

Lecture 34 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2017 Dan Dill dan@bu.edu

[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 ΔH_{sur}
 20% 2. the effect of T on the magnitude of ΔS_{sur}
 20% 3. the relative magnitude of ΔS_{sys} and ΔS_{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: ΔG .

Next lecture: Using temperature to change spontaneity: ΔG versus T .
 The three faces of ΔG . Using temperature to change equilibrium: K versus T .

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How to determine ΔS_{sys} for a chemical reaction?

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

Getting ΔS_{sys} for a chemical reaction requires a different approach.

In principle we could get ΔS_{sys} by analyzing changes in particle and energy dispersal due to the reaction.

But, in practice, it is easier to get ΔS_{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

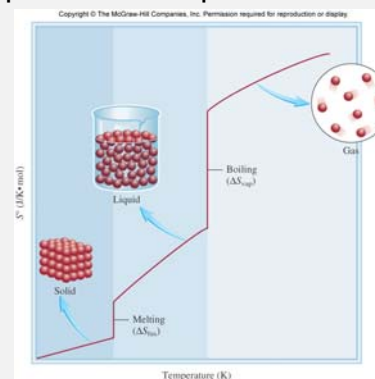
Make a sketch of how you expect the entropy of water to change with temperature, starting from $S = 0$ at $T = 0$ K and ending at the entropy at $T = 400$ K.



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Find S at a particular temperature

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Find S at a particular temperature

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

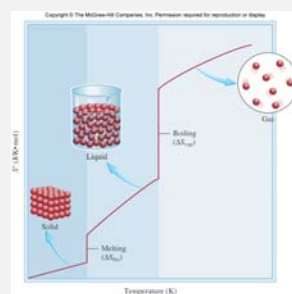
$$S(400 \text{ K}) = S(\text{heating solid}) \dots$$

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

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

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

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



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Find S at a particular temperature

Entropies typically are tabulated at 298 K.

These are called **standard entropies**, S°

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

Selected Thermodynamic Data* at 25 °C

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

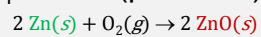


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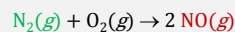
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$$\Delta_r S^\circ = S^\circ(\text{products}) - S^\circ(\text{reactants})$$



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

$\Delta n_g = -1$, 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: ΔG 

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System-only spontaneity measure

Since spontaneity depends on total entropy change, we cannot tell about spontaneity from ΔS_{sys} alone.

We need also to know about ΔS_{sur} .

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

we can express ΔS_{tot} in terms of ...

ΔS_{sys} , ΔH_{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 ΔG 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

ΔG depends only on "sys" quantities, but it reflects ΔS_{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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