L8

REACTIONS AT EQUILIBRIUM

chapter 10

- **One of the most important information in chemistry is whether a reaction will run in one direction or another.**

- **The composition of equilibrium can be specified in terms of a single quantity, equilibrium constant.**

- **It is possible to predict how the position of equilibrium responds to changes in the conditions**

- **It is possible to make quantitative predictions**

A chemical reaction is at *equilibrium* when the composition is stationary and has no further tendency to react

- $2H_2 \quad + \quad 2O_2 \quad \Leftrightarrow \quad 2H_2O$

- **When hydrogen and oxygen are induced to react (by a spark),**

- **they go completely to the product**

Dynamic equilibrium

- **A mixture of nitrogen and hydrogen reacts and forms ammonia:**
- $N_2 + 3H_2 \Leftrightarrow 2NH_3$
- **Ammonia synthesis settled down to to a stationary composition**
- **consisting of a mixture of nitrogen, hydrogen, and ammonia.**

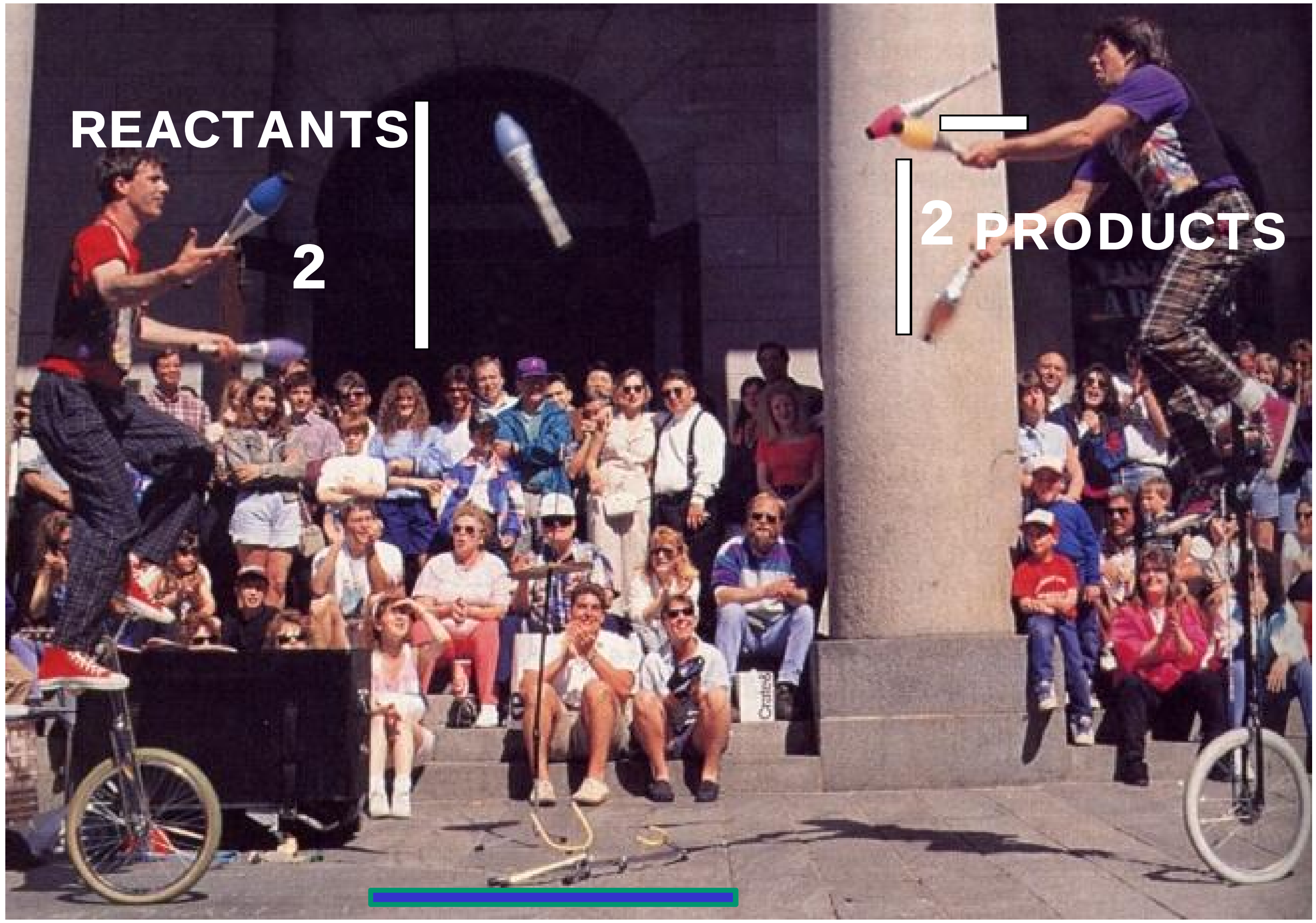
- Chemical equilibria are *dynamic equilibria*
- *when* the forward and backward reactions continue, but there is no net change.
- Rates of movement in either direction are equal.
- **This can be proved by isotopic studies:**

