

# Chemical Equilibrium

## Dynamic Equilibrium

The properties – including chemical composition – of a reacting *system at equilibrium* do not change with time.

However, chemical reactions continue at equilibrium.

At equilibrium, rate of a forward reaction equals rate of reverse reaction – resulting in no net change. This is called *dynamic equilibrium*.

The rate of forward reaction decreases as concentrations of reactants decrease, while the rate of reverse reaction increases as concentrations of products increase (use partial pressures for gas reactions).

Forward or reverse reaction proceeds until the rates of forward and reverse reaction are equal and equilibrium is achieved.

## Equilibrium Constant

Equilibrium occurs when product *activities* are balanced against reactant *activities*.

For a species A *in solution*, at low concentration, *activity* is approximately equal to the *concentration* of the species, [A] in mol L<sup>-1</sup>.

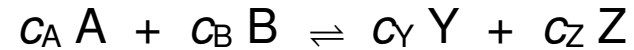
For a gas, activity is approximately the gas partial pressure,  $p_A$  in bar.

For pure (or almost pure) liquids and solids, activity is approximately 1.

$$a_A = \begin{cases} [A] & \text{for A in solution} \\ P_A & \text{for A in the gas phase} \\ 1 & \text{for pure liquid or solid A} \end{cases}$$

Activity is dimensionless – the units are divided out.

The *equilibrium constant*,  $K$ , for the reaction,



is given by

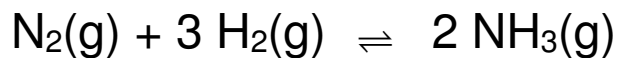
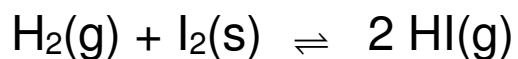
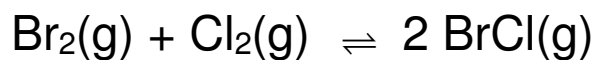
$$K = \frac{a_Y^{c_Y} a_Z^{c_Z}}{a_A^{c_A} a_B^{c_B}}$$

where  $a_A$ ,  $a_B$ ,  $a_Y$  and  $a_Z$  are the activities of A, B, Y and Z under equilibrium conditions.

The equilibrium constant depends only on temperature.

## Examples:

Reaction



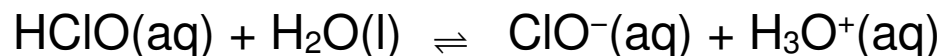
Equilibrium constant

$$K = \frac{P_{\text{BrCl}}^2}{P_{\text{Br}_2} P_{\text{Cl}_2}}$$

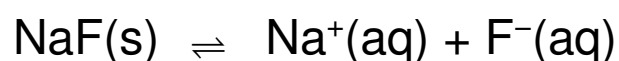
$$K = \frac{P_{\text{HI}}^2}{P_{\text{H}_2}}$$

$$K = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

$$K = [\text{Ca}^{2+}][\text{OH}^{-}]^2$$

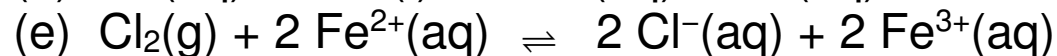
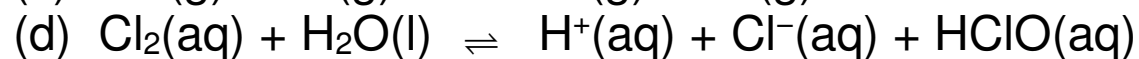
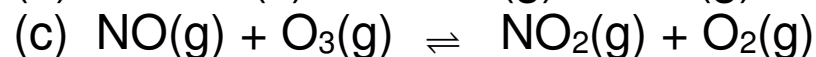
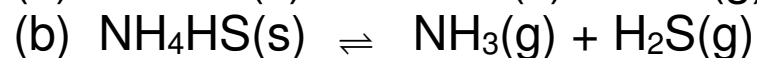
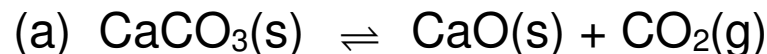


$$K = K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} \quad \text{or} \quad \frac{[\text{H}^+][\text{ClO}^-]}{[\text{HClO}]}$$



$$K = K_{sp} = [\text{Na}^+][\text{F}^-]$$

**Example:** Write down the equilibrium constant,  $K$ , for each of the following reactions.



$$(a) \quad K = P_{\text{CO}_2}$$

Here,  $K$  is the vapor pressure of solid carbon dioxide.

$$(b) \quad K = P_{\text{NH}_3} P_{\text{H}_2\text{S}}$$

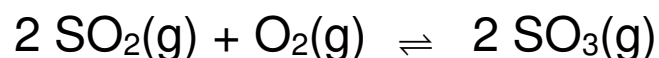
$$(c) \quad K = \frac{P_{\text{NO}_2} P_{\text{O}_2}}{P_{\text{NO}} P_{\text{O}_3}}$$

$$(d) \quad K = \frac{[\text{H}^+][\text{Cl}^-][\text{HClO}]}{[\text{Cl}_2]}$$

$$(e) \quad K = \frac{[\text{Cl}^-]^2 [\text{Fe}^{3+}]^2}{P_{\text{Cl}_2} [\text{Fe}^{2+}]^2}$$

## Application of a known equilibrium constant

The equilibrium constant for combustion of sulfur dioxide at 350°C is  
 $K = 5.60 \times 10^4$ .



If the partial pressures of  $\text{O}_2$  and  $\text{SO}_3$  are both 0.500 bar, what is the partial pressure of  $\text{SO}_2$ ?

$$K = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}} = \frac{0.500^2}{P_{\text{SO}_2}^2 \cdot 0.500} = 5.60 \times 10^4$$

gives

$$P_{\text{SO}_2}^2 = \frac{0.500^2}{5.60 \times 10^4 \times 0.500} = 8.92_9 \times 10^{-6}$$

and

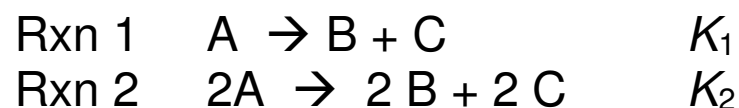
$$P_{\text{SO}_2} = 2.99 \times 10^{-3} \text{ bar}$$

## Combining Equilibrium Constants

First, note that

$$K_{\text{reverse}} = \frac{1}{K_{\text{forward}}}$$

Now consider Rxn 2 = 2× Rxn 1.



$$K_2 = K_1^2$$

In general,

$$K = K_1^{n_1} K_2^{n_2} K_3^{n_3} \cdots,$$

where

$$\text{Reaction of interest} = \sum_i n_i (\text{ith tabulated reaction}),$$

and  $n_i$  is negative for tabulated reactions that need to be reversed.



## The Reaction Quotient

The above expressions for the equilibrium constant only hold under *equilibrium conditions*.

When a reaction mixture is *not* at equilibrium, combining the concentrations and partial pressures as they are in the equilibrium constant gives the *reaction quotient*,  $Q$ .

Under equilibrium conditions,  $Q = K$ .

Under non-equilibrium conditions,  $Q \neq K$  and there is net forward or reverse reaction.

If  $Q < K$ , there is net *forward* reaction.

Net forward reaction *increases*  $Q$  until  $Q = K$ .

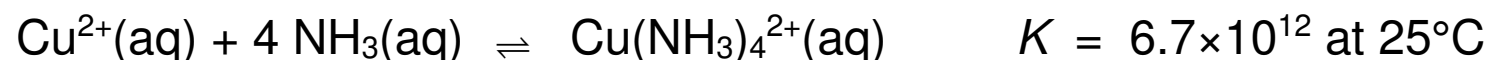
If  $Q > K$ , there is net *reverse* reaction.

Net reverse reaction *decreases*  $Q$  until  $Q = K$ .

**Example:** Consider each of the following reaction mixtures. Is the mixture at equilibrium, or is there net forward or reverse reaction?

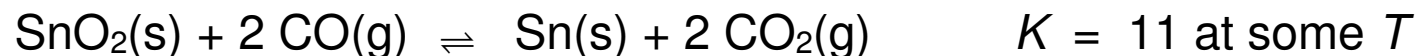
(a) Solid calcium carbonate and calcium oxide at 700°C are in a vessel with 0.1 bar partial pressure carbon dioxide. At 700°C,  $K = 0.056$  for the decomposition of  $\text{CaCO}_3(\text{s})$  into  $\text{CaO}(\text{s})$  and  $\text{CO}_2(\text{g})$ .

(b) Consider the following equilibrium:



Suppose  $[\text{Cu}^{2+}] = [\text{Cu}(\text{NH}_3)_4^{2+}] = 1.0 \text{ mol L}^{-1}$ , while  $[\text{NH}_3] = 5.0 \times 10^{-4} \text{ mol L}^{-1}$  at 25°C.

(c) Consider the following equilibrium:



Suppose the partial pressure of  $\text{CO}_2$  is 3 bar, while that of  $\text{CO}$  is 1 bar at the required  $T$ .

