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[TP] At 300 K, hydrogen and oxygen react explosively to form water. The free energy of formation of water is  $-237$  kJ/mol. Based on this information, to decide what will happen to water at very high temperatures, we need to consider ...

20% 1. the sign of  $\Delta H_{\text{sur}}$   
 20% 2. the effect of  $T$  on the magnitude of  $\Delta S_{\text{sur}}$   
 20% 3. the relative magnitude of  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{sur}}$   
 20% 4. All of the above  
 20% 5. Some other factor(s)

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Response Counter

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 Friday, April 21, 2017

- Absolute entropy.
- Entropy change of reaction.
- System-only measure of total entropy change:  $\Delta G$ .

Next lecture: Using temperature to change spontaneity:  $\Delta G$  versus  $T$ .  
 The three faces of  $\Delta G$ . Using temperature to change equilibrium:  $K$  versus  $T$ .

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### How to determine $\Delta S_{\text{sys}}$ for a chemical reaction?

We have seen that we can get  $\Delta S_{\text{sys}}$  for a phase transition using  $\Delta S_{\text{tot}} = 0$  at the transition temperature.

Getting  $\Delta S_{\text{sys}}$  for a chemical reaction requires a different approach.

In principle we could get  $\Delta S_{\text{sys}}$  by analyzing changes in particle and energy dispersal due to the reaction.

But, in practice, it is easier to get  $\Delta S_{\text{sys}}$  by measuring heat flow between system and surroundings when they are in equilibrium.

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### How to determine $\Delta_r S^\circ$ ?

At equilibrium,  $\Delta S_{\text{tot}} = 0$ , 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  $S = 0$  !

This is known as the **third law of thermodynamics**.

Starting for  $S(T=0) = 0$ , 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

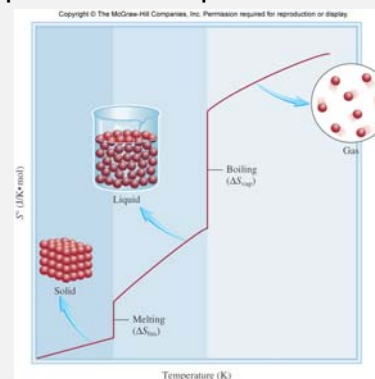
Make a sketch of how you expect the entropy of water to change with temperature, starting from  $S = 0$  at  $T = 0$  K and ending at the entropy at  $T = 400$  K.



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Find  $S$  at a particular temperature

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Find  $S$  at a particular temperature

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

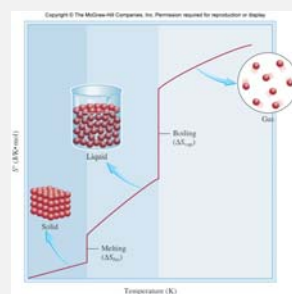
$$S(400 \text{ K}) = S(\text{heating solid}) \dots$$

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

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

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

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



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Find  $S$  at a particular temperature

Entropies typically are tabulated at 298 K.

These are called **standard entropies**,  $S^\circ$

Note, these **absolute entropies**,  
not entropy changes

## Selected Thermodynamic Data\* at 25 °C

Species	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
<i>Aluminum</i>		
Al(s)	0	28.3
AlCl <sub>3</sub> (s)	-705.63	109.29
Al <sub>2</sub> O <sub>3</sub> (s)	-1675.7	50.92
<i>Barium</i>		
BaCl <sub>2</sub> (s)	-858.6	123.68
BaCO <sub>3</sub> (s)	-1213	112.1
BaO(s)	-548.1	72.05
BaSO <sub>4</sub> (s)	-1473.2	132.2
<i>Beryllium</i>		
Be(s)	0	9.5
Be(OH) <sub>2</sub> (s)	-902.5	51.9



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

1. Get absolute entropies  $S^\circ$  (Mahaffy et al., Appendix D)
2.  $\Delta_r S^\circ = S_{\text{products}} - S_{\text{reactants}}$



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Entropy of reaction,  $\Delta_r S^\circ$ 

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

Rules of thumb:

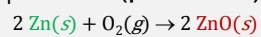
- If more gas moles **formed**,  $\Delta_r S^\circ$  **large and positive**
- If more gas moles **consumed**,  $\Delta_r S^\circ$  **large and negative**
- If gas moles **unchanged**,  $\Delta_r S^\circ$  **small but positive or negative**



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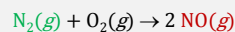
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 $\Delta_r S^\circ = S^\circ(\text{products}) - S^\circ(\text{reactants})$ 

$$\Delta_r S^\circ = 2 \times 43.7 - (2 \times 41.6 + 205.0) = -200.8 \text{ J/K}$$

$\Delta n_g = -1$ , so  $\Delta_r S^\circ$  is **large and negative**



$$\Delta_r S^\circ = 2 \times 210.8 - (191.6 + 205.0) = +25 \text{ J/K}$$

$\Delta n_g = 0$ , so  $\Delta_r S^\circ$  is **small**



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System-only measure of total entropy change:  $\Delta G$ 

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## System-only spontaneity measure

Since spontaneity depends on total entropy change, we cannot tell about spontaneity from  $\Delta S_{\text{sys}}$  alone.

We need also to know about  $\Delta S_{\text{sur}}$ .

But since  $\Delta S_{\text{sur}} = -\Delta H_{\text{sys}}/T \dots$

we can express  $\Delta S_{\text{tot}}$  in terms of ...

$\Delta S_{\text{sys}}$ ,  $\Delta H_{\text{sys}}$  and  $T$  only.



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## System-only spontaneity measure

Gibbs free energy change is defined as

$$\Delta G = -T\Delta S_{\text{tot}} = -T\Delta S_{\text{sur}} - T\Delta S_{\text{sys}}$$

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

The components of  $\Delta G$  are usually written with "sys" omitted ...

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

with the understanding that ...

$$\Delta H \text{ is } \Delta H_{\text{sys}} \text{ and } \Delta S \text{ is } \Delta S_{\text{sys}}$$



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## System-only spontaneity measure

$\Delta G$  depends only on "sys" quantities, but it reflects  $\Delta S_{\text{tot}}$

If  $\Delta G < 0$ , then spontaneous ( $\Delta S_{\text{tot}} > 0$ )

If  $\Delta G = 0$ , then equilibrium ( $\Delta S_{\text{tot}} = 0$ )

If  $\Delta G > 0$ , then non-spontaneous ( $\Delta S_{\text{tot}} < 0$ )



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