Lecture 11 CH131 Summer 1

Thursday, June 11, 2020

- Standard enthalpy of formation of X, $\Delta_f H°(X)$
- Example thermochemistry problems.

Begin ch13: Spontaneous Processes
- The essence of change: Blind chance and dumb luck
- Arrangements (particles) → entropy
- Heat (energy) flow → entropy change

Next lecture: Complete ch13

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Standard enthalpy of formation, $\Delta_f H°$, of X

Form one mole of X ...
... from the elements it contains, ...
... each in their standard state.

25°C

The standard state of an element is its most stable form.

$6C(s) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s)$ $\quad \Delta_r H \equiv \Delta_f H°$ ("formation")

$\frac{1}{2}H_2(g) \rightarrow H(g)$ $\quad \Delta H = 217.96$ kJ

$\Delta H_f°(H,g)$ $\quad 217.96$

$\Delta H_f°(H_2,g)$ $\quad 0$

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$\Delta_f H°$ of glucose, $C_6H_{12}O_6(s)$

Form one mole of glucose ...
→ $C_6H_{12}O_6(s)$
... from the elements it contains, ...
C, H, and O
... each in their standard state,
$C(s)$, $H_2(g)$, and $O_2(g)$

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$\Delta_f H°$ of glucose, $C_6H_{12}O_6(s)$

The standard enthalpy of formation of glucose is defined as the enthalpy change when one mole of sugar is formed from its elements, each in their standard states.

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$\Delta_f H°$ of glucose, $C_6H_{12}O_6(s)$

Task: Write down the balanced chemical equation whose enthalpy change is the standard enthalpy of formation of sugar, $C_6H_{12}O_6(s)$

The enthalpy change of the chemical reaction

$$6\,C(s) + 6\,H_2(g) + 3\,O_2(g) \rightarrow C_6H_{12}O_6(s)$$

is the standard enthalpy of formation of sugar.

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$\Delta_f H°$ of water, $H_2O(l)$

Task: Write down the balanced chemical equation whose enthalpy change is the standard enthalpy of formation of water, $H_2O(l)$

The enthalpy change of the chemical reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$$

is the standard enthalpy of formation of water.

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$\Delta_f H°$ of steam, $H_2O(g)$

Task: Write down the balanced chemical equation whose enthalpy change is the standard enthalpy of formation of steam, $H_2O(g)$.

The enthalpy change of the chemical reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g)$$

is the standard enthalpy of formation of steam.

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$\Delta_f H°$ of water and steam

Is the standard enthalpy of formation of water *the same* as that of steam?

The enthalpy changes of the chemical reactions

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_1$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad \Delta H_2$$

are different, since ...

$H_2O(l) \rightarrow H_2O(g)$ requires energy.

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Example thermochemistry problems

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Heat of combustion

Calculate $\Delta H°$ for the combustion of methane, $CH_4(g)$.

① write chemical equation

$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(\ell)$

②

$\Delta H = \Delta H_f(CO_2, g) + 2\,\Delta H_f(H_2O, \ell) - \Delta H_f(CH_4, g)$

$C(s) + O_2(g) \rightarrow CO_2(g)$

$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell)$

$CH_4(g) \rightarrow C(s) + 2\,H_2(g)$

$\Delta H_f(CO_2, g) = -393.51$

$2\,\Delta H_f(H_2O, \ell) = 2 \times (-285.83)$

$-\Delta H_f(CH_4, g) = -(-74.81)$

$\Delta H = (-393.51 - 2 \times 285.83 + 74.81)$ kJ/mole

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Heat of combustion

Calculate $\Delta H°$ for the combustion of glucose, $C_6H_{12}O_6(s)$.

① $C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(\ell)$

6 + 12 + 6 = 18

② $\Delta H = 6\,\Delta H_f(CO_2, g) + 6\,\Delta H_f(H_2O, \ell) - \Delta H_f(C_6H_{12}O_6, s) - 6\,\Delta H_f(O_2, g)$

$\Delta H_f(O_2, g) = 0$

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Problem 7e & 8e: 12.39

Appendix D is the key

39. Calculate the standard enthalpy change $\Delta H°$ at 25°C for the reaction

$$N_2H_4(\ell) + 3\,O_2(g) \rightarrow 2\,NO_2(g) + 2\,H_2O(\ell)$$

using the standard enthalpies of formation ($\Delta H_f°$) of reactants and products at 25°C from Appendix D.