- $N_2 \quad + \quad 3H_2 \quad \Leftrightarrow \quad 2NH_3$

N^2H_3 deuterium

HH

NHH_2


REACTANTS
2
2 PRODUCTS

Esterification of ethanoic acid

$$CH_3COOH\,(l) + C_2H_5OH\,(l) \Leftrightarrow CH_3COOC_2H_5\,(l) + H_2O\,(l)$$

ethanoic acid + ethanol $\Leftrightarrow$ ester + water

The equilibrium composition of a reaction is characterized by the *equilibrium constant*

$$K_c = \left\{ \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]} \right\}_{eq}$$

eq = = in equilibrium

- **K_c is constant for given temperature**

Esterification of ethanoic acid at 100 ºC

$$K_c = \left\{ \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} \right\}_{eq}$$

- **K_c is constant for given temperature**

mol at start		mol at equilibrium		
acid	alcohol	ester	water	Kc
1	0.18	0.171	0.171	3.9

$$K_c = 0.171 \cdot 0.171 \,/\, (1-0.171)\,(0.18-0.171)$$

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \Leftrightarrow CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \Leftrightarrow CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

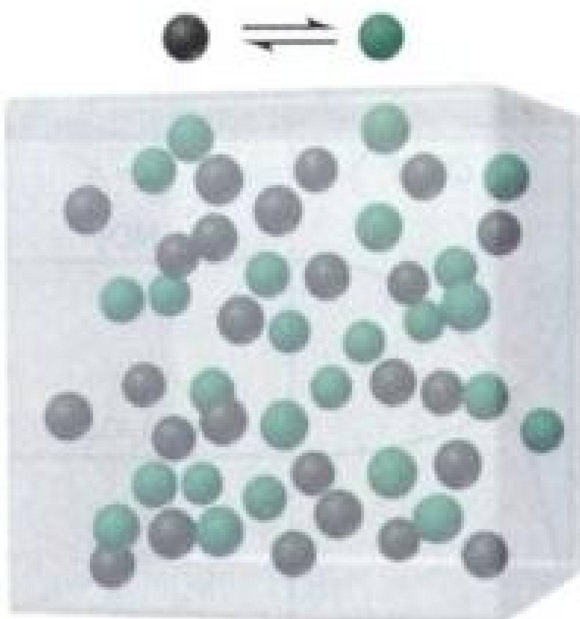
mol at start		mol at equilibrium		
acid	alcohol	ester	water	Kc
1	0.18	0.71	0.171	3.9
1	1	0.667	0.667	4
1	8	0.966	0.966	3.9

