

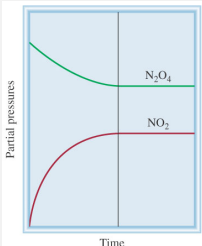
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[TP] The figure shows how the partial pressures of the  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  **change with time** due to the chemical reaction

$$\text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2$$

for **certain initial conditions**. At these **initial conditions** (far left), the following is known about the chemical reaction.

25% 1. It is **spontaneous**  
 25% 2. It is **at equilibrium**  
 25% 3. It is **non-spontaneous**  
 25% 4. Its spontaneity is **not known** without further information



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## Lecture 12 CH102 A2 (MWF 11:15 am) Tuesday, February 19, 2019

- Complete review: Colligative properties

**Begin ch13: Dynamic Chemical Equilibrium**

- Reaction quotient,  $Q$ , spontaneity, and equilibrium

**Next:** Predicting direction of change;  $Q$  depends on how a reaction is written; Knowing  $K$  **does not** fix individual concentrations. Disturbing equilibrium (Le Chatelier)

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## Roadmap of osmotic pressure calculations

Osmotic pressure  $\Pi = i c R T$ .

1. Use measured osmotic pressure,  $\Pi$ , and temperature,  $T$ , to **evaluate concentration**,  $c = \Pi / (i R T)$ , in mol/L.
2. Use cell volume to express concentration in terms of **moles**,  $n = c V$ .
3. Use solute mass to calculate **molar mass**,  $M = \text{mass}/n$ .

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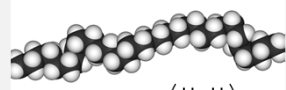
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## Osmotic pressure $\Pi = i c R T$

1.40 g of polyethylene ( $i = 1$ ) dissolved in 100. mL of benzene generates an osmotic pressure of 0.248 kPa at 25 °C. Calculate the molar mass of the polyethylene.

1. Calculate the concentration...



$$\left( \begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{H} \end{array} \right)_n$$

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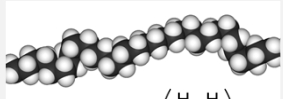
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 $1.00 \times 10^{-4} \text{ mol/L}$



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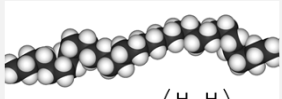
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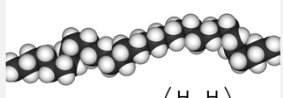
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1. Calculate the concentration...  
 $1.00 \times 10^{-4} \text{ mol/L}$
2. Calculate the moles...  
 $10^{-5} \text{ mol}$



$$\left( \begin{array}{cc} \text{H} & \text{H} \\ | & | \\ -\text{C} & - & \text{C}- \\ | & | \\ \text{H} & \text{H} \end{array} \right)_n$$

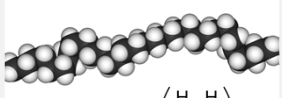
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1. Calculate the concentration...  
 $1.00 \times 10^{-4} \text{ mol/L}$
2. Calculate the moles...  
 $10^{-5} \text{ mol}$
3. Calculate the molar mass...



$$\left( \begin{array}{cc} \text{H} & \text{H} \\ | & | \\ -\text{C} & - & \text{C}- \\ | & | \\ \text{H} & \text{H} \end{array} \right)_n$$

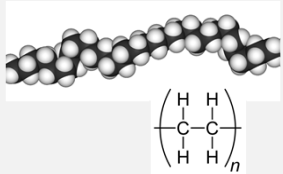
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### Osmotic pressure $\Pi = i c R T$

1.40 g of polyethylene ( $i = 1$ ) dissolved in 100. mL of benzene generates an osmotic pressure of 0.248 kPa at 25 °C. Calculate the molar mass of the polyethylene.

1. Calculate the concentration...  
 $1.00 \times 10^{-4}$  mol/L
2. Calculate the moles...  
 $10^{-5}$  mol
3. Calculate the molar mass...  
 $1.40 \times 10^{+5}$  g/mol



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[TP] 1.0 mg of a substance dissolved in 1.0 mL of water generates an osmotic pressure of 1.0 kPa, at 25 °C. The molar mass of the solute ( $i = 1$ ) is ...

0% 1. 250 g/mol  
0% 2. 500 g/mol  
0% 3. 1000 g/mol  
0% 4. 2500 g/mol  
0% 5. 5000 g/mol  
0% 6. Some other value

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### Practice question

What height column of benzene ( $D = 0.876$  g/mL) generates a pressure of 248 Pa? Express your answer in cm, to the correct number of significant figures. Recall that  $\Pi = Dgh$ ,  $\text{Pa} = \text{kg}/(\text{m s}^2)$ , and  $g = 9.80665$  m/s<sup>2</sup>.

Answer: 2.89 cm

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### Begin ch 13

Dynamic chemical equilibrium

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## Spontaneity of “reactants” → “products”

If products (right side) increase with time, we say ...  
the reaction is **spontaneous**.

If reactants (left side) increase with time, we say ...  
the reaction is **nonspontaneous**.

If the amount of reactants and products do not change with time, we say ...  
the reaction is **at equilibrium**.

