a blue cobalt solution turn pink in ice water and blue again in hot water?
- How can a factory make a lot of ammonia when the reaction itself stops at just 15 to 20% conversion?
- Why does high pressure help some reactions, but does nothing for others?

1 Reactions that refuse to finish

Burn a match and the reaction goes one way only. But many reactions are **reversible**: the products can react to give back the reactants. Take the classic pair N_2O_4 (pale) and NO_2 (brown gas):



Put N_2O_4 in a closed flask and it starts breaking into NO_2 , so the brown colour appears. As NO_2 builds up, it starts recombining. Eventually the flask reaches a point where **the rate of the forward reaction equals the rate of the reverse reaction**. The colour stops changing. This state is called **chemical equilibrium**.

Four things you must remember about equilibrium:

- **It is dynamic, not dead.** Both reactions carry on. Think of a busy metro platform where 100 people get off and 100 get on every minute. The crowd size looks constant, yet nobody is standing still.
- **It needs a closed system.** If a gas can escape, the reaction never settles.
- **Concentrations are constant, but not necessarily equal.** In Fig 1 we end up with 1.6 mol/L of HI and 0.2 mol/L of H_2 .
- **It can be approached from either side.** Start with pure reactants or pure products and the same equilibrium mixture appears (at the same temperature).

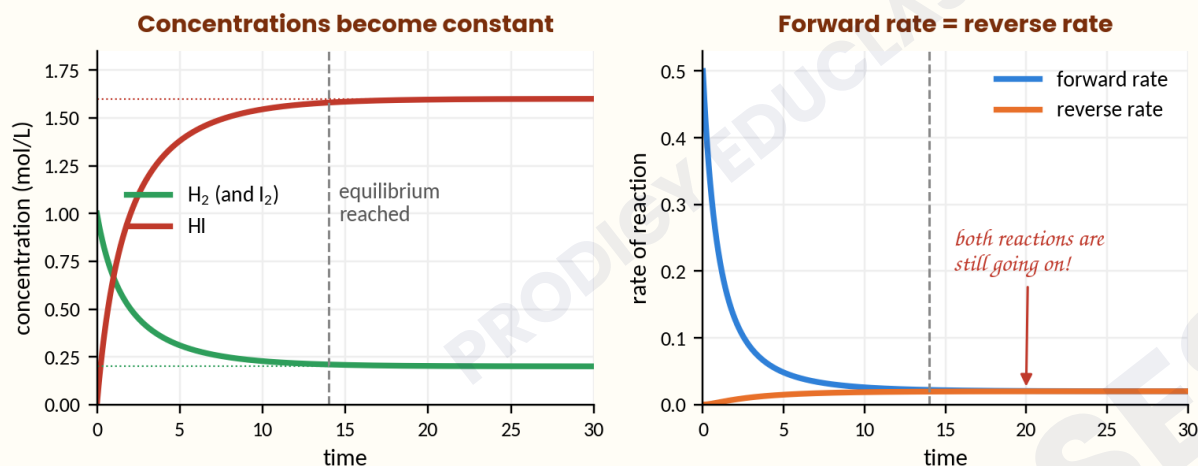


Fig 1. $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ starting from 1 mol/L each of H_2 and I_2 . The curves flatten when the two rates become equal.

⚠ Careful! Common Mistake

Many students write 'at equilibrium the concentrations of reactants and products are equal'. That is **wrong**. They are *constant*, and their ratio is fixed by K . A reaction can sit at equilibrium with 99% products or with 1% products.