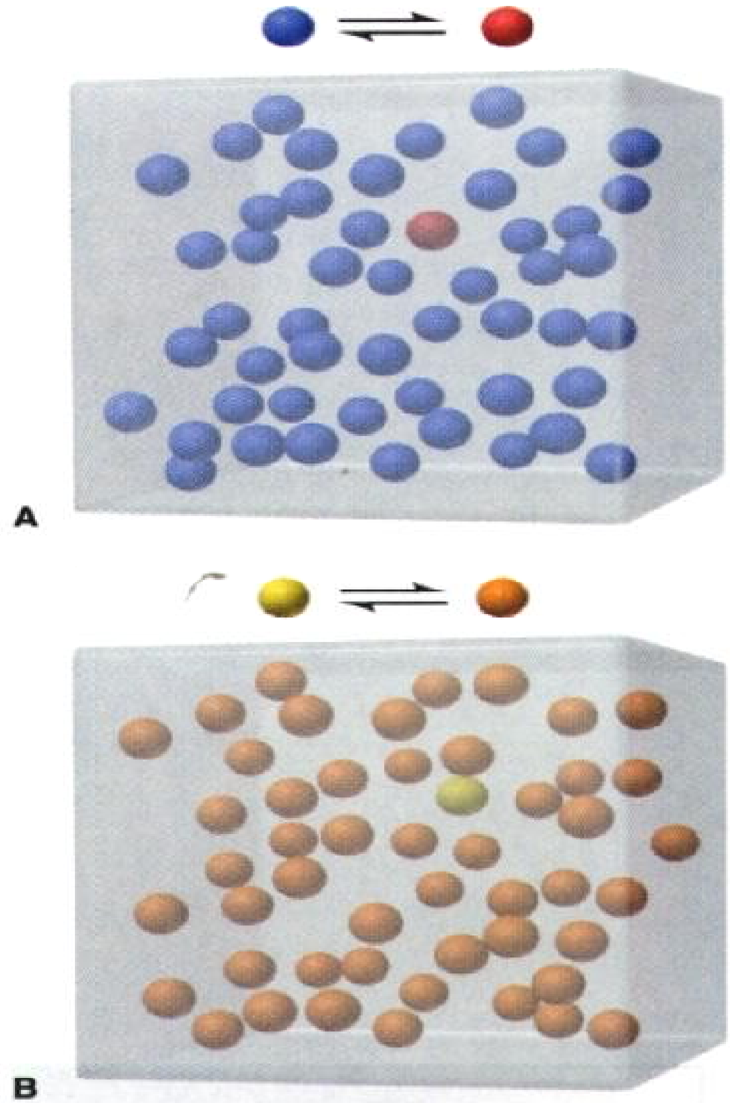
$$K_c = \left\{ \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} \right\}_{eq}$$

$$K_c = 0.667 \cdot 0.667 / (1-0.667)\ (1-0.667) = 4$$

$$K_c = 0.966 \cdot 0.966 / (1-0.966)\ (8-0.966) = 3.9$$

Figure 17.2 The range of equilibrium constants. A, A system that reaches equilibrium with very little product has a small K. For this reaction, $K = \frac{1}{49} = 0.020$. **B,** A system that reaches equilibrium with nearly all product has a large K. For this reaction, $K = \frac{49}{1} = 49$. **C,** A system that reaches equilibrium with significant concentrations of reactant and product has an intermediate K. For this reaction, $K = \frac{25}{25} = 1.0$.





$$CH_3COOH\ (l) + C_2H_5OH\ (l) \Leftrightarrow CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

- N_2 (g) + $3H_2$ (g) $\Leftrightarrow$ $2NH_3$ (g)

- $K_p = p^2_{NH_3} / (p_{N_2} \cdot p^3_{H_2})$

- at 400 K the value of this equilibrium constant is 53 bar^{-2}

How equilibria respond to changes of concentration?

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \Leftrightarrow CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

mol at start		mol at equilibria		
acid	alcohol	ester	water	
1	0,18	0,171	0,171	
1	1	**0,667**	**0,667**	

Henri L. le Chatlier
1850-1936.
Adapted thermodynamics to equilibria; formulated the principle known by his name.

