

Lecture 12 CH102 A1 (MWF 9:05 am) Spring 2018

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[TP] Based on Coulomb's law, which of the following has the **largest magnitude** enthalpy of aqutation,  $[\Delta_{\text{aq}}H]$ ?

- 25% 1. LiCl  
 25% 2. NaCl  
 25% 3. KCl  
 25% 4. Further information required



1

## Lecture 12 CH102 A1 (MWF 9:05 am)

Friday, February 16, 2018

- Complete: Predicting relative values of  $\Delta_{\text{latt}}H$  and  $\Delta_{\text{aq}}H$
- Effect of temperature on solubility
- Review of colligative properties

**Next:** Begin ch13: Dynamic chemical equilibrium



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### Enthalpy of aqutation, $\Delta_{\text{aq}}H$

Make a sketch of **liquid water** at the scale of individual molecules.  
 Represent the molecules as chevrons ( $/\backslash$ ) in various orientations.



6

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### Enthalpy of aqutation, $\Delta_{\text{aq}}H$

Make a sketch of what a **1 M aqueous solution of  $\text{MgS}(s)$**  looks like on the scale of your sketch of liquid water.

Represent water molecules as chevrons ( $/\backslash$ ) in various orientations.



7

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## Enthalpy of aqution, $\Delta_{aq}H$

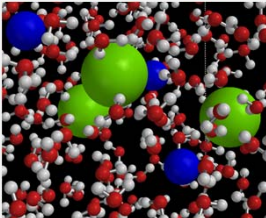
**Key idea:** Electrical attraction (Coulomb's law) between ions and polar water molecules

Energy  $\propto \frac{\text{ion charge}}{\text{distance to water}}$

The **smaller** the ion size, ...  
the **smaller** the **distance** to water and so ...  
the **greater** enthalpy of aqution

$\text{Cl}^- > \text{Br}^- > \text{I}^-$

$\text{Li}^+ > \text{K}^+ > \text{NH}_4^+$



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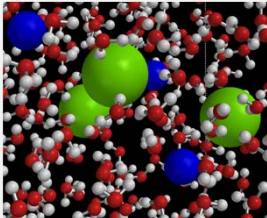
## Enthalpy of aqution, $\Delta_{aq}H$

**Key idea:** Electrical attraction (Coulomb's law) between ions and polar water molecules

Energy  $\propto \frac{\text{ion charge}}{\text{distance to water}}$

The **larger** the **ion charge** ...  
the **greater** enthalpy of aqution

$\text{PO}_4^{3-} > \text{S}^{2-} > \text{Cl}^-$



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## Enthalpy change of solution, $\Delta_{sol}H$

When  $\text{KF}(s)$  is dissolved in water in a beaker, the beaker **becomes warm**. What happens when  $\text{KCl}(s)$  is dissolved in water?

	Lattice	Aqution	Solution
KF	+821	-837	-16 (warmer)
KCl			

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## Enthalpy change of solution, $\Delta_{sol}H$

When  $\text{KF}(s)$  is dissolved in water in a beaker, the beaker **becomes warm**. What happens when  $\text{KCl}(s)$  is dissolved in water?

	Lattice	Aqution	Solution
KF	+821	-837	-16 (warmer)
KCl	+703		

Why is the lattice enthalpy of KCl smaller?

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## Enthalpy change of solution, $\Delta_{\text{sol}}H$

When  $\text{KF}(s)$  is dissolved in water in a beaker, the beaker **becomes warm**. What happens when  $\text{KCl}(s)$  is dissolved in water?

	Lattice	Aquation	Solution
KF	+821	-837	-16 (warmer)
KCl	+703	-700	+3 (colder)

Why is the enthalpy of aquation of KCl smaller?



12

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## Enthalpy change of solution, $\Delta_{\text{sol}}H$

When  $\text{KF}(s)$  is dissolved in water in a beaker, the beaker **becomes warm**. What happens when  $\text{KCl}(s)$  is dissolved in water?

	Lattice	Aquation	Solution
KF	+821	-837	-16 (warmer)
KCl	+703	-700	+3 (colder)

Could we have predicted that when  $\text{KCl}(s)$  dissolves the solution get colder?