$\Delta H = 2\,\Delta H_f(NO_2, g) + 2\,\Delta H_f(H_2O, \ell) - \Delta H_f(N_2H_4, \ell)$

= sum of ΔH_f of products − sum ΔH_f of reactions

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Problem 7e & 8e: 12.43

43. The dissolution of calcium chloride in water

$$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2\ Cl^-(aq)$$

is used in first-aid hot packs. In these packs, an inner pouch containing the salt is broken, allowing the salt to dissolve in the surrounding water.

(a) Calculate the standard enthalpy change $\Delta H°$ for this reaction, using data from Appendix D.

(b) Suppose 20.0 g $CaCl_2$ is dissolved in 0.100 L water at 20.0°C. Calculate the temperature reached by the solution, assuming it to be an ideal solution with a heat capacity close to that of 100 g pure water (418 J K^{-1}).

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Problem 7e & 8e: 12.47

47. A sample of pure solid naphthalene ($C_{10}H_8$) weighing 0.6410 g is burned completely with oxygen to $CO_2(g)$ and $H_2O(\ell)$ in a constant-volume calorimeter at 25°C. The amount of heat evolved is observed to be 25.79 kJ.

(a) Write and balance the chemical equation for the combustion reaction.

(b) Calculate the standard change in internal energy ($\Delta U°$) for the combustion of 1.000 mol naphthalene to $CO_2(g)$ and $H_2O(\ell)$.

(c) Calculate the standard enthalpy change ($\Delta H°$) for the same reaction as in part (b).

(d) Calculate the standard enthalpy of formation per mole of naphthalene, using data for the standard enthalpies of formation of $CO_2(g)$ and $H_2O(\ell)$ from Appendix D.

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[TP] The enthalpy diagram shows changes associated with the reaction

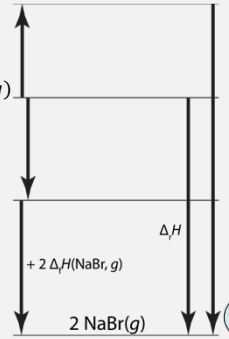
$Na_2(g) + Br_2(g) \rightarrow 2\ NaBr(g)$.

The uppermost line corresponds to the species ...

33% 1. $2\ Na(s) + Br_2(l)$

33% 2. $2\ Na(g) + 2\ Br(g)$

33% 3. $Na_2(g) + Br_2(g)$



Response Counter 10

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Chapter 13: Spontaneous Processes

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The essence of spontaneous change

Why does a drop of ink in water disperse?

Why do salt water and fresh water mix?

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The essence of spontaneous change

"things happen simply because they can happen
and because they are statistically
most likely to happen."

Michael Munowitz, "Principles of Chemistry," W. W. Norton, 2000

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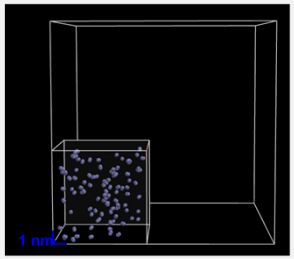
A gas fills its container



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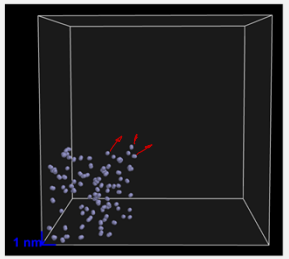
A gas fills its container



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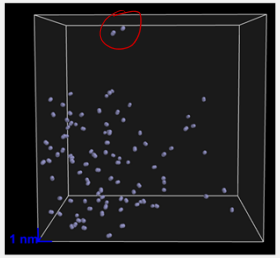
A gas fills its container



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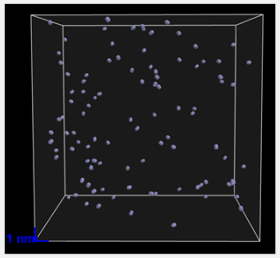
A gas fills its container



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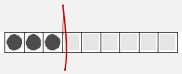
A gas fills its container



Gas all on left of container

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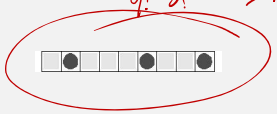
A gas fills its container

$\frac{12!}{9!\,3!} = \frac{12 \cdot 11 \cdot 10 \cdot 9!}{9!\,3!} = 2 \cdot 11 \cdot 10 = 220$