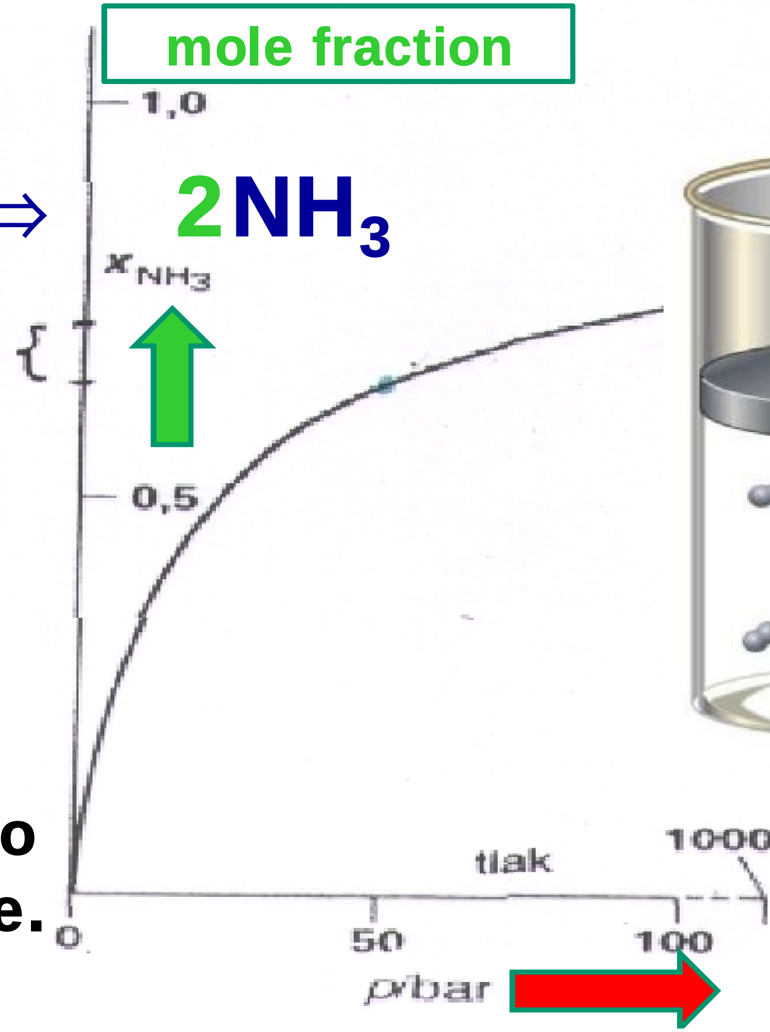
Le Chatelier's principle: when a reaction at equilibrium is subjected to a change of conditions,
the composition adjusts so as to minimize the change.

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \Leftrightarrow CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

mol at start		mol at equilibria		
acid	alcohol	ester	water	
1	0,18	0,171	0,171	
1	1	**0,667**	**0,667**	

If a reaction involving gases is subjected to an *increase in* pressure the reaction adjusts the composition so as to reduce the number of gas-phase molecules (and thereby to minimize the increase in pressure)

$$1N_2 \quad + \quad 3H_2 \quad \Leftrightarrow \quad 2NH_3$$



Le Chatelier: **when a reaction at equilibrium is subjected to a change of conditions,**
the composition adjusts so as to minimize the change.

Is this reaction sensitive to pressure change?

$$CH_4\mathbf{(g)} + 2O_2\mathbf{(g)} \quad \hat{U} \quad CO_2\mathbf{(g)} + 2H_2O\mathbf{(g)}$$

An *increase of temperature,* in the case of endothermic reactions, shifts the position of equilibrium in favour of products

and in favour of reactants for exothermic reactions.

$N_2O_4 \Leftrightarrow NO_2$ $\Delta H = +$

$N_2 + 3H_2 \Leftrightarrow 2NH_3$ $\Delta H = -\ 92\ kJmol^{-1}$ at 25 ^oC

$2NH_3 \Leftrightarrow N_2 + 3H_2$ $\Delta H = ?$

Le Chatelier: when a reaction at equilibrium is subjected to a change of conditions, the composition adjusts so as to minimize the change.

$2NH_3 \Leftrightarrow N_2 + 3H_2$ $\Delta H = +\,92\ kJ\ mol^{-1}$ at 25 ^oC

$$K = [N_2][H_2]^3 / [NH_3]^2$$

$2NH_3 \Leftrightarrow N_2 + 3H_2$ K_1 (25 ^oC)

$2NH_3 \Leftrightarrow N_2 + 3H_2$ K_2 (100 ^oC)

a) $K_2 > K_1$ ■

b) $K_2 = K_1$

c) $K_2 < K_1$

The Universality of Le Châtelier's Principle

ance is attained.