(a)  $Q = P_{\text{CO}_2} = 0.1 > 0.056$ . Therefore, there is net reverse reaction. At this partial pressure,  $\text{CO}_2$  in the gas phase combines with available  $\text{CaO(s)}$  to form  $\text{CaCO}_3\text{(s)}$ .

(b) Here,

$$Q = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{1.0}{1.0(5.0 \times 10^{-4})^4} = 1.6 \times 10^{13} > K$$

Again,  $Q > K$  and there is net reverse reaction.

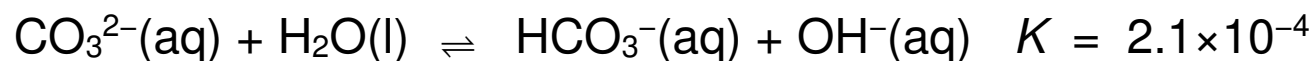
(c) Here,

$$Q = \frac{P_{\text{CO}_2}^2}{P_{\text{CO}}^2} = \frac{3^2}{1} = 9 < 11$$

In this case,  $Q < K$  and there is net forward reaction.

## Shift in Equilibrium – Le Châtelier's Principle

Non-equilibrium conditions can result, starting with an equilibrium mixture, by adding or removing a reactant or a product. For example, if we have an equilibrium solution with the reaction



and we dissolve a small amount of NaOH(s) into the solution, a non-equilibrium initial state results.

Increasing the concentration of hydroxide makes *Q larger* - there is net *reverse* reaction until *Q* decreases back to *K*.

When equilibrium is re-established, hydroxide concentration is smaller than it was immediately after the added NaOH(s) dissolves, but larger than it was before the NaOH(s) was added.

Adding a small amount of concentrated sulfuric acid reduces the hydroxide concentration, making  $Q$  *smaller*. Net *forward* reaction results until equilibrium is re-established.

*Le Châtelier's principle:*

When a change is imposed on an equilibrium system, the change is followed by net reaction that reduces the change.

Le Châtelier's principle also applies to the effect of changing temperature.

## Changing Temperature

Thermodynamics shows that  $K$  *increases* with *increasing temperature* for *endothermic* reactions ( $\Delta H > 0$ ), and *decreases* for *exothermic* reactions ( $\Delta H < 0$ ).

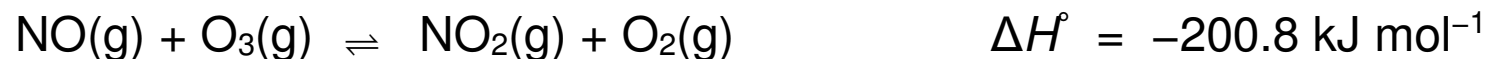
Increasing  $K$  shifts the equilibrium *toward products* – the *endothermic* direction.

Heating a system, initially at equilibrium, results in net *forward* reaction that *consumes* some of the heat added – countering the change.

Decreasing  $K$  shifts the equilibrium *toward reactants* – the *exothermic* direction.

Heating a system, initially at equilibrium, results in net *reverse* reaction that *consumes* some of the heat added – countering the change.

**Example:** Predict the direction each of the following equilibria shifts when the indicated changes are imposed.



- (a) The  $\text{O}_3$  partial pressure is increased
- (b) Some  $\text{NO}_2$  is removed from the reaction mixture
- (c) The reaction mixture is transferred to a vessel with twice the volume
- (d) Temperature is increased



- (e) The  $\text{HCl}$  partial pressure is increased
- (f) Some solid  $\text{NH}_4\text{Cl}$  is added to the mixture
- (g) Temperature is decreased

- (a)  $\text{O}_3$  is a reactant. Increasing its partial pressure results in net forward reaction – to consume some of the added  $\text{O}_3$ .
- (b)  $\text{NO}_2$  is a product. Removing it from the reaction mixture results in net forward reaction. This is a common means of improving product yield. Removing the product from a reaction mixture drives the reaction in the forward direction.
- (c) Doubling the volume of the vessel reduces all partial pressures to  $1/2$  their initial values. However, this does not change the reaction quotient because there are two partial pressure factors in both the numerator and denominator of  $Q$  and they have the same exponents. Decreasing all partial pressures by the same factor thus has no effect on the reaction quotient. Therefore, the system is still at equilibrium. This is consistent with le Châtelier's principle, which says that the reaction will shift to the side with more moles of gas so as to counter the reduction in total pressure caused by the increase in volume. However, neither forward nor reverse reaction increases the moles of gas. Therefore, the mixture remains at equilibrium.



- (d) The reaction is exothermic. Increasing temperature favors reactants (the endothermic direction of reaction) – i.e., there is net reverse reaction.
- (e) HCl is a product. Increasing its partial pressure results in net reverse reaction.
- (f)  $\text{NH}_4\text{Cl(s)}$  is a pure solid. Adding it or removing some of it from the reaction mixture has no effect on the equilibrium as long as some of the solid remains. No net reaction results.
- (g) The reaction is endothermic. Decreasing temperature favors reactant (the exothermic direction of reaction) – i.e., there is net reverse reaction.

## Final Equilibrium Conditions - ICE Tables

Consider the reaction of water vapor and carbon monoxide, both initially at 1.00 bar partial pressure.  $K = 0.63$  for this reaction at a certain temperature,  $T$ .

	$\text{H}_2\text{O}(\text{g})$	+	$\text{CO}(\text{g})$	$\rightleftharpoons$	$\text{H}_2(\text{g})$	+	$\text{CO}_2(\text{g})$
<b>Initial</b>	1.00		1.00		0		0
<b>Change</b>	$-x$		$-x$		$+x$		$+x$
<b>Equilibrium</b>	$1.00 - x$		$1.00 - x$		$x$		$x$

$x$  is the *extent of reaction* – appearing here as a change in partial pressure.

$$K = \left( \frac{P_{\text{H}_2} P_{\text{CO}_2}}{P_{\text{H}_2\text{O}} P_{\text{CO}}} \right)_{\text{eqm}} = \frac{x x}{(1.00 - x)(1.00 - x)} = 0.63$$

or

$$\left( \frac{x}{(1.00 - x)} \right)^2 = 0.63$$
$$\frac{x}{(1.00 - x)} = \sqrt{0.63} = 0.79_4$$

$$x = 0.79_4 (1.00 - x)$$

$$x = \frac{0.79_4}{1.79_4} = 0.44_3$$

$x = 0.44_3$ , gives the equilibrium partial pressures – the bottom row in the ICE table. Specifically,

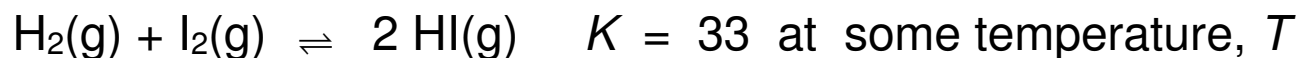
$$P_{\text{H}_2\text{O}} = P_{\text{CO}} = 1.00 - x = 0.56 \text{ bar}$$

and

$$P_{\text{H}_2} = P_{\text{CO}_2} = x = 0.44 \text{ bar} .$$

Sometimes a linear equation for  $x$  results – as it does above – and sometimes it is a quadratic equation.

**Example:** Consider the gas phase equilibrium of hydrogen and iodine,



- (a) Suppose a vessel is filled to 0.100 bar of both  $\text{H}_2$  and  $\text{I}_2$ . What is the partial pressure of HI when equilibrium is established at  $T$ ?
- (b) Suppose the vessel is filled to 1.00 bar of  $\text{H}_2$  and 0.100 bar of  $\text{I}_2$ . What is the partial pressure of HI when equilibrium is established at  $T$ ?

(a)

	<b>H<sub>2</sub></b>	<b>+</b>	<b>I<sub>2</sub></b>	<b>⇌</b>	<b>2 HI</b>
<b>Initial</b>	0.100		0.100		0
<b>Change</b>	-x		-x		+2 x
<b>Equilibrium</b>	0.100 - x		0.100 - x		2 x

Substitute the equilibrium partial pressures into the equilibrium constant equation.

$$K = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}} = \frac{(2x)^2}{(0.100 - x)(0.100 - x)} = 33$$

This equation simplifies.

$$\left( \frac{2x}{(0.100 - x)} \right)^2 = 33$$

$$\frac{2x}{(0.100 - x)} = \sqrt{33} = 5.7_4$$

$$2x = 5.7_4(0.100 - x)$$

$$x = \frac{0.57_4}{7.7_4} = 0.074_2$$

The final equilibrium partial pressure of HI is

$$P_{\text{HI}} = 2x = 2 \times 0.074_2 = 0.148 \text{ bar} .$$

(b)

	<b>H<sub>2</sub></b>	<b>+</b>	<b>I<sub>2</sub></b>	<b><math>\rightleftharpoons</math></b>	<b>2 HI</b>
<b>Initial</b>	1.00		0.100		0
<b>Change</b>	$-x$		$-x$		$+2x$
<b>Equilibrium</b>	$1.00 - x$		$0.100 - x$		$2x$

Substitute the equilibrium partial pressures into the equilibrium constant equation.