Gas evenly distributed throughout container

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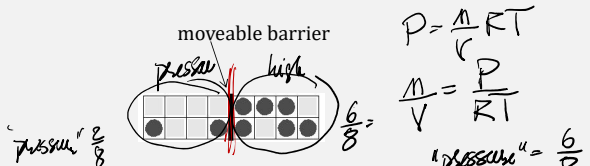
Pressure in a gas is uniform



P proportional to n/V ("lattice gas")
P higher on the right

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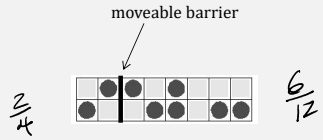
Pressure in a gas is uniform



P proportional to n/V ("lattice gas")
P the same on the left and right

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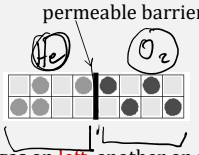
Gases mix evenly



One gas on left, another on right

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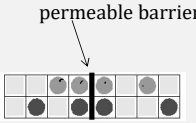
Gases mix evenly



Equal amounts throughout

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The essence of spontaneous change

The essential similarity in all of these behaviors…

gas particles spontaneously spread uniformly thought their container, so that pressure is everywhere the same;

an ink drop spontaneously disperses throughout water;

gases spontaneously mix uniformly, so that their partial pressures are everywhere the same;

…

The essence of spontaneous change

The essential similarity in all of these behaviors…

is that all spontaneous change results in the possible arrangements (W) of particles that is as large as it can be:

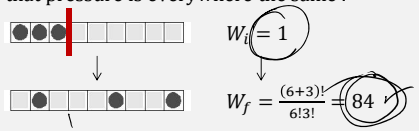
$W_i \rightarrow W_f = W_{\max}$

The essence of spontaneous change

Spontaneous change always results in the possible arrangements (W) of particles that is as large as it can be.

For example,

gas particles spontaneously spread uniformly thought their container, so that pressure is everywhere the same .



$W_i = 1$

$W_f = \frac{(6+3)!}{6!3!} = 84$

The essence of spontaneous change

"things happen simply because they can happen
and because they are statistically
most likely to happen."

Michael Munowitz, "Principles of Chemistry," W. W. Norton, 2000

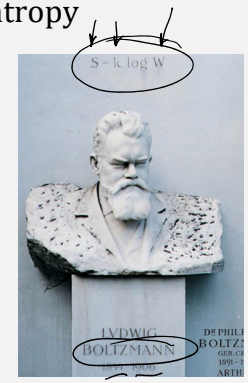
All spontaneous change results in the possible arrangements (W) of particles that is as large as it can be:

$W_i \rightarrow W_f \neq W_{\max}$

Arrangements → entropy

$S = k_B \ln(W)$

$k_B = \frac{R}{N_A} = 1.4 \times 10^{-23}$ J/K



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$S = k_B \ln(W)$

Why natural log?

So that doubling the size of the system double the value of the spontaneity measure:

$W \rightarrow W \times W = W^2$

$S \rightarrow k_B \ln(W^2) = 2k_B \ln(W) = 2S$, so ...

Boltzmann's definition in terms of natural log makes S extensive ...

S scales with size of system

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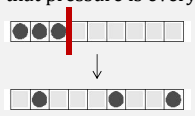
The essence of spontaneous change

Gas particles spontaneously spread uniformly thought their container, so that pressure is everywhere the same:



$W_i = 1$

$W_f = \frac{(6+3)!}{6!3!} = 84$

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[TP] What is the value of $\frac{\Delta S}{k_B}$ for $W_i = 1 \rightarrow W_f = 84$?

0% 1. 1
81% 2. 4.4
6% 3. 83
13% 4. 84
0% 5. Something else

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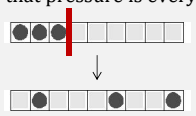
The essence of spontaneous change

Gas particles spontaneously spread uniformly thought their container, so that pressure is everywhere the same:



$W_i = 1$

$W_f = \frac{(6+3)!}{6!3!} = 84$

All spontaneous processes have an increase in W

Since $\Delta S \propto \ln\left(\frac{W_f}{W_i}\right)$

$\Delta S = S_f - S_i = k_B \ln\left(\frac{W_f}{W_i}\right) = k_B \ln\left(\frac{84}{1}\right) = k_B 4.4 > 0$

and since $\frac{W_f}{W_i} > 0$

$\Delta S > 0$ for spontaneous process

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[TP] Boltzmann's definition of entropy is proportional to the natural logarithm of the number of arrangements, $S \sim \ln(W)$. Could Boltzmann's definition of entropy just as well be defined in terms of base-10 logarithm, $S \sim \log(W)$?