2 The equilibrium constant K and the quotient Q

In 1864, the Norwegians Guldberg and Waage found a striking pattern. For a general reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$, the ratio below always settles to the same number at a given temperature:

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

For the Haber reaction, $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$, this gives $K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$. The coefficients become powers. Here are the ground rules:

Rule	Meaning
Pure solids and pure liquids are left out	Their concentration is constant. For $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, $K_c = [\text{CO}_2]$
Large K (much greater than 1)	Products are favoured at equilibrium
Small K (much less than 1)	Reactants are favoured at equilibrium
Reverse the reaction	K becomes $1 \div K$
Multiply the equation by n	K becomes K^n
Only temperature changes K	Concentration, pressure and catalysts do not
For gases, use pressures	$K_p = K_c (RT)^{\Delta n}$, where Δn = moles of gaseous products – moles of gaseous reactants

Worked example 1: finding K_c . 1 mol of H_2 and 1 mol of I_2 are heated in a 1 L vessel. At equilibrium the mixture contains 1.6 mol of HI.

HI = 1.6 mol, so 0.8 mol each of H_2 and I_2 reacted, leaving $[\text{H}_2] = [\text{I}_2] = 0.2 \text{ M}$. $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.6)^2}{(0.2 \times 0.2)} = 2.56 \div 0.04 = 64$.

Suppose the system is disturbed, or we simply do not know if a mixture is at equilibrium. We calculate the same ratio with the concentrations at that moment. This is called the **reaction quotient, Q** . Compare it with K and you

know which way the reaction will go:

Compare the reaction quotient Q with the equilibrium constant K

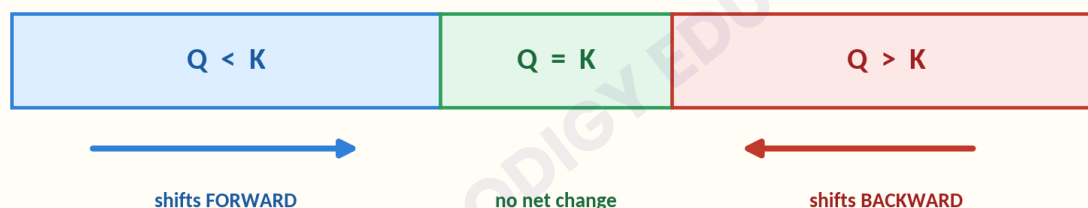


Fig 2. Q compared with K tells you the direction of change.

Worked example 2: which way will it go? To the mixture above (0.2 M H_2 , 0.2 M I_2 , 1.6 M HI) we add 0.4 mol of H_2 .

New $[\text{H}_2] = 0.6 \text{ M}$. $Q = (1.6)^2 \div (0.6 \times 0.2) = 2.56 \div 0.12 \approx 21.3$. Since $Q < K$ (64), the reaction shifts **forward**, making more HI .

Solving for the new equilibrium (let $y \text{ mol/L}$ react): $(1.6 + 2y)^2 \div ((0.6 - y)(0.2 - y)) = 64$ gives $y \approx 0.10$. So $[\text{HI}] \approx 1.80 \text{ M}$, $[\text{H}_2] \approx 0.50 \text{ M}$, $[\text{I}_2] \approx 0.10 \text{ M}$. Check: $1.80^2 \div (0.50 \times 0.10) \approx 64$. $\checkmark$. More HI , less I_2 , and the system has counteracted (but not completely undone) our addition of H_2 .

3 Le Chatelier's principle: the stubborn system

If a system at equilibrium is disturbed, it shifts in the direction that partly cancels the disturbance.

Think of equilibrium as a seesaw with a very stubborn child on each side. Add weight to one side and the seesaw tips, and the system spends its energy re-balancing. Notice the word *partly*. Nature counteracts the change but never erases it completely (in Worked example 2, the H_2 was 0.6 M at first and ended at 0.5 M , not back to 0.2 M).

