Lecture 21 CH102 A3 (TuTh 5 pm)
Thursday, April 7, 2016

For today ...

- Continue Ch. 17   Spontaneous change – how far?
  - The role of ΔS in colligative properties
  - Absolute entropies
  - Entropy change for chemical reactions
  - A system–only measure of spontaneity: Free energy ΔG

Next lecture:
- Continue Ch. 17   Spontaneous change – how far?
  - ΔG vs. temperature
  - The three faces of ΔG
  - Effect of temperature on the equilibrium constant K

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No lecture next Thursday, April 14

No office hour wed. 4/13
                        Fri 4/15

Taking stock

Spontaneity **means** that ...
$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur} > 0$$

Spontaneity **does not** require that ...
$$\Delta S_{sys} > 0 \text{ or } \Delta S_{surr} > 0$$

A neat illustration of the **separate roles** of ΔS_{sys} and ΔS_{surr} is understanding why **steam condenses** and **water boils**

The same approach works for **melting** and for **sublimation**

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$$H_2O \ (g) \longrightarrow H_2O \ (l) \quad \text{CONDENSATION}$$

$$\Delta S_{TOTAL} = \Delta S_{SYS} - \frac{\Delta H_{SYS}}{T} \quad \longleftarrow \quad +40.65 \times 10^3 \ \frac{J}{mol}$$

$$= -108.9 \ \frac{J}{mol} + \frac{40.65 \times 10^3}{T} \qquad = \Delta H_{VAP}$$

$$\Delta H_{COND} = -\Delta H_{VAP}$$

$$\frac{T}{25\,^{\circ}C} \qquad \Delta S_{TOT} = -108.9 + 110.46 = + 1.56 \ \frac{J}{mol}$$

SPONT.

$$104\,^{\circ}C \qquad \Delta S_{TOT} = -108.9 + 107.8 = -1.10 \ \frac{J}{mol}$$

NON-SPONT

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The role of ΔS in colligative properties

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Freezing point depression and ΔS

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

S_{liquid}

S

S_{solid}

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Freezing point depression and ΔS

What is the length of the arrow?

S

S_{liquid}

$-\Delta H_{\text{fus}}/T^0{}_{fp}$

S_{solid}

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$$\Delta S_{sys} = \ominus \quad \text{for freezing}$$

Freezing point depression and ΔS

What is the length of the arrow?

$$-\Delta H_{fus} = \Delta H_{\text{"freezing"}}$$
$$S \rightarrow \ell \qquad \ell \rightarrow S$$

"freezing"

S_{liquid}

S

$-\Delta H_{fus}/T^0_{fp}$

freezing point of
pure $H_2O \Rightarrow 273 K$

S_{solid}

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$$solid \rightarrow liquid$$

$$\Delta H_{fusion} \Rightarrow \text{refers to enthalpy}$$
change accompanying
MELTING - need to
add heat $\Rightarrow$ ENDOTHERMIC

$$\Delta H_{fus} = \oplus$$

FREEZING IS EXOTHERMIC

Freezing point depression and ΔS

How is S_{liquid} changed by adding a small amount of solute, to make a solution?

$S_{solution}$ ———
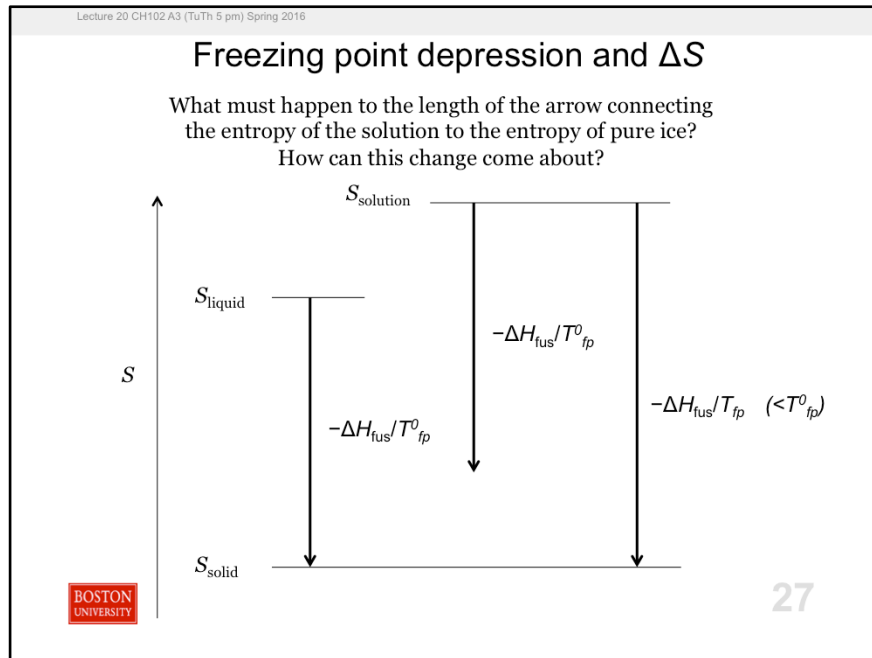
S_{liquid} ———

S

$-\Delta H_{fus}/T^0_{fp}$

S_{solid} ———

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a solution has more arrangements (ways) than a pure liquid,