$$K = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}} = \frac{(2x)^2}{(1.00 - x)(0.100 - x)} = 33$$

This equation requires solution of a quadratic equation.

$$\frac{4x^2}{(0.100 - 1.10x + x^2)} = 33$$

$$4x^2 = 33(0.100 - 1.10x + x^2)$$

$$29x^2 - 36.3x + 3.3 = 0$$

$$ax^2 + bx + c = 0$$

The solution of this quadratic equation is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{36.3 \pm \sqrt{36.3^2 - 4 \times 29 \times 3.3}}{2 \times 29}$$

$$= \begin{cases} 1.1_5 \\ 0.098_7 \end{cases} \quad \text{Two solutions for } x - \text{only one of them is admissible.}$$



The choice of  $x = 1.15$  yields negative equilibrium partial pressures for  $\text{H}_2$  and  $\text{I}_2$ . It is an inadmissible solution. Therefore,

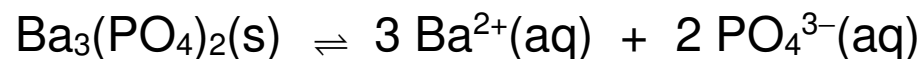
$$x = 0.0987$$

and

$$P_{\text{HI}} = 2x = 2 \times 0.0987 = 0.197 \text{ bar}$$

## Solubility

Example: The equilibrium constant for



is  $K_{\text{sp}}$  for  $\text{Ba}_3(\text{PO}_4)_2(\text{s})$ .

The overall concentration of the salt is called the *molar solubility*.

The molar solubility of  $\text{Ba}_3(\text{PO}_4)_2(\text{s})$  is 1/3 the barium concentration, or 1/2 the phosphate concentration, at equilibrium.

**Example:** Determine the molar solubilities of the following salts at 25°C. ( $K_{sp}$  values are for 25°C.)

- (a)  $\text{BaCO}_3$        $K_{sp} = 2.6 \times 10^{-9}$   
(b)  $\text{CaF}_2$        $K_{sp} = 3.45 \times 10^{-11}$

(a)

	$\text{BaCO}_3(\text{s})$	$\rightleftharpoons$	$\text{Ba}^{2+}(\text{aq})$	+	$\text{CO}_3^{2-}(\text{aq})$
<b>Initial</b>			0		0
<b>Change</b>			+ $x$		+ $x$
<b>Equilibrium</b>			$x$		$x$

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}] = x^2 = 2.6 \times 10^{-9}$$

which gives

$$x = \sqrt{2.6 \times 10^{-9}} = 5.1 \times 10^{-5}$$

At equilibrium,  $[\text{Ba}^{2+}] = [\text{CO}_3^{2-}] = 5.1 \times 10^{-5} \text{ mol L}^{-1}$

The molar solubility is just the barium or carbonate concentration, i.e.,  $5.1 \times 10^{-5} \text{ mol L}^{-1}$ .

(b)

	<b>CaF<sub>2</sub>(s)</b>	<b>Ca<sup>2+</sup>(aq)</b>	<b>+</b>	<b>2 F<sup>-</sup>(aq)</b>
<b>Initial</b>		0		0
<b>Change</b>		+x		+2 x
<b>Equilibrium</b>		x		2 x

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2 = x(2x)^2 = 3.45 \times 10^{-11}$$

which gives

$$x = \left( \frac{3.45 \times 10^{-11}}{4} \right)^{1/3} = 2.05 \times 10^{-4}$$

At equilibrium,

$$[\text{Ca}^{2+}] = x = 2.05 \times 10^{-4} \text{ mol L}^{-1}$$

$$[\text{F}^{-}] = 2x = 4.10 \times 10^{-4} \text{ mol L}^{-1}$$

Molar solubility is just the calcium concentration or 1/2 the fluoride concentration, i.e.,  $2.05 \times 10^{-4} \text{ mol L}^{-1}$ .

In general, the molar solubility of  $\text{M}_i\text{X}_j$  equals  $x$ , where

$$K_{sp} = (ix)^i (jx)^j = i^i j^j x^{i+j}$$

or

$$x = \left( \frac{K_{sp}}{i^i j^j} \right)^{\frac{1}{i+j}}.$$

## The Common Ion Effect

Less of a salt dissolves in a solution containing an ion in common with the salt, than in pure water.

For example, consider dissolving  $\text{CaCO}_3(\text{s})$  in a saturated solution of  $\text{CaF}_2(\text{s})$ .  $K_{sp} = 3.36 \times 10^{-9}$  for calcium carbonate at  $25^\circ\text{C}$ . Construct the ICE table for this process.

	$\text{CaCO}_3(\text{s})$	$\rightleftharpoons$	$\text{Ca}^{2+}(\text{aq})$	+	$\text{CO}_3^{2-}(\text{aq})$
<b>Initial</b>			$2.05 \times 10^{-4}$		0
<b>Change</b>			$+ x$		$+ x$
<b>Equilibrium</b>			$2.05 \times 10^{-4} + x$		$x$

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = (2.05 \times 10^{-4} + x)x = 3.36 \times 10^{-9}$$

which gives

$$x^2 + 2.05 \times 10^{-4} x - 3.36 \times 10^{-9} = 0$$

Using the quadratic formula,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-2.05 \times 10^{-4} \pm \sqrt{(2.05 \times 10^{-4})^2 + 4 \times 3.36 \times 10^{-9}}}{2}$$

$$= \begin{cases} 1.52_6 \times 10^{-5} \\ -2.20_3 \times 10^{-4} \end{cases}$$

The negative solution produces a negative carbonate concentration at equilibrium and is therefore inadmissible.

At equilibrium,

$$[\text{Ca}^{2+}] = 2.05 \times 10^{-4} + 1.53 \times 10^{-5} \text{ mol L}^{-1} = 2.20 \times 10^{-4} \text{ mol L}^{-1}$$

$$[\text{CO}_3^{2-}] = 1.53 \times 10^{-5} \text{ mol L}^{-1}$$

If the initial calcium concentration had been zero,  $K_{sp}$  equation would have given

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = x^2 = 3.36 \times 10^{-9}$$

$$x = \sqrt{3.36 \times 10^{-9}} = 5.80 \times 10^{-5}$$

In the absence of an initial calcium ion concentration, the extent of reaction (dissolution of calcium carbonate) is larger;  $5.80 \times 10^{-5}$  versus  $1.53 \times 10^{-5}$ .



# Thermochemistry

## System, State and Properties (state functions)

Universe = *system(s)* + *surroundings* (i.e., everything else)

The *system* is the portion of the universe we are currently considering.

Systems have *properties* – *state functions*:

amount of each substance in the system,  $n$   
volume,  $V$   
temperature,  $T$   
pressure,  $P$

Other properties:

energy,  $U$   
the sum total of potential and kinetic energy of all  
particles in the system.  
enthalpy,  $H$

## Heat

Heat flows from a hot system to a cold system – in *thermal contact*.

Heat flows until the temperatures no longer change – they are equal at equilibrium.

$q$  = heat flow *into* a system

When heat flows *from* system 2 *to* system,

$$q_2 = -q_1$$

heat flowed into system 1:  $q_1 > 0$

heat flowed from system 2:  $q_2 < 0$

If there are no phase transitions ...

The temperature of system 1 increases:

$$q_1 = C_1 \Delta T_1$$

$C_1$  is the *heat capacity* of the system 1, and

$$\Delta T_1 = T_{1, \text{final}} - T_{1, \text{initial}}$$

$C_1$  is proportional to the amount of substance – the size of the system.

Heat capacity is an *extensive* property.

Specific heat capacity – a characteristic of a substance

$$s = \frac{C}{m}$$

$C$  is the heat capacity of mass,  $m$ , of the substance – mass measured in grams. Units are  $\text{J K}^{-1} \text{g}^{-1}$ .

$s$  is the heat capacity per gram of substance; i.e.,  $m$  is the mass in grams.

An *intensive* property – independent of size of system.

$$s_{\text{water}} = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$$

and

$$s_{\text{copper}} = 0.385 \text{ J K}^{-1} \text{ g}^{-1},$$

at 25°C and 1 bar pressure

In this course, we treat  $s$  as independent of temperature and pressure for all substances.

In terms of  $s$ ,

$$q = ms \Delta T$$

**Example:** How much heat must flow into a 100. g sample of water to raise its temperature from 20.00°C to 25.00°C? ( $s_{\text{water}} = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$ )

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 25.00\text{ }^{\circ}\text{C} - 20.00\text{ }^{\circ}\text{C} = 5.00\text{ }^{\circ}\text{C} \text{ or } 5.00\text{ K} .$$

A 1  $^{\circ}\text{C}$  difference is the same as 1 K difference.

