How to influence chemical equilibriums?

- Well-defined starting point: at a given T, there is only one equilibrium constant (K; but $K_p = K \frac{RT}{D^N}$)

- Le Chatelier's principle:
  
  “If stress is applied to a system at equilibrium, the system responds by achieving a new equilibrium position at which the stress is counteracted or reduced.”

  in plain English: introduce a change and the equilibrium changes to reduce the effect of that change

  a) concentration: cause: remove product → response: do something to increase products → effect: convert more reactants

  b) pressure: (note that the textbook is incorrect – inert gas changes the mol% and partial pressures)
  cause: introduce inert gas → response: do something the reduce pressure → $K = \frac{\sum n_{prod}^i}{\sum n_{react}^i} \cdot \frac{V_{total}^D}{D^N}$
  $\Delta N > 0$ : more product particles than reactant, to reduce pressure reduce $c_{prod}$, thus increase $c_{react}$

  c) volume:
  cause: compress the vessel→ response: do something the increase volume → $K = \frac{n_{prod}}{n_{react}} \cdot V_{total}^D$ \hspace{1cm} $\Delta N > 0$ : the negative sign means reduce the number of molecules to counteract the volume change

  in all above conditions K stays constant; however

  d) temperature: (K changes!)
  exothermic reaction: cause: increase temperature by heating → response: need to reduce the heat by consuming energy → effect: shifts to the left and $K$ decreases
  analytically: $\Delta G = 0 = \Delta H^o - T \Delta S^o + RT \ln K$
  $\ln K = - \frac{\Delta H^o}{R} \frac{1}{T} + \frac{\Delta S^o}{R}$ or van't Hoff expression $\ln \frac{K_2}{K_1} = \frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$

\[3 \text{H}_2(g) + \text{N}_2(g) \leftrightarrow 2 \text{NH}_3(g) \quad \Delta H^o = -46 \text{kJ/mol} \quad \Delta S^o = -68 \text{J/molK} \quad \Delta G^o = -17 \text{kJ/mol} \quad T_{eq} = 676 \text{K}\]

- add H₂ →
- add N₂ → $K = (c_{NH3} + 2/3x)^2 / (c_{H2} - x)(c_{N2} - 1/3x)$
- add NH₃ ←

  Ben's dilemma: $2\text{CO}_2(g) \leftrightarrow 2 \text{CO}(g) + \text{O}_2(g)$
  K = 2 · 10⁶ starting from 2 moles of CO₂ in 5 L
  -2x +2x +x changes or
  -x +x +½x
  $K = (2x)^2x / (0.4 - 2x)^2$ or $K = x^2 \frac{1}{2}x / (0.4 - x)^2$
  note that if K is small you can neglect the consumption of the starting material (negligible small)
  $K = 4x^3/0.4^2$ or $K = \frac{1}{2}x^3/0.4^2$
  solve and get $x = 0.0043$ or $x = 0.0086$
  → does not matter as long as you know what change you consider

- increase p → $K = \frac{c_{NH3}^2}{c_{H2}^3} \cdot \frac{c_{N2}^3}{p_{total}^2}$
- increase V ← $K = \frac{n_{NH3}^2}{n_{H2}^3} \cdot \frac{n_{N2}^3}{V_{total}^2}$
- raise T ← reducing exothermicity (negative entropy takes over)
'Candy for the hungry minds': special properties of $\Delta N = 0$ equilibria

examples: $\text{H}_2\text{O}(g) \leftrightarrow \text{H}_2\text{O}(l)$  \hspace{1cm} \text{n-butane} \leftrightarrow \text{isobutane}  \hspace{1cm} \text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI}

- changes in V or p $\rightarrow$ conserves the relative concentrations
  $\rightarrow$ conserves the reaction quotient (Q)
  $\rightarrow$ conserves the number of particles n

What changes? $\Rightarrow$ collisions $\Rightarrow$ kinetics

- consider above butane isomerization reaction (important in petrochemistry – increase the octane number)

$$K = \frac{[\text{iC}_4]}{[\text{nC}_4]} \text{ at a given temperature}$$

$\text{iC}_4 = K \text{[nC}_4] \quad \rightarrow$ plot and get a linear function with slope of K and intersection at 0

<table>
<thead>
<tr>
<th>change the equilibrium</th>
<th>starting</th>
<th>$[\text{nC}_4]_0$</th>
<th>$[\text{iC}_4]_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>change</td>
<td>-x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>new equilibrium concentrations</td>
<td>$[\text{nC}_4]_0-x$</td>
<td>$[\text{iC}_4]_0+x$</td>
<td></td>
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$$K = (\frac{[\text{iC}_4]_0+x}{([\text{nC}_4]_0-x)} = \frac{[\text{iC}_4]_0}{[\text{nC}_4]_0}$$

$$x = (\frac{[\text{iC}_4]_0-K[\text{nC}_4]_0}{(K+1)})$$

graphical approach: equilibrium points are along the $[\text{iC}_4] = K\text{[nC}_4]$ line $\rightarrow$ plot A

new equilibrium $[\text{iC}_4] = [\text{iC}_4]_0 + x$

$$= [\text{iC}_4]_0 + [\text{nC}_4]_0 - [\text{nC}_4]$$

$$= -1[\text{nC}_4] + \Sigma [\text{C}_4]_0$$ $\rightarrow$ plot B

intersections of plots A and B gives the equilibrium point