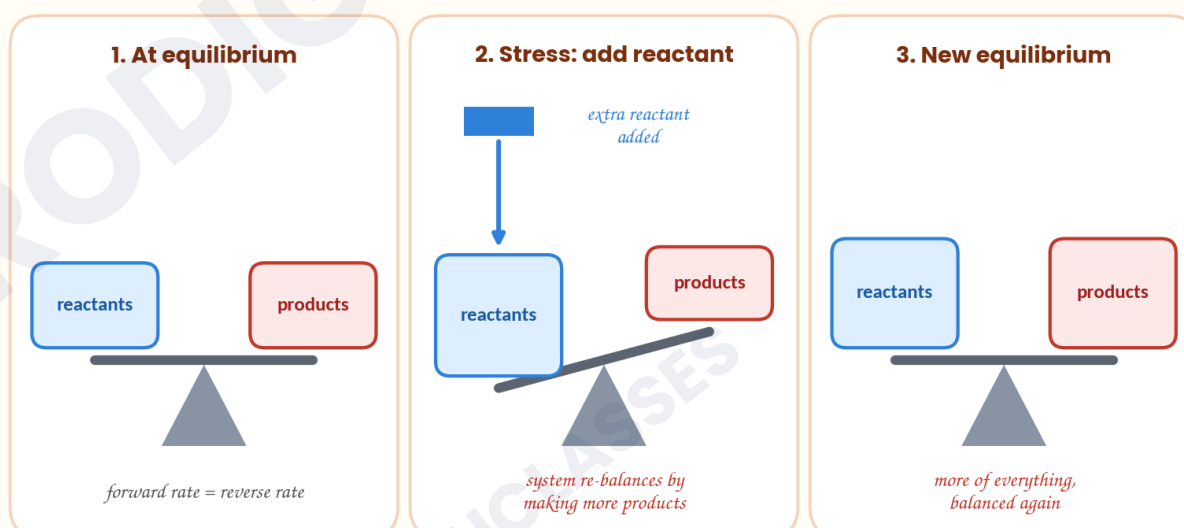


Fig 3. Adding a reactant tips the seesaw. The system re-balances by shifting forward, ending with more products.

Stress 1: change in concentration. Add a reactant or remove a product, and the system shifts *forward* to use up the extra reactant or replace the product. Add a product or remove a reactant, and it shifts *backward*. This is why industries keep removing the product as it forms: a lime kiln keeps blowing away CO_2 so that $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ keeps moving forward.

Stress 2: change in pressure or volume (only matters for gases). Increasing the pressure favours the side with **fewer moles of gas**. For $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$, we have 4 moles on the left and 2 on the right, so high pressure pushes the reaction forward. For $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$, it is 1 mole against 2, so high pressure pushes it backward. For $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$, we have 2 moles on both sides, so pressure makes **no difference**.

Stress 3: change in temperature. This is the only stress that changes the value of K. Heat behaves like a reactant or a product. For an **endothermic** forward reaction, heat is a reactant, so raising the temperature shifts it forward and K increases. For an **exothermic** forward reaction, heat is a product, so raising the temperature shifts it backward and K decreases.