- **In *homogeneous reactions* all the species are in the same phase;**

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \Leftrightarrow CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g); \qquad K_p = \left\{ \frac{p_C^c p_D^d}{p_A^a p_B^b} \right\}_{eq}$$

- **in *heterogeneous reactions* the species are in more than one phase.**

- **Corresponding equilibria are called h*omogeneous equilibria and heterogeneous equilibria,* respectively.**

Heterogeneous equilibria

$CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$ $K=\{[CaO]pCO_2/ [CaCO_3]\}_{eq}$

The *concentrations of pure solids* are constant, and may be absorbed into the definition of the equilibrium constant for a heterogenous reaction.

$K=\{pCO_2\}_{eq}$ = **24.4 kPa at 800 ºC**

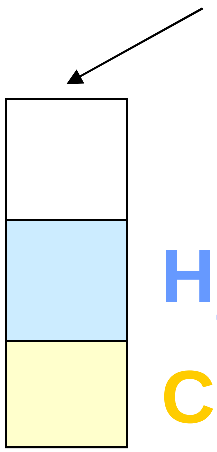
j (CO_2) = 0.0003; p(CO_2) = 0.03 kPa

$CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$ $K = \{[CaO]pCO_2 / [CaCO_3]\}_{eq}$

$K = \{pCO_2\}_{eq}$ = **24.4 kPa**

Partition equilibria

Cl_2



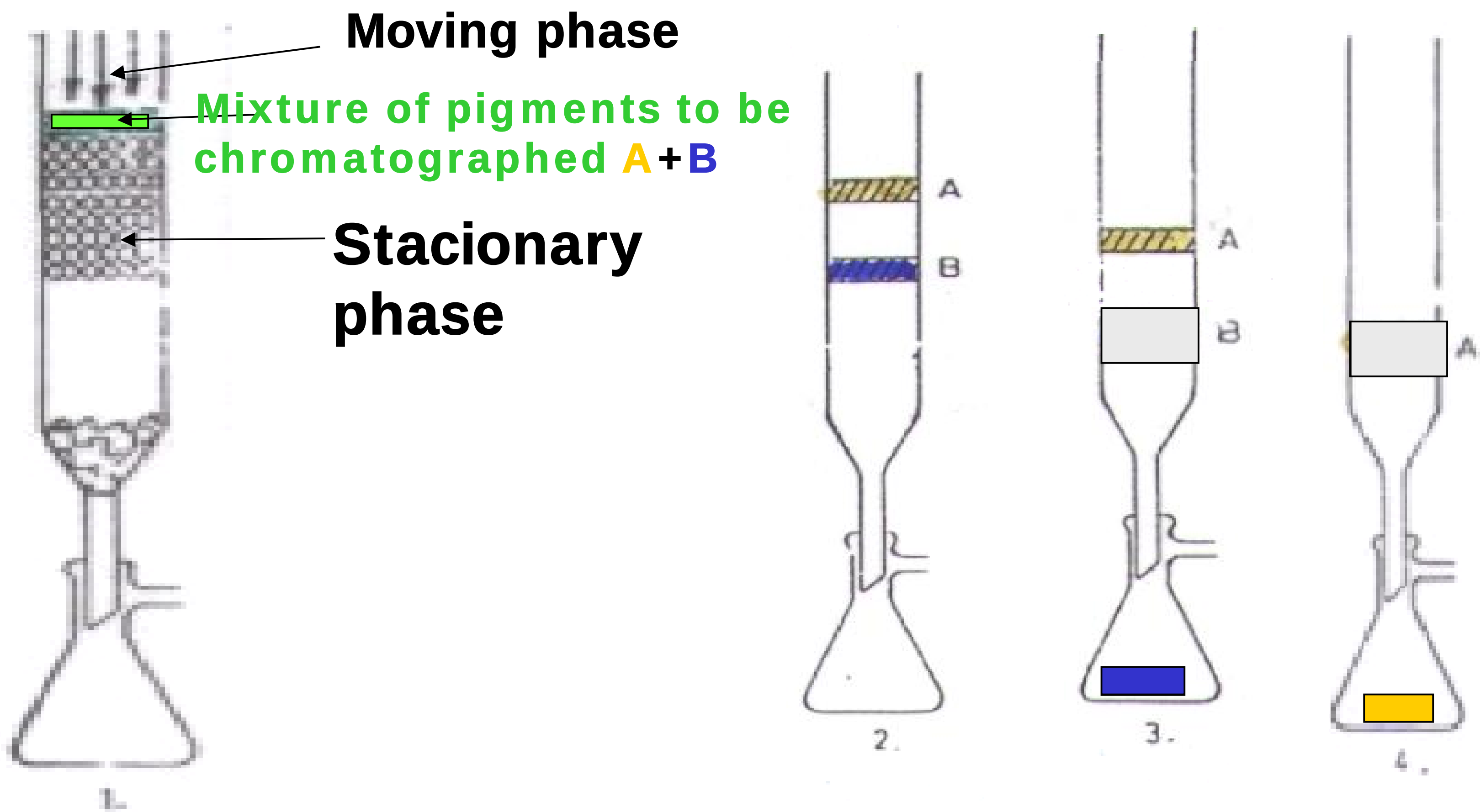
H_2O (B_1)