57% 1. Yes
36% 2. No
7% 3. Not sure

$\ln(W^2) = 2\ln(W)$

$\log(W^2) = 2\log(W)$

$\ln(W) = 2.303 \log(W)$

$S = k_B \ln(W)$

$= 2.303 k_B \log(W)$

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0

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$S = k_B \ln(W)$

The extensive property of entropy is true for any logarithm base.

For example, if base-10 logarithm were used, the only change needed would be the numerical value of the proportionality constant.

$S = k_B \ln(W) = k_B 2.303 \log(W)$

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Heat (energy) flow → entropy change

Adding energy increases the units of energy in the system.

More units of energy mean more arrangements of energy (W_e)

This means that adding energy increases entropy, $S = k_B \ln(W_e)$.

Does the entropy increase depend on how much energy is initially present?

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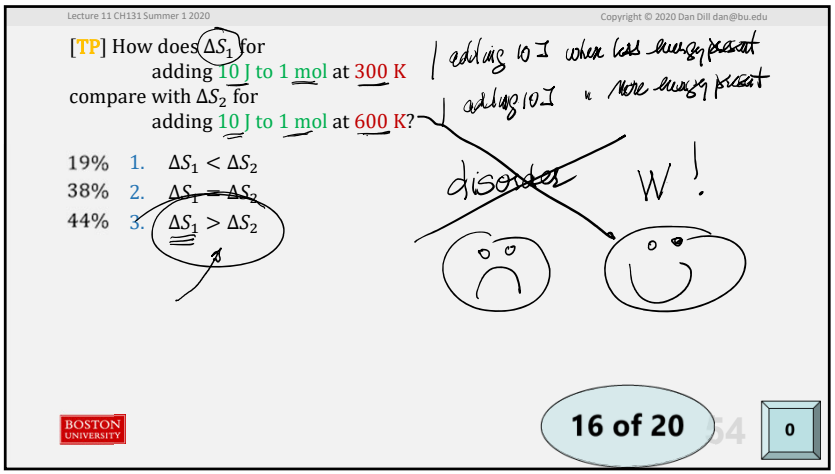
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Copyright © 2020 Dan Dill dan@bu.edu
[TP] How does ΔS_1 for adding 10 J to 1 mol at 300 K compare with ΔS_2 for adding 10 J to 1 mol at 600 K?
19% 1. $\Delta S_1 < \Delta S_2$
38% 2. $\Delta S_1 = \Delta S_2$
44% 3. $\Delta S_1 > \Delta S_2$
adding 10 J when less energy present
adding 10 J " more energy present
disorder
W !
16 of 20
54
0
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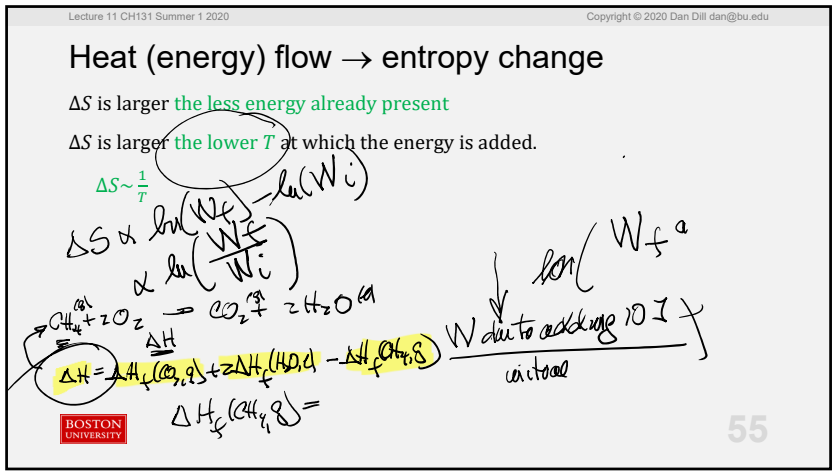
54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Heat (energy) flow → entropy change
ΔS is larger the less energy already present
ΔS is larger the lower T at which the energy is added.
$\Delta S \sim \frac{1}{T}$
$\Delta S \propto \ln\left(\frac{W_f}{W_i}\right)$
$\propto \ln(W_f) - \ln(W_i)$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$\Delta H = \Delta H_f(CO_2,g) + 2\Delta H_f(H_2O,l) - \Delta H_f(CH_4,g)$
$\Delta H_f(CH_4,g) =$
W due to adding 10 J
critical
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