The heat transferred is

$$\begin{aligned} q &= ms \Delta T \\ &= 100. \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times 5.00 \text{ K} \\ &= 209_2 \text{ J} = 2.09 \text{ kJ} . \end{aligned}$$

**Example:** A 20.0 g sample of copper at 300. $^{\circ}\text{C}$  is placed within a thermally insulated vessel containing 100. g of water at 20.0 $^{\circ}\text{C}$ . What is the final temperature when thermal equilibrium is re-established? ( $s_{\text{water}} = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$  and  $s_{\text{copper}} = 0.385 \text{ J K}^{-1} \text{ g}^{-1}$ )

The heat lost by copper is

$$\begin{aligned} -q_{\text{copper}} &= -m_{\text{copper}} s_{\text{copper}} \Delta T_{\text{copper}} \\ &= -20.0 \text{ g} \times 0.385 \text{ J K}^{-1} \text{ g}^{-1} \times (T_{\text{f}} - 300. \text{ }^{\circ}\text{C}) \\ &= 7.70 \text{ J K}^{-1} (300. \text{ }^{\circ}\text{C} - T_{\text{f}}) \end{aligned}$$

The heat gained by water is

$$\begin{aligned} q_{\text{water}} &= m_{\text{water}} s_{\text{water}} \Delta T_{\text{water}} \\ &= 100. \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times (T_{\text{f}} - 20. \text{ }^{\circ}\text{C}) \\ &= 418 \text{ J K}^{-1} (T_{\text{f}} - 20. \text{ }^{\circ}\text{C}) \end{aligned}$$

Heat lost by copper is gained by water. So

$$q_{\text{water}} = -q_{\text{copper}}$$

or

$$418 \text{ J K}^{-1} (T_{\text{f}} - 20. \text{ }^{\circ}\text{C}) = 7.70 \text{ J K}^{-1} (300. \text{ }^{\circ}\text{C} - T_{\text{f}})$$

which rearranges to

$$(418 + 7.70) T_{\text{f}} = 7.70 \times 300. + 418 \times 20.$$

$$T_{\text{f}} = 10670/425.7 \text{ }^{\circ}\text{C} = 25.1 \text{ }^{\circ}\text{C}$$

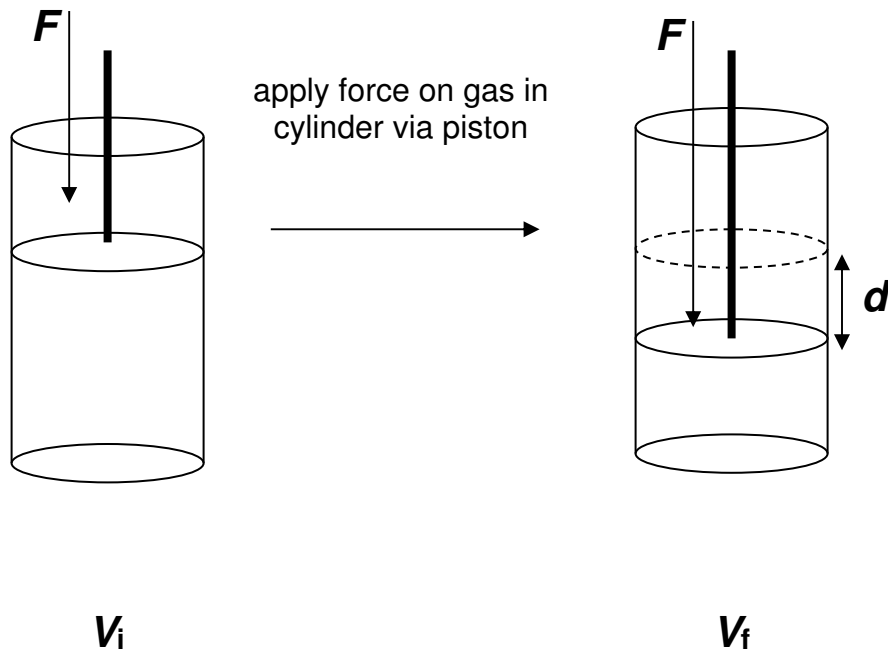
## Phase transitions

Heat is **absorbed** – at a constant temperature – by a solid when it **melts** or **sublimates**, and by a liquid when it **evaporates** (**boils**)

Heat is released in the reverse processes – i.e., **condensation** (gas to liquid), **deposition** (gas to solid) and **freezing** (solid to liquid).

## Work

Doing work *on* a gas:



**Compressed gas has higher energy**



Work done *on* the gas is

$$\begin{aligned}w &= F d \\&= P A d \\&= -P \Delta V\end{aligned}$$

**Example:** How much work is done on the air in a bicycle pump when the volume of air is decreased by 50 mL under 5.0 bar pressure?

$$\begin{aligned}w &= -P \Delta V \\&= -5.0 \text{ bar} \times 0.050 \text{ L} = -0.25 \text{ L bar} \\&= -100 \text{ J L}^{-1} \text{ bar}^{-1} \times 0.25 \text{ L bar} \\&= 25 \text{ J}\end{aligned}$$

Note:

$$100 \text{ J} = 1 \text{ L bar}$$

since

$$1 \text{ L} = 10^3 \text{ mL} = 10^3 \times (10^{-2} \text{ m})^3 = 10^{-3} \text{ m}^3$$

and

$$1 \text{ bar} = 10^5 \text{ Pa} = 10^5 \text{ J m}^{-3}$$

## Work done when there is a chemical reaction.

Chemical reactions (or physical processes) can change the volume of a system.

Volume of a system is determined (almost entirely) by the number of moles of gas,  $n_{\text{gas}}$ .

Work is *positive* (volume *decreases*) for reactions that *decrease moles of gas*.

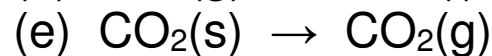
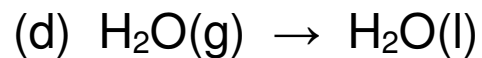
$$w > 0 \quad \Delta n_{\text{gas}} < 0$$

Work is *negative* (volume *increases*) for reactions that *increase moles of gas*.

$$w < 0 \quad \Delta n_{\text{gas}} > 0$$

**Example:** For which of the following processes is work positive – i.e., work is done on the system?

- (a)  $2 \text{Na(s)} + 2 \text{H}_2\text{O(l)} \rightarrow 2 \text{NaOH(aq)} + \text{H}_2\text{(g)}$
- (b)  $\text{C}_3\text{H}_8\text{(g)} + 5 \text{O}_2\text{(g)} \rightarrow 3 \text{CO}_2\text{(g)} + 4 \text{H}_2\text{O(l)}$
- (c)  $2 \text{NI}_3\text{NH}_3\text{(s)} \rightarrow 2 \text{N}_2\text{(g)} + 3 \text{I}_2\text{(s)} + 3 \text{H}_2\text{(g)}$



(a) The only gas here is a product.  $\Delta n_{\text{gas}} = n_{\text{product gas}} - n_{\text{reactant gas}} = 1$ .

Work is done by the system.  $w < 0$

**(b)**  $\Delta n_{\text{gas}} = -3$ . Work is done **on** the system.  $w > 0$

(c)  $\Delta n_{\text{gas}} = 5$ . Work is done by the system.  $w < 0$

**(d)**  $\Delta n_{\text{gas}} = -1$ . Work is done **on** the system.  $w > 0$

(e)  $\Delta n_{\text{gas}} = 1$ . Work is done by the system.  $w < 0$

## Energy Conservation – the First Law of Thermodynamics

$$\Delta U = q + w$$

Change in *energy* results from heat flow to/from the system, and/or work done on/by the system.

**Example:** What is the change in energy for the following combinations of  $q$  and  $w$ ?

(a)  $q = 50 \text{ J}$  and  $w = 50 \text{ J}$

(b)  $q = 0 \text{ J}$  and  $w = 100 \text{ J}$

(a)  $q = 100 \text{ J}$  and  $w = 0 \text{ J}$

(a)  $\Delta U = q + w = 50 \text{ J} + 50 \text{ J} = 100 \text{ J}$

(b)  $\Delta U = q + w = 0 \text{ J} + 100 \text{ J} = 100 \text{ J}$

(c)  $\Delta U = 100 \text{ J}$

Different combinations of  $q$  and  $w$  produce the same change in the energy.

Heat and work are *not* state functions. However, their sum is the *change* in a state function – *energy*,  $U$ .

## Bomb Calorimetry

*Bomb calorimeters* are *calorimeters* with *constant volume*.

Measuring heat (via change in temperature) gives  $\Delta U$ , since the work term is zero:

$$\Delta U = q + 0 = q_v$$

Bomb calorimeters require a strong, rigid (steel) container to withstand large pressure differences that can result from chemical reactions inside the calorimeter.

## Coffee Cup Calorimetry

*Coffee cup calorimeters* are calorimeters with *constant pressure*.

Much safer, but do not give  $\Delta U$  directly – not a problem ...

## Enthalpy

*Enthalpy* is another state function – it is energy plus the product of pressure and volume:

$$H = U + P V$$

For solids and liquids, which occupy small volumes,  $P V$  is negligible compared to  $U$ .

For gases, the  $P V$  term is not negligible. However, it is small.

Under constant pressure conditions – in a coffee cup calorimeter – the change in energy is not equal to the measured  $q$ . The first law gives

$$\begin{aligned}\Delta U &= q + w \\ &= q - P \Delta V\end{aligned}$$

Under constant pressure conditions, the volume can change.