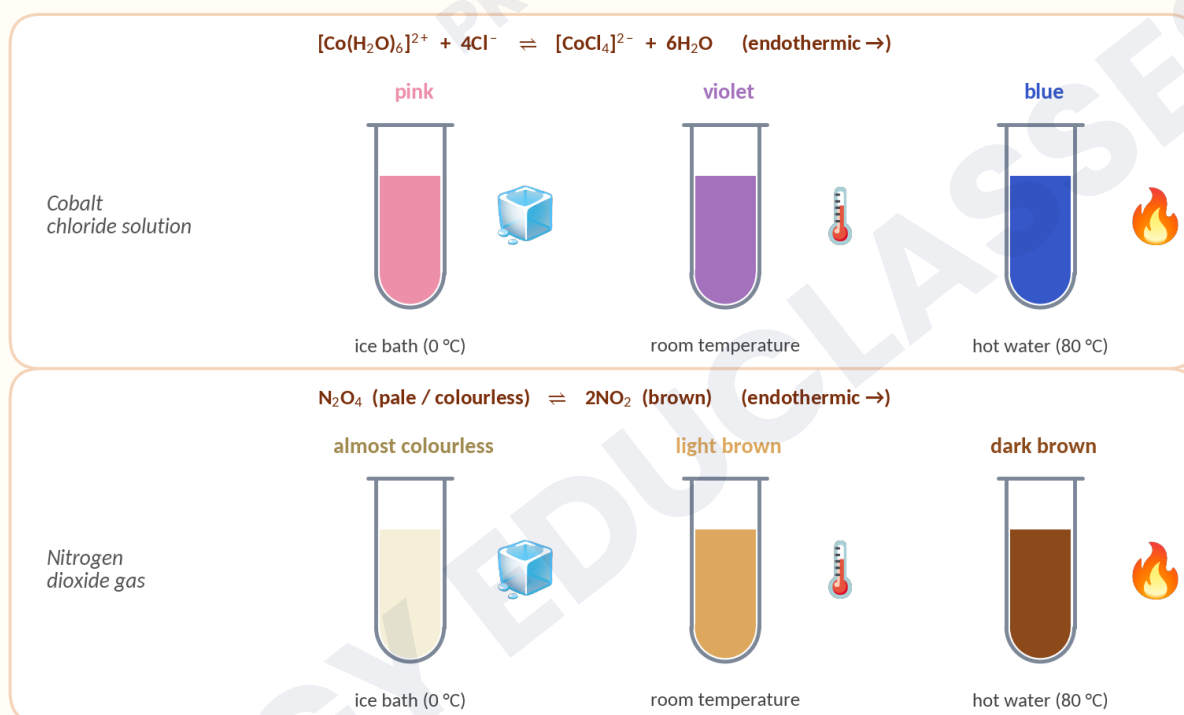


Fig 4. You can see Le Chatelier's principle. Heating an endothermic equilibrium pushes it towards the coloured product on the right.

Stress 4: adding a catalyst. A catalyst speeds up the forward and reverse reactions *equally*. It gets you to equilibrium faster, but the equilibrium position and K stay exactly the same.

Stress 5: adding an inert gas. At *constant volume*, the partial pressures of the reacting gases do not change, so there is no shift. At *constant pressure*, the volume must expand, which behaves like a pressure decrease, so the shift is towards the side with more moles of gas.

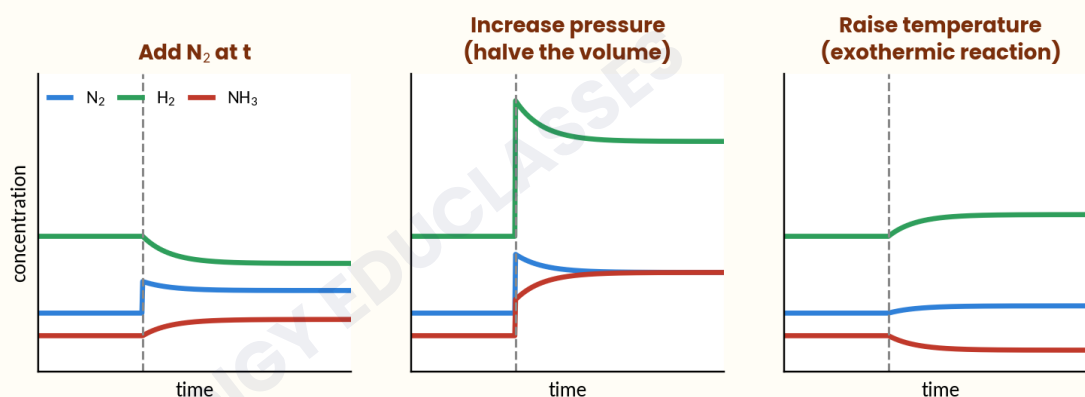


Fig 5. How the concentrations respond. Notice the instant jump at the disturbance, followed by a gradual re-adjustment.

Change applied	Shift	Does K change?
Add reactant / remove product	Forward $\rightarrow$	No
Add product / remove reactant	$\leftarrow$ Backward	No
Increase pressure (decrease volume)	Towards fewer moles of gas	No
Decrease pressure (increase volume)	Towards more moles of gas	No
Increase temperature	Towards the endothermic direction	Yes
Decrease temperature	Towards the exothermic direction	Yes
Add a catalyst	No shift; equilibrium reached faster	No
Add inert gas at constant volume	No shift	No

Did you know?