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## Reaction quotient Q measures progress

$A \rightarrow B + C$

$$Q = \frac{\text{products}}{\text{reactants}} = \frac{[B][C]}{[A]}$$

Q at  $t_1$  is **smaller** (less products)

Q at  $t_2$  is **larger** (more products)

Q for  $t > t_2$  **no longer changes**

For  $t > t_2$ ,  $Q = K$ , **equilibrium constant**

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## Writing Q

For a  $A + b B \rightarrow c C$

$$Q = (C)^c / ((A)^a (B)^b)$$

(X) = conc of X/ref value

As discussed in Mahaffy et al., 2e, p498, such ratios are called **activities**, dimensionless measures of **effective concentration**.

**Reference concentrations**

Solutes:	ref value = 1 M
Gases:	ref value = 1 bar
Liquids:	ref value = conc of pure liquid
Solids:	ref value = conc of pure solid

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## Writing Q

$2 A(aq, .20 M) \rightarrow B(g, .60 \text{ bar})$   
 $Q = .60 / (.20)^2 = 15$  (no units, always!)

$2 A(aq, .10 M) \rightarrow B(g, 1.20 \text{ bar})$   
 $Q = 1.20 / (.10)^2 = 120$

$2 A(aq, 1.5 M) \rightarrow B(g, 0 \text{ bar})$   
 $Q = 0 / (1.5)^2 = 0$  (only reactants)

$2 A(aq, 0 M) \rightarrow B(g, 4 \text{ bar})$   
 $Q = 4 / (0)^2 = \infty$  (only products)

$2 C(aq, 3 M) \rightarrow 3 D(s)$   
 $Q = (1)^3 / (3)^2 = 1/9$  (solids and liquid contribute 1)

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**Reaction quotient  $Q$  measures progress**For  $A \rightarrow B + C$ , the **reaction quotient** is ...

$$Q = \frac{[B][C]}{[A]}$$

The numerical value of the reaction quotient when the concentrations have their **equilibrium values**  $[A]_e$ ,  $[B]_e$  and  $[C]_e$  ...and so **no longer change** with time, is called the **equilibrium constant** ...

$$Q = K = \frac{[B]_e[C]_e}{[A]_e}$$



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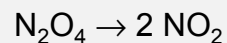
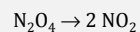
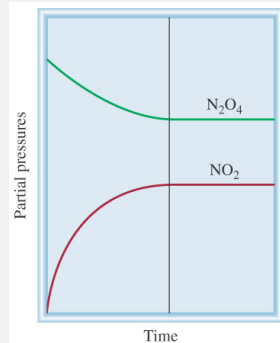
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 **$Q$  versus  $K$  is the key to assessing spontaneity**If  $Q < K$ , product must form to get to equilibrium,  
so **spontaneous**If  $Q > K$ , reactants must form to get to equilibrium,  
so **nonspontaneous**If  $Q = K$ , no change in amounts of reactants and products,  
so **equilibrium**So,  $Q/K$  is the key quantity to monitor.

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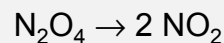
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The figure shows how the partial pressures of the  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  **change with time** due to the chemical reactionfor **certain initial conditions** (far left).

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The **reaction quotient** is

$$Q = [\text{NO}_2]^2 / [\text{N}_2\text{O}_4]$$

The numerical value of the reaction quotient when the concentrations have their **equilibrium values**

$$[\text{N}_2\text{O}_4]_e \text{ and } [\text{NO}_2]_e$$

and so no longer change with time, is called the **equilibrium constant**

$$K = [\text{NO}_2]_e^2 / [\text{N}_2\text{O}_4]_e$$



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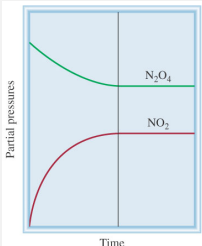
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$$\text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2$$

for **certain initial conditions**. At these **initial conditions** (far left), the following is known about the chemical reaction.

- 25% 1. It is **spontaneous**
- 25% 2. It is **at equilibrium**
- 25% 3. It is **non-spontaneous**
- 25% 4. Its spontaneity is **not known** without further information



Partial pressures

Time

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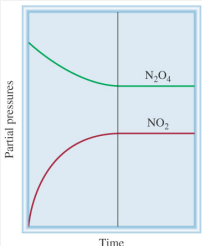
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**[TP]** At the **initial conditions** (far left) for the reaction

$$\text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2$$

the following is known about the ratio  $Q/K$ .

- 25% 1. It is **greater** than 1
- 25% 2. It is **equal** to 1
- 25% 3. It is **less** than 1
- 25% 4. The ratio is not known without further information



Partial pressures

Time

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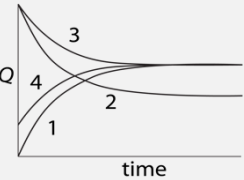
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**[TP]** For the reaction

$$\text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2$$

which curve on the right shows the corresponding **change of  $Q$  with time**?

- 20% 1. 1
- 20% 2. 2
- 20% 3. 3
- 20% 4. 4
- 20% 5. None



Q

time

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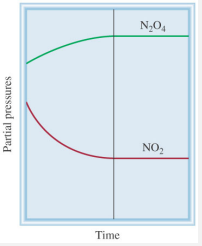
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Partial pressures

Time

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## Q versus $K$ is the key to assessing spontaneity

If  $Q < K$ , product must form to get to equilibrium,  
so **spontaneous**

If  $Q > K$ , reactants must form to get to equilibrium,  
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