However, if pressure is constant,

$$P \Delta V = \Delta(P V)$$

and

$$\begin{aligned}\Delta U &= q + w \\ &= q - P \Delta V = q - \Delta(P V)\end{aligned}$$

or

$$\begin{aligned}\Delta U + \Delta(P V) &= q \\ \Delta(U + P V) &= q \\ \Delta H &= q = q_p\end{aligned}$$

Heat measured in a *coffee cup calorimeter* equals the *change in enthalpy*, a state function.

An *enthalpy scale* for all substances can be constructed from a series of coffee cup calorimeter experiments.

Each experiment measures the *enthalpy difference* between the reactants and products for some reaction – i.e., the *enthalpy of reaction*.

## Calorimetry

A calorimeter is thermally insulated from the surroundings.

*No* heat transferred *to* or *from* the interior of the calorimeter:

$$q_1 = 0$$

However, the temperature changes.

- a. Temperature *increases* – the *reaction releases* heat – the heat is trapped in the calorimeter.
- b. Temperature *decreases* – the *reaction absorbs* heat – heat is absorbed from the contents of the calorimeter.

In either case, we imagine a second step – a *thought experiment* (*not* actually performed).



Remove the thermal insulation and allow the temperature to return to its initial value.

- a. The trapped heat is *released* to the surroundings – heat is *negative*

$$q_2 < 0$$

- b. The absorbed heat *returns* to the system from the surroundings – heat is *positive*

$$q_2 > 0$$

If steps 1 and 2 occur at constant pressure,

$$\Delta H_1 = q_1$$

and

$$\Delta H_2 = q_2 = C (-\Delta T),$$

Under constant volume conditions – i.e., a *bomb calorimeter* –

$$\Delta U = C (-\Delta T)$$

$C$  is the heat capacity of the calorimeter including contents, and

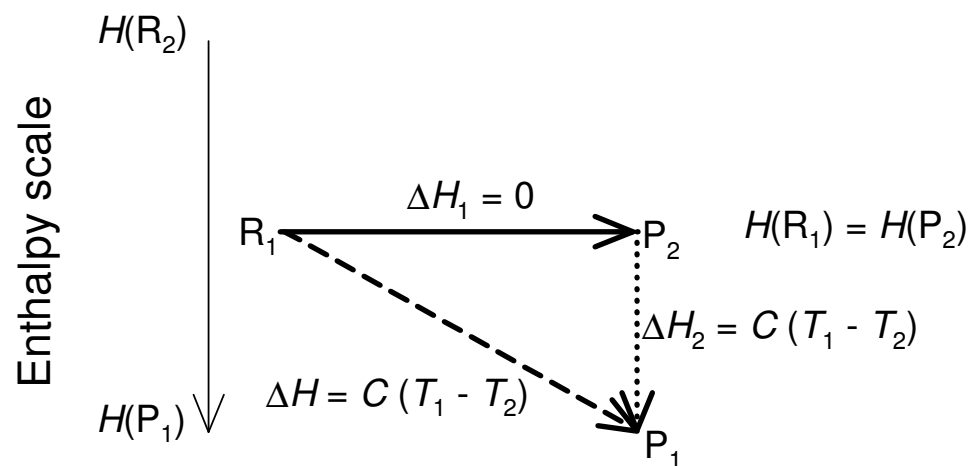
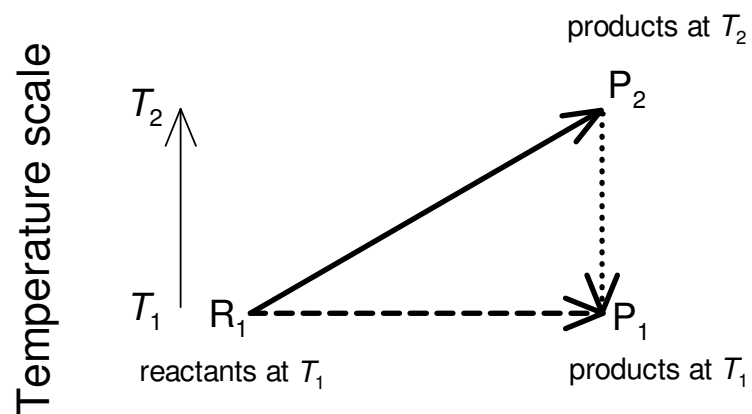
$-\Delta T = T_{\text{initial}} - T_{\text{final}}$  is the change in temperature of the second step – the thought experiment.

$\Delta T = T_{\text{final}} - T_{\text{initial}}$  is the change in temperature of the calorimetry experiment – the first step.

Since  $H$  is a state function, the change in enthalpy upon conversion of reactants to products (at the same temperature – the initial temperature) is

$$\Delta H = \Delta H_1 + \Delta H_2 = -C \Delta T$$

a. Temperature increases



$\Delta H$  depends upon the amount of reactant converted to product – it is proportional.

The *enthalpy of reaction* is the change in enthalpy for extent of reaction = one mole; i.e., it is the change in enthalpy *per mole* of *extent of reaction*.

$$\Delta H_{\text{rxn}} = \Delta H / n,$$

$n$  is the extent of reaction in the calorimetry experiment.

**Example:** The neutralization of 100. mL 0.200 M NaOH solution with 100. mL 0.200 HCl solution is performed in a coffee cup calorimeter. The temperature of the combined solution rises from 20.00°C to 21.34°C. What is the enthalpy of this reaction in kJ mol<sup>-1</sup>? Assume the solution has density 1.00 g mL<sup>-1</sup> and specific heat capacity 4.18 J K<sup>-1</sup> g<sup>-1</sup> – i.e., the properties of pure water at 20.00°C.

Here,

$$C = m s$$

and

$$q = m s (-\Delta T)$$

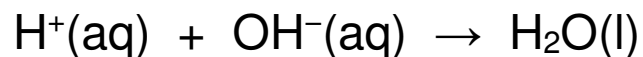
The total mass of solution:

$$\begin{aligned} m &= V d \\ &= (100. + 100. \text{ mL}) \times 1.00 \text{ g mL}^{-1} = 200. \text{ g} \end{aligned}$$

Heat:

$$\begin{aligned} q &= -200. \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} (21.34 - 20.00) \text{ K} \\ &= -1120 \text{ J} = -1.12 \text{ kJ} \\ &= q_P = \Delta H \end{aligned}$$

The *net balanced reaction* is



Number of moles of  $\text{H}^+(\text{aq})$  equals volume of HCl solution  $\times$  its concentration – i.e.,

$$0.100 \text{ L} \times 0.200 \text{ mol L}^{-1} = 0.0200 \text{ mol}$$

Number of moles of  $\text{OH}^-$  is the same. They are both totally consumed.

Number of moles reacted – the *extent of reaction* – is  $n = 0.0200 \text{ mol}$ .

The *enthalpy of reaction* (per mole of extent of reaction).

$$\begin{aligned}\Delta H_{\text{rxn}} &= \Delta H / n \\ &= -1.12 \text{ kJ} / 0.0200 \text{ mol} \\ &= -56.0 \text{ kJ mol}^{-1}\end{aligned}$$

The reaction of NaOH and HCl *released heat* and  $\Delta H_{\text{rxn}}$  is *negative* - an *exothermic* reaction.

Other exothermic processes include *freezing*, *condensation*, *deposition* and *bond formation*.

Bonds (covalent, ionic or intermolecular) are stronger in a solid, than in a liquid. In the gas phase intermolecular forces are essentially absent.

Also, all *redox reactions* that occurs naturally – e.g., combustion.

Processes with *positive*  $\Delta H_{\text{rxn}}$  *absorb heat* – they are called *endothermic* processes.

For example, dissolution of ammonium nitrate in water is endothermic:



Here, strong ionic bonds in the reactant are broken to form weaker intermolecular forces (solvation of the separated ions) in solution.

Other endothermic processes include *melting*, *vaporization*, *sublimation* and *bond breaking*.

Exothermic reactions *break weaker* bonds to *form stronger* bonds.

Condensation (the reverse of vaporization) is *exothermic* because it *forms intermolecular bonds* in the liquid *without breaking* any bonds.



## Hess' Law

The *enthalpy of reaction* for a “*target reaction*” equals the *sum of the enthalpies of reaction* for any set of reactions that “add” up to the target reaction.

Follows because enthalpy is a state function;

$$\begin{aligned}\Delta H &= H_{\text{final}} - H_{\text{initial}} \\ &= \Delta H_1 + \Delta H_2 + \dots\end{aligned}$$

for any set of steps with the same *initial* and *final* states  
*reactants* *products*

A reaction plus the associated reverse reaction yields no net change. Thus,

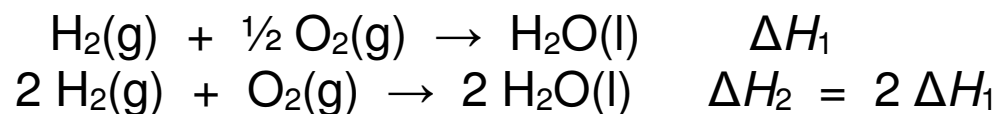
$$\Delta H = \Delta H_{\text{forward}} + \Delta H_{\text{reverse}} = 0$$

and

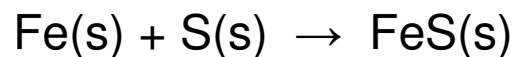
$$\Delta H_{\text{reverse}} = -\Delta H_{\text{forward}}$$

When a reaction is scaled – e.g., the stoichiometric coefficients are twice as big – the enthalpy of reaction is scaled by the same factor.