The syringe trick. Fill a glass syringe with brown $\text{NO}_2/\text{N}_2\text{O}_4$ gas and push the plunger in. The gas *instantly* becomes darker, because everything is squeezed into a smaller volume. Then, over a few seconds, the colour fades: the pressure pushed the equilibrium towards N_2O_4 (fewer moles of gas). First a jump, then a shift. Two-step thinking is exactly what examiners want.

Exam Alert

Always decide the shift **first**, then say what happens to K. Only temperature changes K. Also remember: Le Chatelier's principle tells you the **direction** of the shift, never the **speed**.

4 Chemistry in the factory: Haber and Contact

Le Chatelier's principle is not a classroom toy. Two of the world's most important chemicals depend on it. Let us use the tools of this note like an industrial chemist.

The Haber process (ammonia).



- **Pressure:** 4 moles $\rightarrow$ 2 moles. High pressure favours ammonia. Industry uses about **200 atm**.
- **Temperature:** the reaction is exothermic, so low temperature would give a higher yield. But at low temperature the reaction is painfully slow.
- **The compromise:** about **450 to 500 °C** with an **iron catalyst** (with promoters like Al_2O_3 and K_2O). Each pass converts only about 15 to 20% of the gases.
- **The rescue:** ammonia is cooled and liquefied, removed, and the unreacted N_2 and H_2 are recycled. Removing the product keeps the reaction moving forward (Stress 1!).

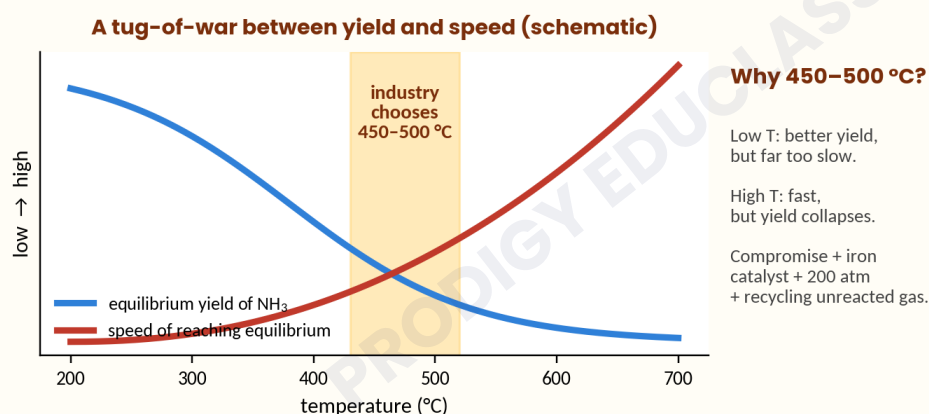


Fig 6. Why the Haber process runs where it does. The curves are schematic: they show the trend, not exact values.

The Contact process (sulphuric acid). The key step is:



	Haber process	Contact process
Gas moles (left → right)	$4 \rightarrow 2$	$3 \rightarrow 2$
Heat change	Exothermic (–92 kJ)	Exothermic (–196 kJ)
Pressure used	High, about 200 atm	Low, about 1 to 2 atm
Temperature	About 450 to 500 °C	About 450 °C
Catalyst	Iron (with promoters)	Vanadium(V) oxide, V_2O_5
Why that pressure?	Yield per pass is low, so high pressure helps a lot	Conversion is already very high (over 95% with several catalyst beds), so extra pressure is not worth the cost and corrosion

Did you know?

Air into bread. The Haber process was developed by Fritz Haber and Carl Bosch in the early 1900s. It fixes nitrogen from the air into ammonia, which becomes fertiliser. Estimates suggest that nitrogen fertiliser made this way helps grow food for roughly half of the world's population, and the process uses about 1 to 2% of the world's energy. A reaction that stops at 15% per pass ended up changing the population of the planet.