so $S_{solution} > S_{liquid}$

.

Freezing point depression and ΔS

What must happen to the length of the arrow connecting
the entropy of the solution to the entropy of pure ice?
How can this change come about?

$S_{solution}$

S_{liquid}

S

$-\Delta H_{fus}/T^0_{fp}$

$-\Delta H_{fus}/T^0_{fp}$

$-\Delta H_{fus}/T_{fp}$ $(<T^0_{fp})$

S_{solid}

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What is happening? the water in
the solution freezes to give
pure ice , so S_{solid} is the
same for freezing a solution
or a pure liquid.

But, entropy change must be
greater for freezing a solution.
SO, TEMP. MUST CHANGE (DECREASE)

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/handouts.html

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

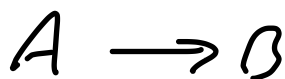We can get ΔS_{sys} by analyzing changes in particle and energy dispersal in the system.

But, in practice, it is easier to get ΔS_{sys} by measuring heat flow between the system and surroundings when they are in equilibrium.

At equilibrium, $\Delta S_{tot} = 0$, and so ...

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

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$$\Delta H_{rxn}$$

$$A \longrightarrow B \qquad\qquad \Delta H_{f_B} - \Delta H_{f_A} = \Delta H_{rxn}$$

$$\Delta S^{\circ}_{rxn} ?$$

$$\Delta S_{sys} \qquad S^{\circ}_{products} - S^{\circ}_{reactants} = \Delta S^{\circ}_{rxn}$$

absolute entropies !

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How to determine $\Delta_r S^o$?

At equilibrium, $\Delta S_{tot} = 0$, and so ...

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

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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for any substance

at 0 K   perfect $\Rightarrow$ $W = 1$
              order

$$S_{0K} = k_B \ln 1 = 0 \ !!$$

_____

as we heat the substance,

ENTROPY goes up !!

heat to desired temp (298 K,
                                                                    25°C)
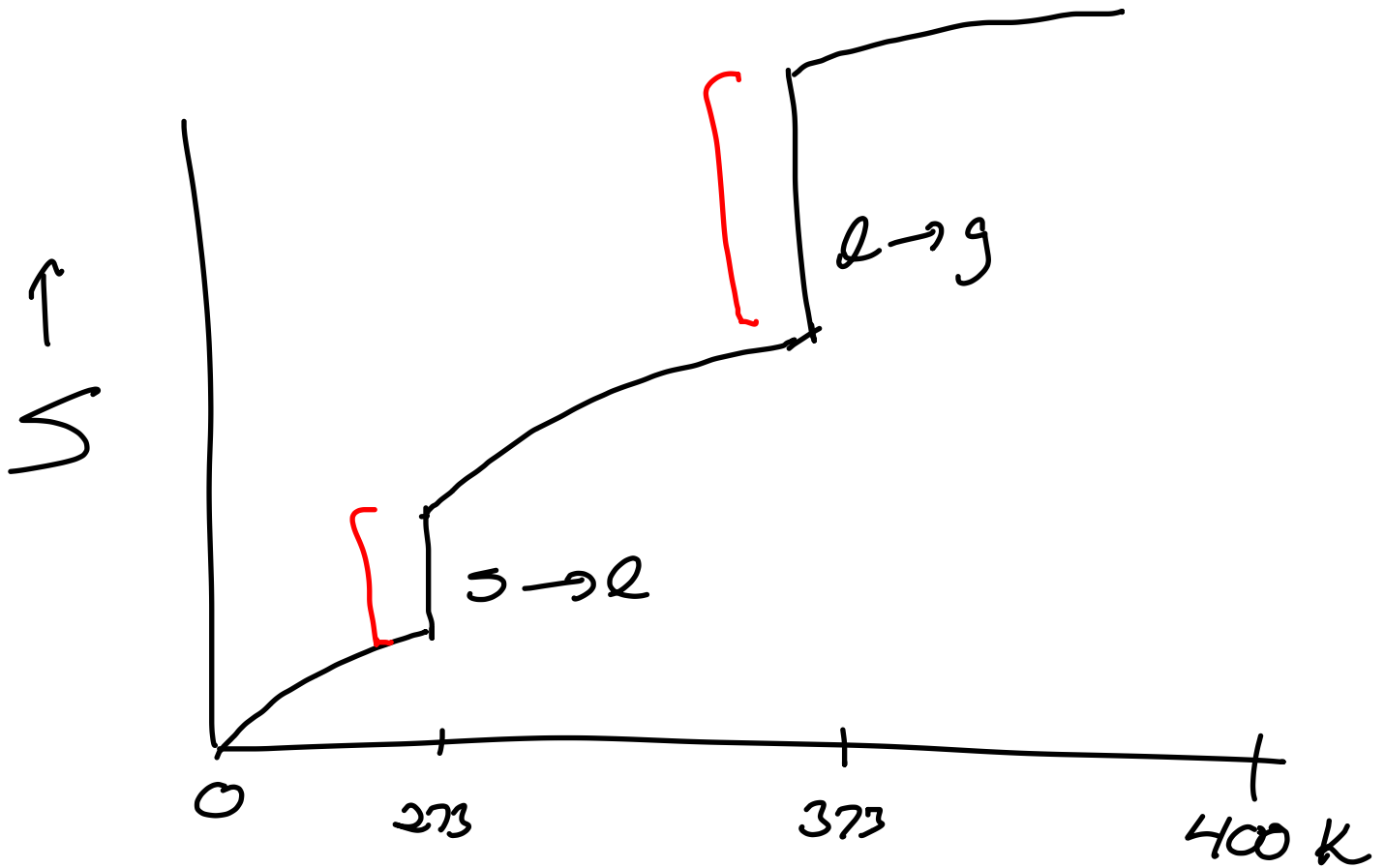
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Find *S* at a particular temperature

