

Lecture 31 CH102 A1 (MWF 9:05 am) Spring 2018 Copyright © 2018 Dan Dill dan@bu.edu

[TP] For the reaction $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$, at what temperature range will result in the **greatest amount of products (largest K)**?

25% 1. Very low T
 25% 2. Very high T
 25% 3. The amount will be the same at all T
 25% 4. More information needed

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Response Counter

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 Wednesday, April 11, 2018

- Complete: Absolute entropy
- Entropy change of reaction
- Free energy change, ΔG
- ΔG , E , ΔH , ΔS , Q , K , and T

Next lecture: Complete: ΔG , E , ΔH , ΔS , Q , K , and T

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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

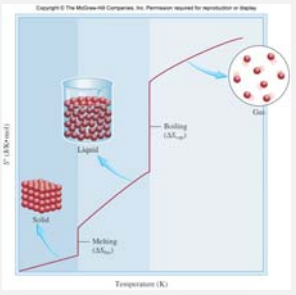
$$S(\text{heating } \dots) = \int dq/T = \int c_p dT/T$$

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

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

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

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

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


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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, $\Delta_r S^\circ$

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

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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Free energy change, ΔG

In electrochemistry (lecture 24) we learned that free energy change is the work that can be done **on the surroundings** (excluding any pressure volume work).

For an electrochemical cell, this work **available to the surroundings** is

$$\Delta G_{\text{cell}} = -n_e F E_{\text{cell}}$$

The fundamental, general expression for free energy change—the work **available to the surroundings**—is

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

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Free energy change, ΔG

The general expression for free energy change can be rewritten in terms on the system enthalpy change and system entropy change,

$$\begin{aligned} \Delta G &= -T\Delta S_{\text{tot}} \\ &= -T\Delta S_{\text{sur}} - T\Delta S_{\text{sys}} \\ &= +\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \end{aligned}$$

The components of ΔG are usually written with “sys” **omitted** ...

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

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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** ($\Delta S_{\text{tot}} > 0$) and process **provides work**

If $\Delta G = 0$, then **equilibrium** ($\Delta S_{\text{tot}} = 0$) and **no work** is involved

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

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Using temperature to change equilibrium: K versus T
 $\Delta G, E, \Delta H, \Delta S, Q, K,$ and T

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$\Delta G, \Delta H, \Delta S, E, Q, K,$ and T

Just as we did to discover that spontaneity in an electrochemical cell is proportional to $\ln(Q/K)$, ...

let's see if we can guess how ΔG must depend on Q and K ...

$$\Delta G = -nFE_{\text{cell}} = RT \ln(Q/K) = \Delta H - T\Delta S$$

where RT has units J/mol

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$\Delta G, \Delta H, \Delta S, E, Q, K,$ and T

Rearranging

$$\Delta G = -nFE_{\text{cell}} = RT \ln(Q/K) = \Delta H - T\Delta S$$

we see that this means

$$E_{\text{cell}} = -\left(\frac{RT}{n_e F}\right) \ln(Q/K) = -\left(\frac{RT}{n_e F}\right) 2.303 \log\left(\frac{Q}{K}\right)$$

since if $x = 10^{\log(x)}$, then $\ln(x) = \ln(10) \log(x) = 2.303 \log(x)$

At 25 °C

$$\left(\frac{R298.15K}{n_e F}\right) 2.303 = \frac{0.05912}{n_e} \text{V}$$

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$\Delta G, \Delta H, \Delta S, E, Q, K,$ and T

$$\Delta G = -nFE_{\text{cell}} = RT \ln(Q/K) = \Delta H - T\Delta S$$

How about for standard states?

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = RT \ln(1/K) = \Delta H^\circ - T\Delta S^\circ$$

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