For example,



**Example:** Determine the enthalpy of the following reaction given the data below.



$n$	Reaction	$\Delta H_n$ (kJ mol <sup>-1</sup> )
1	$2 \text{Fe}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{FeO}(\text{s})$	-544.0
2	$2 \text{S}(\text{s}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$	-791.4
3	$\text{FeO}(\text{s}) + \text{SO}_3(\text{g}) \rightarrow \text{FeSO}_4(\text{s})$	-260.7
4	$\text{FeS}(\text{s}) + 2 \text{O}_2(\text{g}) \rightarrow \text{FeSO}_4(\text{s})$	-828.4

Reaction 1 has reactant 2 Fe(s) among reactants. Scale reaction 1 by 1/2 to match the Fe(s) coefficient in the target reaction. Reaction 2 has 2 S(s) among reactants. Again, scale by 1/2. Reaction 4 has FeS(s) as a reactant, whereas FeS(s) is a product in the target reaction. Reverse reaction 4. Reaction 3 is needed to cancel out compounds that do not participate in the target reaction. Note that the  $\Delta H$  values must be adjusted similarly.

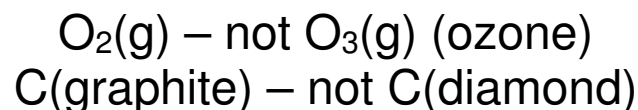
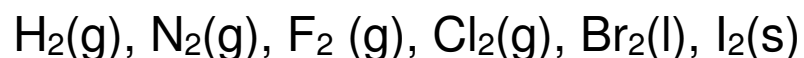
		$\Delta H_n$ (kJ mol <sup>-1</sup> )
1/2 × Rxn 1	Fe(s) + 1/2 O <sub>2</sub> (g) → FeO(s)	-272.0
1/2 × Rxn 2	S(s) + 3/2 O <sub>2</sub> (g) → SO <sub>3</sub> (g)	-395.7
-Rxn 4	FeSO <sub>4</sub> (s) → FeS(s) + 2 O <sub>2</sub> (g)	828.4
Rxn 3	FeO(s) + SO <sub>3</sub> (g) → FeSO <sub>4</sub> (s)	-260.7
	<hr/> Fe(s) + S(s) → FeS(s)	<hr/> -100.0

## Formation reactions

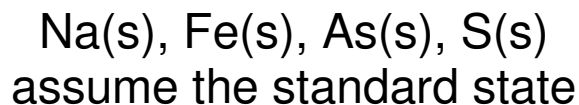
The *formation reaction* of a compound forms the compound from its *elements* in their *standard state*.

Standard state of an element = its stable form at 1.00 bar pressure and 25°C.

Some standard states – most stable structure at 1.00 bar pressure and 25°C.



Most elements are solids written as, for example,



$\text{S}(\text{s})$  is a convenient shorthand for  $\text{S}_8(\text{rhombic})$  a molecular solid

## A Universal Enthalpy Scale

A table of enthalpies of formation provides a universal enthalpy scale.

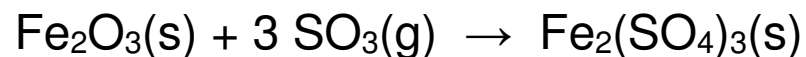
The enthalpy of reaction – for any reaction (under *standard conditions* of 1.00 bar pressure and 25°C) – with reactants and products in the table is given by

$$\Delta H^{\circ} = \sum_{\text{products, P}} c_{\text{P}} \Delta H_f^{\circ}[\text{P}] - \sum_{\text{reactants, R}} c_{\text{R}} \Delta H_f^{\circ}[\text{R}]$$

Superscript “<sup>0</sup>” denotes standard conditions.

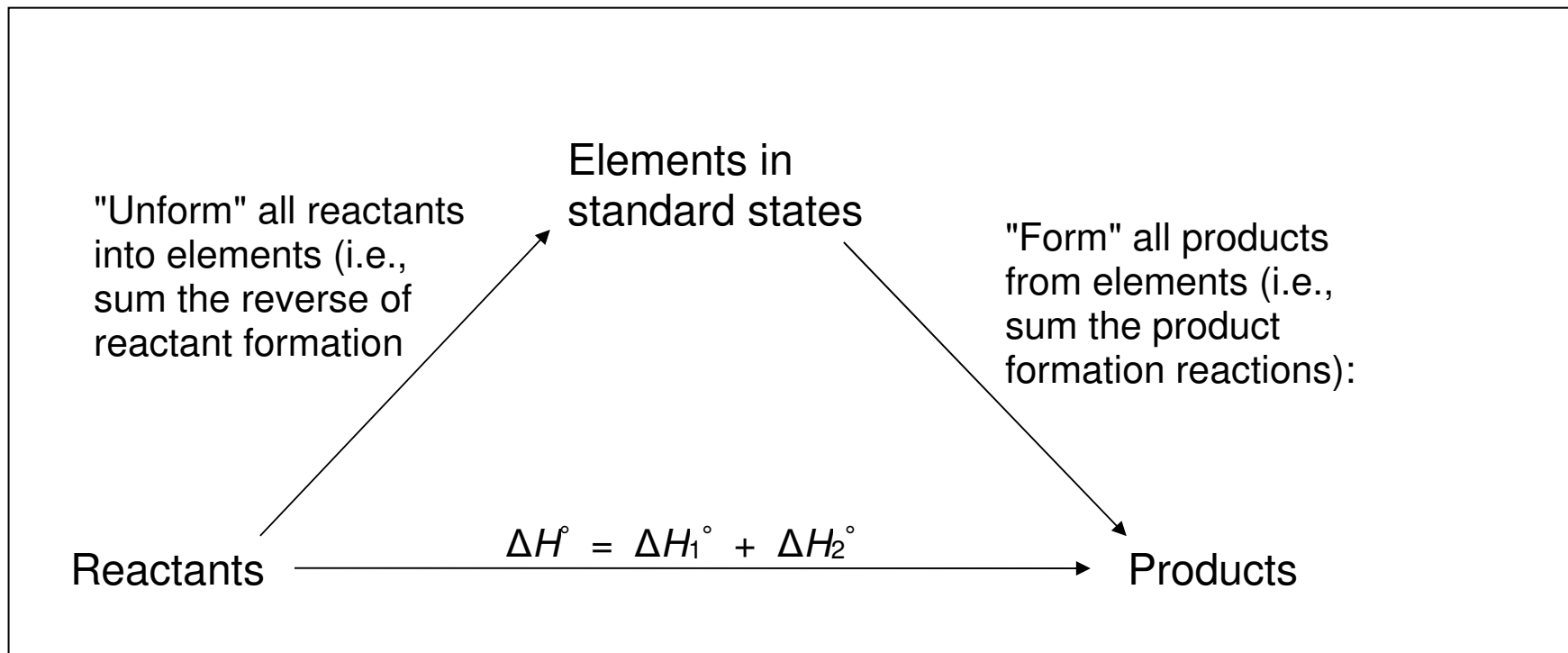
$c_{\text{P}}$  and  $c_{\text{R}}$  are the stoichiometric coefficients of products and reactants, respectively.

For example, the enthalpy of reaction of



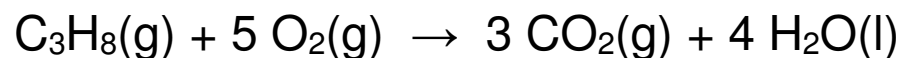
is

$$\Delta H^{\circ} = \Delta H_f^{\circ}[\text{Fe}_2(\text{SO}_4)(\text{s})] - \Delta H_f^{\circ}[\text{Fe}_2\text{O}_3(\text{s})] - 3\Delta H_f^{\circ}[\text{SO}_3(\text{g})]$$



**Example:** Determine the enthalpy of combustion of propane from the given enthalpies of formation.

Compound	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )
CO <sub>2</sub> (g)	-393.5
H <sub>2</sub> O(l)	-285.8
C <sub>3</sub> H <sub>8</sub> (g)	-103.8



$$\begin{aligned}\Delta H^\circ &= 3\Delta H_f^\circ[\text{CO}_2(\text{g})] + 4\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] - \Delta H_f^\circ[\text{C}_3\text{H}_8(\text{g})] \\ &= 3(-393.5) + 4(-285.8) - (-103.8) \text{ kJ mol}^{-1} = -2219.9 \text{ kJ mol}^{-1}\end{aligned}$$

## Bond Enthalpies

*Bond enthalpy* is the change in enthalpy when a bond is broken – the enthalpy of a *bond dissociation reaction*.