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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S

$\ell \rightarrow g$

$s \rightarrow \ell$

0   273   373   400 k

$$\frac{\Delta H}{T} = \Delta S \searrow$$

$$S_{heating} = \int \frac{dq}{T} = \int \frac{C_p \, dT}{T}$$

Get absolute entropies S

$$S(300 \text{ K}) = S(\text{heating solid}) + \Delta H_{fus}/T_{fus} + S(\text{heating liquid}) + \ldots$$
$$S(\text{heating}) = \int dq/T = \int C_P \, dT/T$$

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read out
S°

Boiling
(ΔS_{vap})

Gas

Liquid

S° (J/K·mol)

Solid

Melting
(ΔS_{fus})

Temperature (K)

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melting

$$S_{400K} = S_{\substack{heat \; solid \\ 0 \to 273 K}} + \frac{\Delta H_{fus}}{T_{fus}}$$

273K

boiling

$$+ \; S_{\substack{heat \; liquid \\ 273K - 373K}} + \frac{\Delta H_{vap}}{T_{vap}}$$

373

$$+ \; S_{\substack{heat \; gas \\ 373K - 400K}}$$

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Get absolute entropies *S*

Absolute entropies typically tabulated at 298 K.
Called standard entropies, S^o

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S^o in Tables $\Rightarrow$ at 298 K, absolute entropy of 1 mole substance

How to determine $\Delta_r S^o$?

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

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Entropy of reaction, ΔS^o_{rxn}

$$S^o(300 \text{ K}) = S(\text{heating solid}) + \Delta H_{fus}/T_{fus} + S(\text{heating liquid}) + ...$$
$$S(\text{heating}) = \int \mathrm{d}q/T = \int C_P \, \mathrm{d}T/T$$

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

Rules of thumb:
- If more gas moles formed, $\Delta_r S^o$ large and positive
- If more gas moles consumed, $\Delta_r S^o$ large and negative
- If gas moles unchanged, $\Delta_r S^o$ small but positive or negative

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① FORM MORE gas ⟹ LARGE ⊕ ΔS^o_r

② CONSUME MORE gas ⟹ LARGE ⊖ ΔS^o_r

③ gas moles unchanged, small ΔS^o_r
can't predict sign

LARGE
—
(-)

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

$2\ \text{Zn}(s) + \text{O}_2(g)\ \boxed{?}\ 2\ \text{ZnO}(s)$

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

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

$\text{N}_2(g) + \text{O}_2(g)\ \boxed{?}\ 2\ \text{NO}(g)$

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

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

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$$S^o_{\text{gas}} \gg S^o_{\text{solid}}\ !!$$