13

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[TP] Based on Coulomb's law, which of the following has the **largest magnitude** enthalpy of aquation,  $|\Delta_{\text{aq}}H|$ ?

- 0% 1. LiCl
- 0% 2. NaCl
- 0% 3. KCl
- 0% 4. Further information required



14

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[TP] Based on Coulomb's law, which of the following has the **largest magnitude** enthalpy of aquation,  $|\Delta_{\text{aq}}H|$ ?

- 0% 1. MgS
- 0% 2.  $\text{MgCO}_3$
- 0% 3. Further information required



15

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[Quiz] Based on Coulomb's law, which of the following has the **largest magnitude** enthalpy of change of **solution**,  $|\Delta_{\text{sol}}H|$ ?

- 0% 1.  $\text{MgCO}_3$   
 0% 2.  $\text{MgS}$   
 0% 3. More information needed



16

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## Summary

$\Delta_{\text{latt}}H$  and  $\Delta_{\text{aq}}H$  reflect **ion size** and **ion charge**

$\Delta_{\text{sol}}H$  reflects **competition** between  $\Delta_{\text{latt}}H$  and  $\Delta_{\text{aq}}H$

In general, we **cannot predict sign** of  $\Delta_{\text{sol}}H$



17

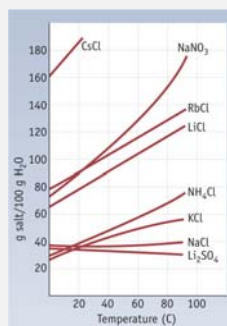
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## Effect of temperature on solubility

Sign of  $\Delta_{\text{sol}}H$  **does not** predict relative solubility (cold packs and hot packs!)

Usually solubility **increases** with temperature



18

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## Effect of temperature on solubility

But not always!

Compound	SOLUBILITY (g per 100 mL)	
	10 °C	40 °C
$\text{Li}_2\text{SO}_4$	35.5	33.7
$\text{LiCl}$	74.5	89.8

What could be going on?



19

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## Summary

$\Delta_{\text{latt}}H$  and  $\Delta_{\text{aq}}H$  reflect **ion size** and **ion charge**

$\Delta_{\text{sol}}H$  reflects **competition** between  $\Delta_{\text{latt}}H$  and  $\Delta_{\text{aq}}H$

In general, we **cannot predict sign** of  $\Delta_{\text{sol}}H$

Sign of  $\Delta_{\text{sol}}H$  **does not** predict relative solubility (cold packs and hot packs!)

Effect of temperature means there is **more to learn**



20

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## Colligative properties review

Non-volatile solute (negligible vapor pressure) ...

- **lowers** vapor pressure of solvent
- **raises** boiling point of solvent
- **lowers** freezing point of solvent

If solute cannot pass through a membrane ...

- the solvent will create an **osmotic pressure**

Details and practice in lab and in discussion



21

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[TP] A non-volatile solute lowers the vapor pressure of the solvent. This in turn means the boiling point of the solvent **must** increase. **Why?** Because ...

- 0% 1. higher temperature is necessary to evaporate the solute
- 0% 2. the solute particles stick to the solvent particles, analogous to van der Waals  $a$
- 0% 3. at the normal boiling point the vapor pressure of the solvent will be too low
- 0% 4. the solute vapor pressure is so low
- 0% 5. Some other reason



22

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[TP] The vapor pressure of water at 32 °C is 4.76 kPa. A glass of water is sealed in a 1.00 L container filled with air at 32 °C. After the water comes to equilibrium with the air in the container, the total pressure is 1 bar and there is 500. g of liquid water in the glass, and the partial pressure of water vapor in the container is ...

- 0% 1. less than 4.76 kPa
- 0% 2. 4.76 kPa
- 0% 3. more than 4.76 kPa
- 0% 4. Further information required



23

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**[Group Quiz]** Then, 35.0 g of ethylene glycol is dissolved in the liquid water. After the water returns to equilibrium, the mass of the liquid water ...

- 0% 1. will have decreased
- 0% 2. will be unchanged
- 0% 3. will have increased
- 0% 4. Further information required



24