Did you know?

Breathless on the mountain. Haemoglobin picks up oxygen in your lungs: $\text{Hb} + \text{O}_2 \rightleftharpoons \text{HbO}_2$. At high altitude the oxygen pressure is low, so the equilibrium shifts *backward* and less oxygen is carried. That is why trekkers feel tired and dizzy above 3,000 m. After a couple of weeks the body makes more red blood cells to fix the problem. This is acclimatisation, and it is Le Chatelier's principle written in your blood.

5 One-page cheat sheet

- ✓ Equilibrium is **dynamic**: forward rate = reverse rate; concentrations constant (not equal); needs a closed system.
- ✓ $K_c = \frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$. Solids and pure liquids are omitted. K depends only on temperature.
- ✓ $K_p = K_c(RT)^{\Delta n}$. Reverse reaction: $1/K$. Equation $\times n$: K^n .
- ✓ $Q < K \rightarrow$ forward. $Q = K \rightarrow$ equilibrium. $Q > K \rightarrow$ backward.
- ✓ **Le Chatelier**: the system shifts to oppose the disturbance (partly).
- ✓ Concentration: add reactant $\rightarrow$ forward. Pressure: increase $\rightarrow$ fewer gas moles. Temperature: heat $\rightarrow$ endothermic direction (K changes). Catalyst: no shift.
- ✓ Haber: 200 atm, 450 to 500 °C, Fe catalyst. Contact: about 1 to 2 atm, 450 °C, V_2O_5 catalyst.

6 Test yourself

- Q1. For $N_2 + 3H_2 \rightleftharpoons 2NH_3$ ($\Delta H = -92$ kJ), predict the shift for: (a) adding H_2 (b) raising pressure (c) raising temperature (d) adding a catalyst (e) removing NH_3 .
- Q2. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is endothermic. Which conditions of temperature and pressure give the maximum yield of Cl_2 ?
- Q3. Write K_c for (a) $2SO_2 + O_2 \rightleftharpoons 2SO_3$ and (b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$.
- Q4. At equilibrium, $[H_2] = [I_2] = 0.2$ M and $[HI] = 1.6$ M. Find K_c . If a mixture has $[H_2] = [I_2] = 0.4$ M and $[HI] = 0.8$ M, which way will it react?
- Q5. The Haber process is exothermic, so why is it run at 450 to 500 °C and not at room temperature?
- Q6. The Contact process is run at just 1 to 2 atm even though gas moles decrease. Why?
- Q7. Explain why the colour of NO_2 in a syringe first darkens and then fades when the plunger is pushed in.
- Q8. For $A \rightleftharpoons B$, $K = 0.01$. What are K for $B \rightleftharpoons A$, and for $2A \rightleftharpoons 2B$?

Peek only after trying!

Answers. 1) (a) forward (b) forward (fewer gas moles) (c) backward (exothermic) (d) no shift (e) forward. 2) High temperature and low pressure. 3) (a) $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ (b) $K_c = [CO_2]$. 4) $K_c = 1.6^2 \div (0.2 \times 0.2) = 64$. For the second mixture $Q = 0.8^2 \div (0.4 \times 0.4) = 4$, which is less than 64, so it moves forward. 5) At low temperature the rate is far too slow, so a compromise temperature with a catalyst gives an economical rate with a reasonable yield. 6) The equilibrium already lies far to the right at normal pressure, so extra pressure would cost more than it gains and cause corrosion. 7) Compression raises all concentrations instantly (darker), then equilibrium shifts towards N_2O_4 , which has fewer moles of gas, so the colour lightens. 8) 100, and $(0.01)^2 = 1 \times 10^{-4}$.



A last word from your teacher

Equilibrium teaches a lesson beyond chemistry: systems resist change, but the wise ones adapt without breaking. Practise the shifts until they feel like common sense, and this chapter will become one of your favourites. **Keep exploring!** - Surajit Sir