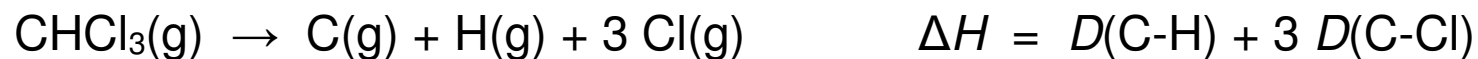
For example, the bond enthalpy of the Cl-Cl bond,  $D(\text{Cl-Cl})$ , is  $\Delta H$  for



Bond dissociation is endothermic.

$D$  is always positive.

Another example,





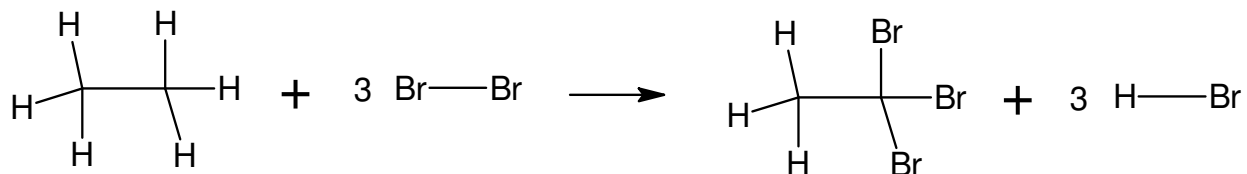
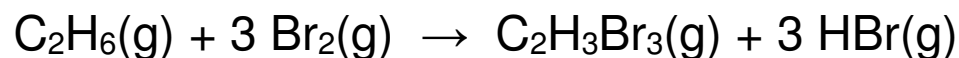
An *approximate* formula for the *enthalpy of any reaction*:

$$\Delta H = \sum_{\text{reactant bonds, r}} n_r D[r] - \sum_{\text{product bonds, p}} n_p D[p]$$

$n_r$  is the number of bonds of type r (e.g., C-Cl bond) among reactants.

$n_p$  is the number of bonds of type p among products.

The enthalpy of reaction for



is approximated by

$$\Delta H = D[\text{C-C}] + 6D[\text{C-H}] + 3D[\text{Br-Br}] - D[\text{C-C}] - 3D[\text{C-H}] - 3D[\text{C-Br}] - 3D[\text{H-Br}]$$

$$= 3D[\text{C-H}] + 3D[\text{Br-Br}] - 3D[\text{C-Br}] - 3D[\text{H-Br}] .$$

Note that bond enthalpies of unchanged bonds cancel out.

Structures of reactants and products are required.

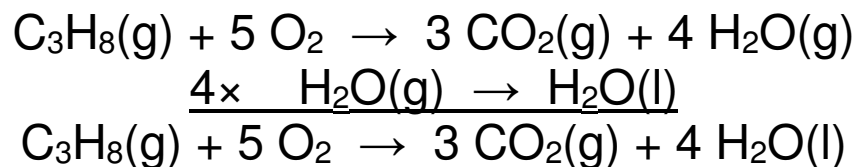
Double bonds are stronger – larger  $D$  – than single bonds (same atoms).

Triple bonds are stronger than double bonds.

Gas phase reactions only.

However, other reactions can be converted to gas phase reactions via sublimation and/or vaporization steps.

For example,

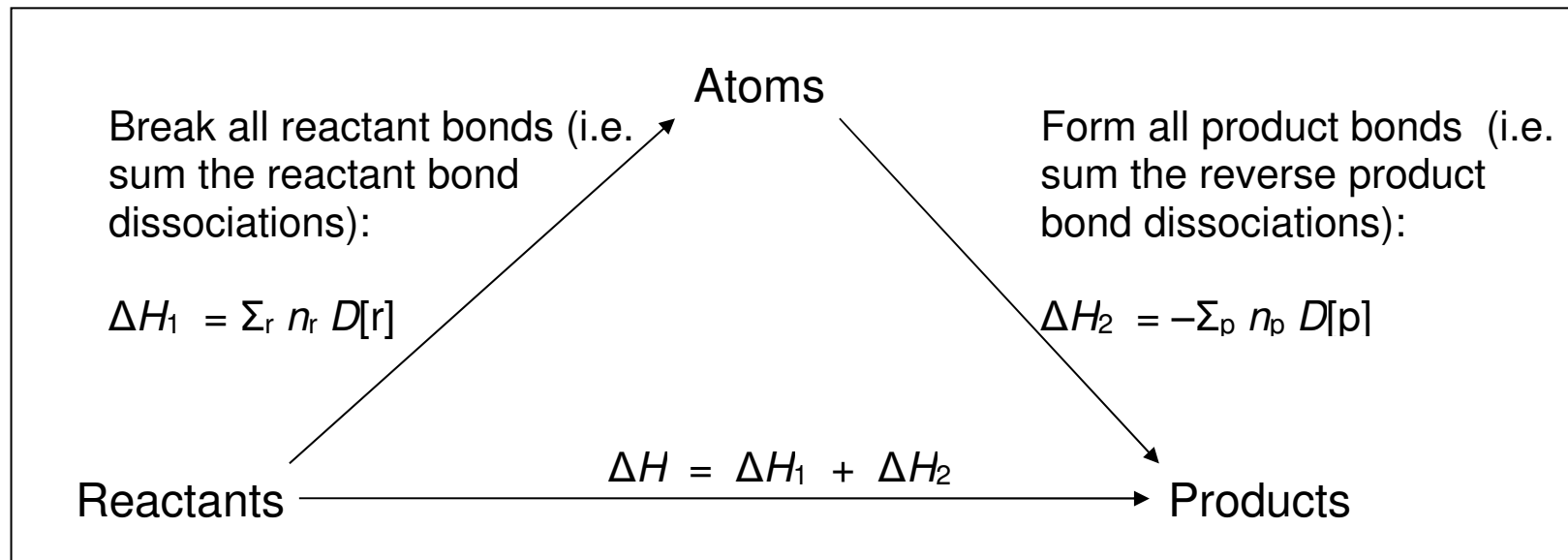


The *enthalpy of combustion* of propane is just

$$\Delta H = \Delta H_{\text{gas phase rxn}} - 4\Delta H_{\text{vap}}[\text{H}_2\text{O}]$$

where

$$\Delta H_{\text{gas phase rxn}} \cong 2D[\text{C-C}] + 8D[\text{C-H}] + 5D[\text{O=O}] - 3 \times 2D[\text{C=O}] - 4 \times 2D[\text{O-H}] .$$

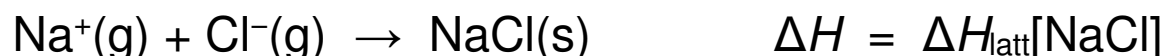


## Lattice Enthalpy and the Born-Haber Cycle

Ionic solids – bonding results from the electrostatic attraction of cations to anions.

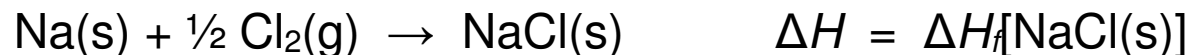
Arrangement of the ions in the solid gives net *negative electrostatic potential energy* = *lattice enthalpy*.

For example, the lattice enthalpy of NaCl(s) is  $\Delta H$  for

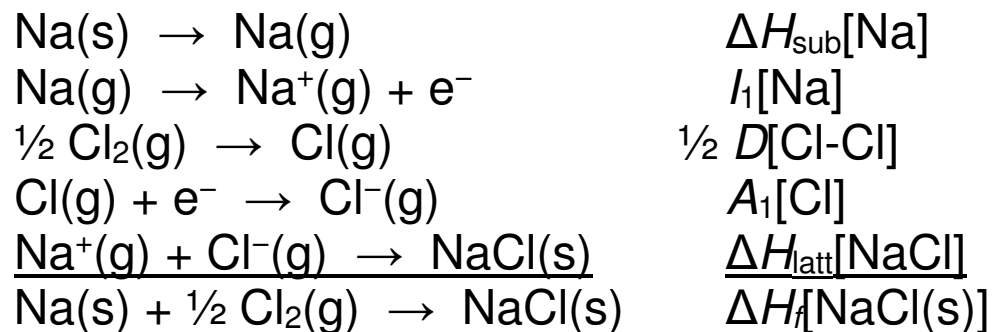


Lattice enthalpy is determined from enthalpy of the formation, ionization energy and electron affinity data.

For example, the formation reaction of sodium chloride is



This is the sum of the following steps:



Thus,

$$\Delta H_f[\text{NaCl(s)}] = \Delta H_{\text{sub}}[\text{Na}] + I_1[\text{Na}] + \frac{1}{2} D[\text{Cl-Cl}] + A_1[\text{Cl}] + \Delta H_{\text{latt}}[\text{NaCl}] ,$$

where

- (1)  $\Delta H_{\text{sub}}[\text{Na}]$  is the enthalpy of sublimation of sodium,
- (2)  $I_1[\text{Na}]$  is the first ionization energy of sodium,
- (3)  $D[\text{Cl-Cl}]$  is the bond enthalpy of a chlorine-chlorine bond, and
- (4)  $A_1[\text{Cl}]$  is the first electron affinity of chlorine.