CCl_4 (B_2)

$$K_{dist} = \{[B]_1 \,/\, [B]_2\}_{eq}$$

Distribution coefficients at 25 ºC between water (1) i another solvent (2):

Solute B	solvent (2)	$K_{dist} = \{[B]_1 \,/\, [B]_2\}eq$
Cl_2	CCl_4	0,1 / 1
CH_3COOH	C_6H_6	16

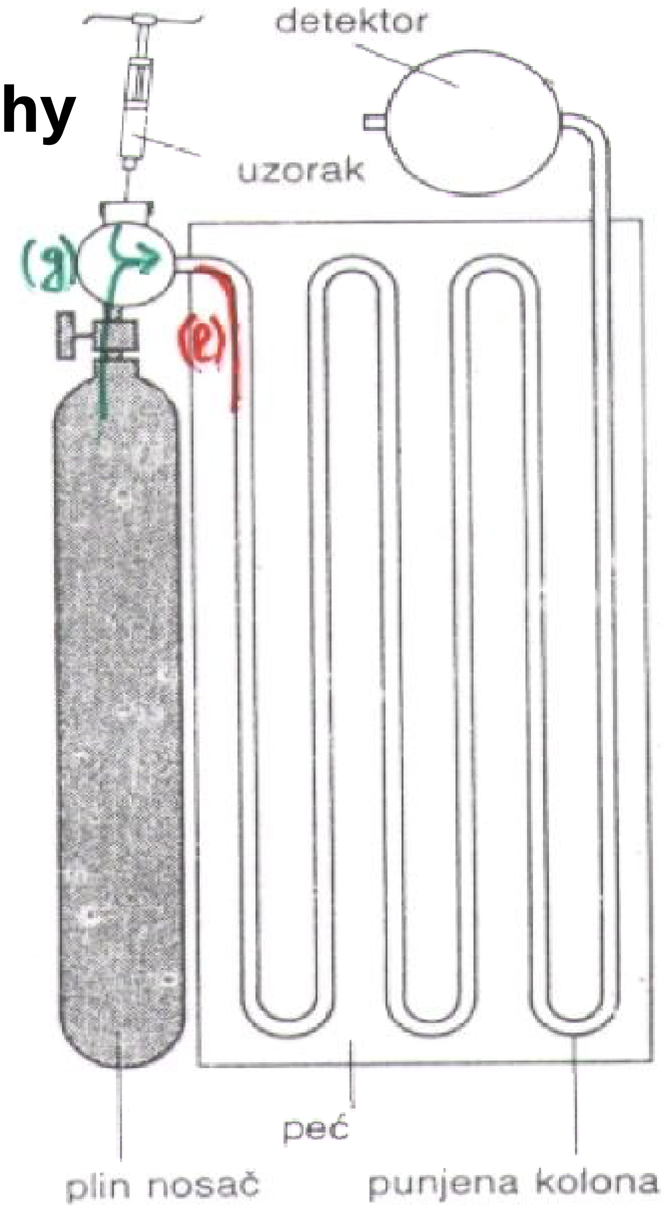


2.-4. Washing process

with moving phase = elution

Gas-liquid chromatography

If whiskey is analysed, which fraction will appear fisrt at detector: water or alcohol?

