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Slides on colligative properties, absolute entropies, and entropy of reaction  
CH102 Spring 2016, A1 and A2 lecture 30

- The role of  $\Delta S$  in colligative properties
- Absolute entropies
- Entropy change of reaction

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$$\Delta S = \Delta H / T = -\Delta H / T$$

The role of  $\Delta S$  in colligative properties

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### $\Delta S$ and freezing point depression

Make a diagram of  $S$  (vertical axis) for liquid and solid water (ice).  
Connect the two entropies with an arrow corresponding to liquid  $\rightarrow$  solid.  
What is the length of the arrow?

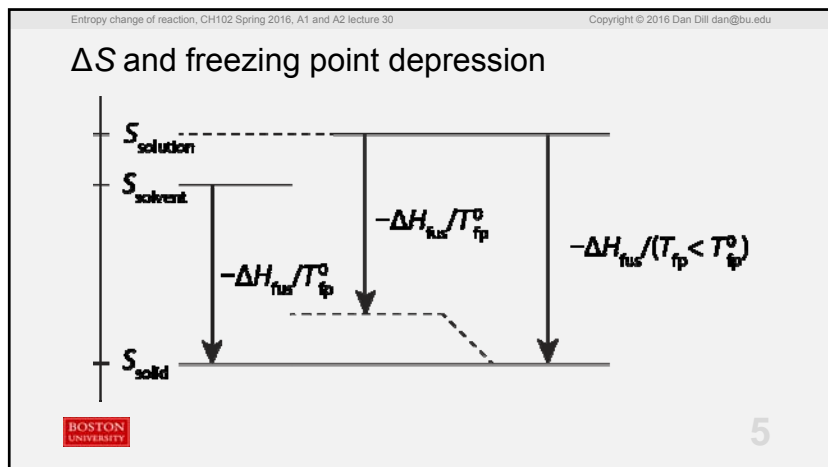
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### $\Delta S$ and freezing point depression

How is  $S$ (liquid) changed by adding a small amount of solute?  
What must happen to the length of the arrow connecting the water solution to pure ice?  
How can this change come about?

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### ΔS and colligative properties

Each of the four colligative properties can be understood in terms of entropy changes.

See the notes on colligative properties at ...

<http://quantum.bu.edu/courses/ch102-spring-2016/handouts.html>

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### How to determine ΔS<sub>sys</sub> for a chemical reaction?

We can get ΔS<sub>sys</sub> by analyzing changes in particle and energy dispersal in the system.

But, in practice, it is easier to get ΔS<sub>sys</sub> by measuring heat flow between system and surroundings when they are in equilibrium.

At equilibrium, ΔS<sub>tot</sub> = 0, and so ...

$$\Delta S_{\text{sys}} = -\Delta S_{\text{sur}} = -\Delta H_{\text{sur}}/T = +\Delta H_{\text{sys}}/T$$

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### How to determine Δ<sub>r</sub>S° ?

At equilibrium, ΔS<sub>tot</sub> = 0, and so ...

$$\Delta S_{\text{sys}} = -\Delta S_{\text{sur}} = -\Delta H_{\text{sur}}/T = +\Delta H_{\text{sys}}/T$$

At 0 K, for each substance  $W = 1$  and so  $S = 0$  !

Therefore, by heating, we can find  $S$  for each substance at a particular temperature.


These values are called **absolute entropies**.

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### Find $S$ at a particular temperature

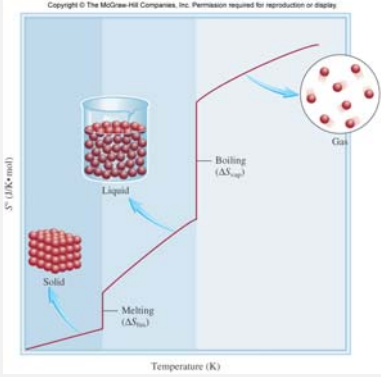

Make a sketch of how you expect the entropy of water to change with temperature, starting from  $S = 0$  at  $T = 0$  K and ending at the entropy at  $T = 400$  K.



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### Find $S$ at a particular temperature

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### Find $S$ at a particular temperature

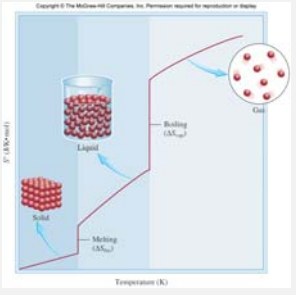

$$S(\text{heating } \dots) = \int dq/T = \int C_p dT/T$$

$$S(400 \text{ K}) = S(\text{heating solid}) \dots$$

$$+ \Delta H_{\text{fus}}/T_{\text{fus}} \dots$$

$$+ S(\text{heating liquid}) \dots$$

$$+ \Delta H_{\text{vap}}/T_{\text{vap}} \dots$$


$$+ S(\text{heating gas})$$



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### Find $S$ at a particular temperature

Entropies typically are tabulated at 298 K.  
Called **standard entropies**,  $S^\circ$   
Note, these **absolute entropies**, not entropy changes



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### How to get entropy change of reaction, $\Delta_r S^\circ$ ?

1. Get absolute entropies  $S^\circ$
2.  $\Delta_r S^\circ = S_{\text{products}} - S_{\text{reactants}}$

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### Entropy of reaction, $\Delta S^\circ_{\text{rxn}}$

$$\Delta_r S^\circ = S^\circ(\text{products}) - S^\circ(\text{reactants})$$

Rules of thumb:

- If more gas moles **formed**,  $\Delta_r S^\circ$  **large and positive**
- If more gas moles **consumed**,  $\Delta_r S^\circ$  **large and negative**
- If gas moles **unchanged**,  $\Delta_r S^\circ$  **small but positive or negative**

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$$\Delta_r S^\circ = S^\circ(\text{products}) - S^\circ(\text{reactants})$$

$2 \text{Zn}(s) + \text{O}_2(g) \rightarrow 2 \text{ZnO}(s)$   
 $\Delta_r S^\circ = 2 \times 43.7 - (2 \times 41.6 + 205.0) = -200.8 \text{ J/K}$   
 $\Delta n_g = -1$ , so  $\Delta_r S^\circ$  is **large and negative**

$\text{N}_2(g) + \text{O}_2(g) \rightarrow 2 \text{NO}(g)$   
 $\Delta_r S^\circ = 2 \times 210.8 - (191.6 + 205.0) = +25 \text{ J/K}$   
 $\Delta n_g = 0$ , so  $\Delta_r S^\circ$  is **small**

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