$\Delta H_{\text{sub}}[\text{Na}]$  is sometimes written as  $\Delta H_{\text{atom}}[\text{Na}]$ , the enthalpy of atomization of sodium.

$\Delta H_{\text{sub}}$  and  $\Delta H_{\text{atom}}$  are the same for sodium, since sodium sublimates to form an atomic gas.

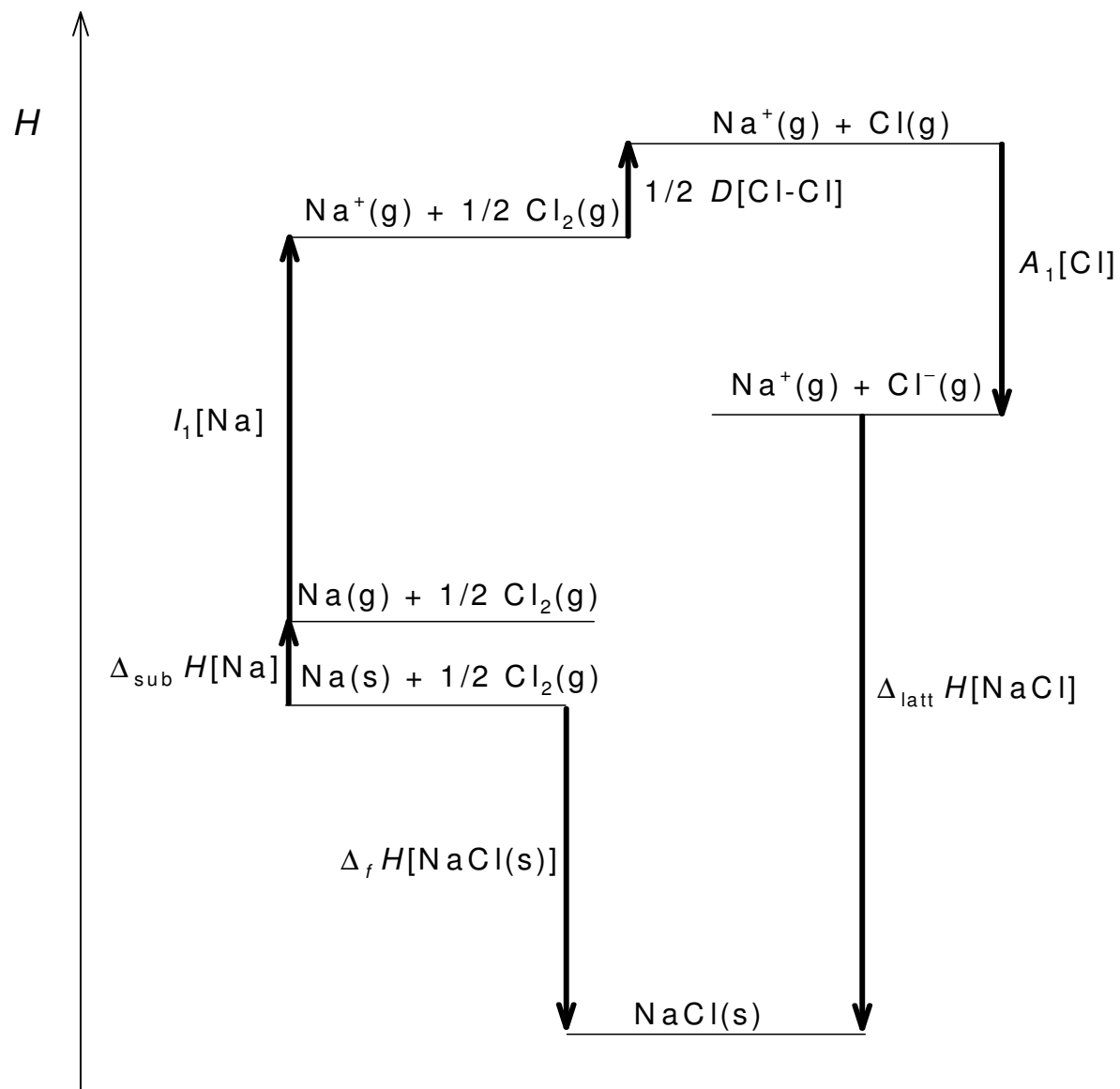
Rearranging gives

$$\Delta H_{\text{latt}}[\text{NaCl(s)}] = \Delta H_{\text{f}}[\text{NaCl(s)}] - \Delta H_{\text{sub}}[\text{Na}] - I_1[\text{Na}] - \frac{1}{2} D[\text{Cl-Cl}] - A_1[\text{Cl}]$$

For sodium chloride,

$$\begin{aligned}\Delta H_{\text{latt}}[\text{NaCl(s)}] &= -411.2 - 107.5 - 495.8 - \frac{1}{2} \times 242.9 - (-348.5) \text{ kJ mol}^{-1} \\ &= -787.5 \text{ kJ mol}^{-1} .\end{aligned}$$

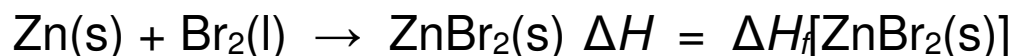
The *Born-Haber cycle* of sodium chloride ...



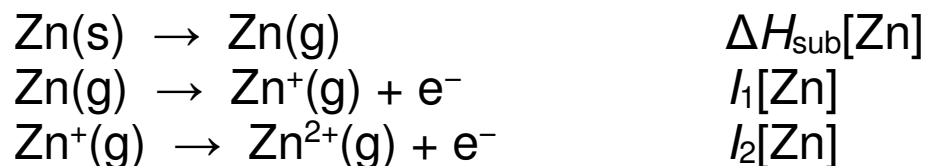
**Example:** Determine the enthalpy of formation of zinc bromide from the following data (in kJ mol<sup>-1</sup>):

$\Delta H_{\text{latt}}[\text{ZnBr}_2]$	-2674.3
$\Delta H_{\text{sub}}[\text{Zn}]$	130.4
$I_1[\text{Zn}]$	906.3
$I_2[\text{Zn}]$	1733.1
$\Delta H_{\text{vap}}[\text{Br}_2]$	30.9
$D[\text{Br-Br}]$	193.9
$A_1[\text{Br}]$	-324.5

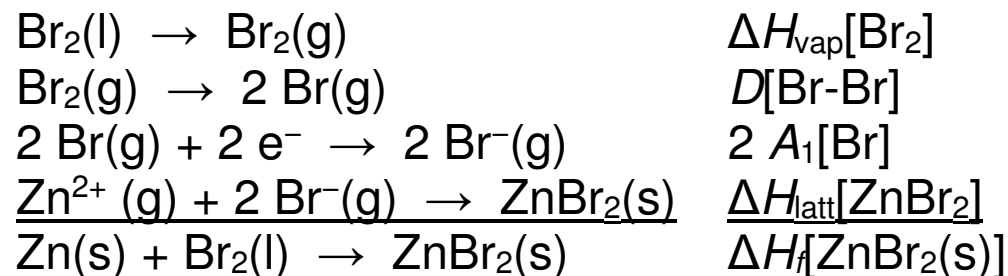
The formation reaction of zinc bromide is



This reaction is the sum of the following steps:







The sum of the enthalpy changes equals the enthalpy of formation of zinc bromide:

$$\Delta H_f[\text{ZnBr}_2(\text{s})] = \Delta H_{\text{sub}}[\text{Zn}] + I_1[\text{Zn}] + I_2[\text{Zn}] + \Delta H_{\text{vap}}[\text{Br}_2] + D[\text{Br}-\text{Br}] + 2 A_1[\text{Br}] + \Delta H_{\text{latt}}[\text{ZnBr}_2]$$

$$= 130.4 + 906.3 + 1733.1 + 30.9 + 193.9 + 2 \times (-324.5) + (-2674.3) \text{ kJ mol}^{-1}$$

$$= -328.7 \text{ kJ mol}^{-1} .$$

## The Magnitude of Lattice Enthalpy

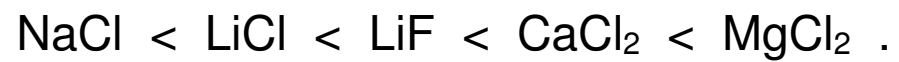
$$E = K \frac{Ze(-Ye)}{r} \quad \text{Coulomb's law}$$
$$= -Ke^2 \frac{ZY}{r_Z + r_Y} \quad \text{at closest approach.}$$

- (1) the largest magnitude lattice enthalpies are associated with the largest ion charges. For sets of solids with same ion charges,
- (2) the largest magnitude lattice enthalpies occur for the smallest ions.

**Example:** Order the following sets of ionic solids according to the magnitude of lattice enthalpy:

- (a) LiF, LiCl, NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>  
(b) CaO, SrS, NaF, Al<sub>2</sub>O<sub>3</sub>, SrBr<sub>2</sub>

(a)



(b)