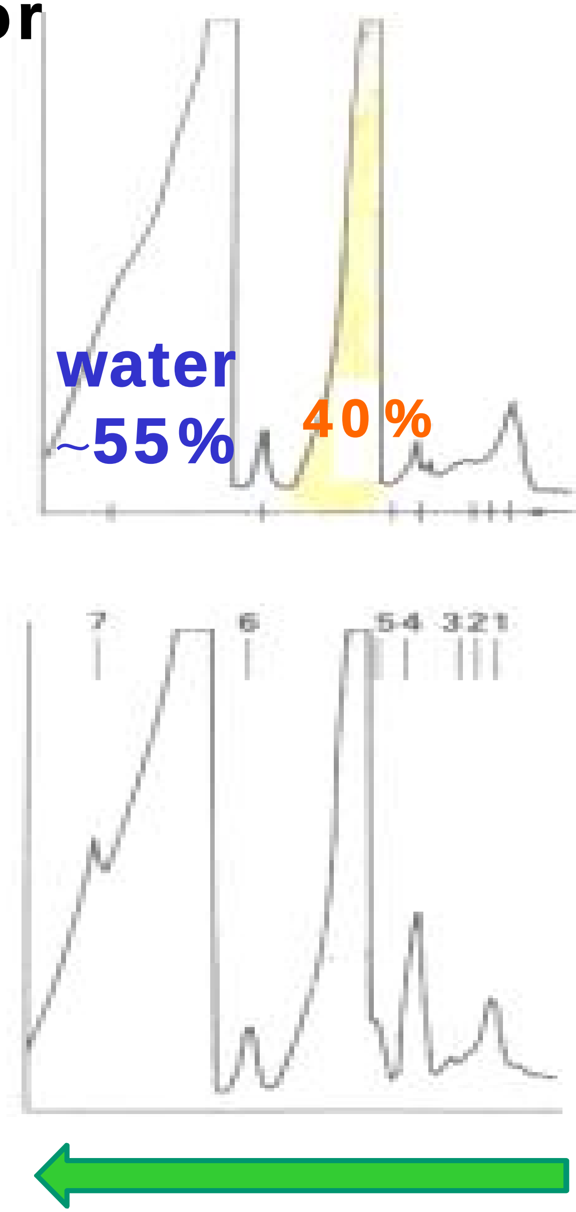


Plinsko-tekućinska kromatografija

y = detector signal

Scotch whiskey

Buorbon whiskey



x = Elution time

peak:

1. Formaldehid
2. Etil-metanoat
3. Etil-acetat
4. Methanol

At the end of statement write YES or NO

During reaction toward products

$CH_4(g) + 2O_2(g) \Leftrightarrow CO_2(g) + 2H_2O(g)$ $\Delta_c H = - 890\ kJmol^{-1}$
the heat is released

YES

Increase of temperature will result in increased concentration of NO_2 in reaction:

$N_{2(g)} + 2\ O_{2(g)} \Leftrightarrow 2\ NO_{2(g)}$ $\Delta_r H = -33.2\ kJ/mol$

NO

At the end of statement write YES or NO

For the reaction $CH_4\,(g) + 2O_2\,(g) \Leftrightarrow CO_2\,(g) + 2H_2O\,(g)$ $\Delta_r H = -\,890\ kJmol^{-1}$

it is correct the statement:

increased total pressure will move reaction more towards products

NO

During reaction toward products

$CH_4(g) + 2O_2(g) \Leftrightarrow CO_2(g) + 2H_2O(g)$ $\Delta_c H = -\,890\ kJmol^{-1}$ the heat is released

YES

Write the ratio (K_{dist}) between concentration of $CH_2ClCOOH$ in C_6H_6 and concentration of $CH_2ClCOOH$ in water

- based on the data for distribution coefficients between water (1) and another solvent (2)

Solute B	Solvent 2	$K_{dist}=\{[B]_1 / [B]_2\}_{eq}$
$CH_2ClCOOH$	C_6H_6	28
CH_3COOH	C_6H_6	16