[TP] The enthalpy diagram shows changes associated with the reaction
$$Na_2(g) + Br_2(g) \rightarrow 2\ NaBr(g).$$
The uppermost horizontal line corresponds to the species ...

0% 1. $2\ Na(s) + Br_2(l)$

0% 2. $2\ Na(g) + 2\ Br(g)$

30% 3. $Na_2(g) + Br_2(g)$

0% 4. Something else

70% 5. Not sure

ΔH_{rxn}

$+2\Delta H°_f[NaBr, g]$

$2\ NaBr(g)$

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1

Lecture 11 CH131 Summer 1 2021
Tuesday, June 15, 2021

- Complete: Enthalpy changes are additive: Hess's law
- Practice problem: Limiting reagent, $\Delta n_{gas}, w_{PV}, q_P, q_V$
- Standard enthalpy of formation, $\Delta H°_f$
- Using $\Delta H°_f$ to compute $\Delta H°_{rxn}$

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

Next lecture: Continue chapter 13

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$\Delta H°_{rxn}$ via Hess's law
Consider

$C(s) + O_2(g) \longrightarrow CO_2(g)\ \ \Delta H_1$

$S(s) + O_2(g) \longrightarrow SO_2(g)\ \ \Delta H_2$

$CS_2(l) + 3\ O_2(g) \longrightarrow CO_2(g) + 2\ SO_2(g)\ \ \Delta H_3$

$C(s) + 2\ S(s) \longrightarrow CS_2(l)\ \ \Delta H_4 = ?$

Since energy is conserved ...

$\Delta H_4 = \Delta H_1 + 2\ \Delta H_2 - \Delta H_3$

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$\Delta H°_{rxn}$ via Hess's law
Consider

$C(s) + O_2(g) \longrightarrow CO_2(g)\ \ \Delta H_1 = -393.5\ kJ$

$S(s) + O_2(g) \longrightarrow SO_2(g)\ \ \Delta H_2 = -296.8\ kJ$

$CS_2(l) + 3\ O_2(g) \longrightarrow CO_2(g) + 2\ SO_2(g)\ \ \Delta H_3 = -1103.9\ kJ$

$C(s) + 2\ S(s) \longrightarrow CS_2(l)\ \ \Delta H_4 = ?$

Since energy is conserved ...

$\Delta H_4 = \Delta H_1 + 2\ \Delta H_2 - \Delta H_3 = ...$

$\Delta H_4 = +116.8\ kJ$

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Slide 13

Recipe for $\Delta H°_{rxn}$ via Hess's law

First, get expression for $\Delta H°_{rxn}$.

Then, substitute in values in the expression for $\Delta H°_{rxn}$ to get its numerical value.

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Slide 14

Practice problem

$2\,Al(s) + 6\,HCl(aq) \rightarrow 2\,AlCl_3(aq) + 3\,H_2(g)\ \ \Delta H_1 = -1049\,\frac{kJ}{mol}$

$HCl(g) \rightarrow HCl(aq)\ \ \Delta H_2 = -79\,\frac{kJ}{mol}$

$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)\ \ \Delta H_3 = -185\,\frac{kJ}{mol}$

$AlCl_3(s) \rightarrow AlCl_3(aq)\ \ \Delta H_4 = -323\,\frac{kJ}{mol}$

Show that

$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)\ \ \Delta H_{rxn} = -1432\,\frac{kJ}{mol}$

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Slide 15

Practice problem

$2\,Al(s) + 6\,HCl(aq) \rightarrow 2\,AlCl_3(aq) + 3\,H_2(g)\ \ \Delta H_1 = -1049\,\frac{kJ}{mol}$

$HCl(g) \rightarrow HCl(aq)\ \ \Delta H_2 = -79\,\frac{kJ}{mol}$

$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)\ \ \Delta H_3 = -185\,\frac{kJ}{mol}$

$AlCl_3(s) \rightarrow AlCl_3(aq)\ \ \Delta H_4 = -323\,\frac{kJ}{mol}$

$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)\ \ \Delta H_{rxn} = \ldots$

Show that

$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)\ \ \Delta H_{rxn} = -1432\,\frac{kJ}{mol}$

$\Delta H_{rxn} = \Delta H_1 + 3\Delta H_3 - 2\Delta H_4 + 6\,\Delta H_2 = 1432\,\frac{kJ}{mol}$

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Slide 16

Practice problem

$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)\ \ \Delta H_{rxn} = -1432\,\frac{kJ}{mol}$

Calculate q_P and q_V for the reaction of 1.350 g of $Al(s)$ reacts with 0.7100 g of $Cl_2(g)$. Assume 100.0% yield.

q_P = heat at constant P for the actual amount consumed.

$q_V = q_P + w_{PV}$

$\Delta H_{rxn} = 2\,\Delta H_f°(AlCl_3, s) - 2\,\Delta H_f°(Al, s) \quad 3\,\Delta H_f°(Cl_2, g)$

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Slide 17

Practice problem

$$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s) \quad \Delta H_{rxn} = -1432\,\frac{kJ}{mol}$$

Calculate q_P and q_V for the reaction of 1.350 g of $Al(s)$ reacts with 0.7100 g of $Cl_2(g)$. Assume 100.0% yield.

Limiting reagent is …

$\Delta n_{Cl_2} = \cdots$ mol

$w_{PV} = -\Delta n_{Cl_2} R\,T$

$q_P = \cdots$ kJ

$q_V = q_P + w_{PV} = \cdots$ kJ

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Practice problem

$$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s) \quad \Delta H_{rxn} = -1432\,\frac{kJ}{mol}$$

Calculate q_P and q_V for the reaction of 1.350 g of $Al(s)$ reacts with 0.7100 g of $Cl_2(g)$. Assume 100.0% yield.

Limiting reagent is Cl_2

$\Delta n_{Cl_2} = -0.01001$ mol

$w_{PV} = -\Delta n_{Cl_2} R\,T = +0.02482$ kJ

$q_P = -4.780$ kJ

$q_V = q_P + w_{PV} = -4.755$ kJ

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Slide 19

Standard enthalpy of formation, $\Delta H°_f$

We have seen that using Hess's law, we can calculate the enthalpy change of a reaction in terms of enthalpy changes of other reactions.

$A \rightarrow B \qquad \Delta H_1 = +85$ kJ

$C \rightarrow B \qquad \Delta H_2 = -52$ kJ

$A \rightarrow C \qquad \Delta H_3 = \Delta H_1 - \Delta H_2 = +85\text{ kJ} - (-52\text{ kJ}) = +137$ kJ

To use this method systematically, a set of reference reactions is needed.

These reference reactions of called formation reactions.

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Slide 20

Standard enthalpy of formation, $\Delta H°_f$

A formation reaction has just single product, one mole of substance X.

The formation reaction of substance X is defined as the balanced chemical equation having as the single product one mole of X, and as reactants the elements that X contains, each element in it standard state.

$$H_2(g) + \tfrac{1}{2}\,O_2(g) \rightarrow H_2O(l) \qquad \Delta H_{rxn} \equiv \Delta H_f(H_2O, g)$$

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Standard enthalpy of formation, $\Delta H°_f$

The standard state of an element is its most stable form at SATP
(1 bar and 25°C).

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Standard enthalpy of formation, $\Delta H°_f$

The enthalpy change of reaction of the formation reaction of substance X is
defined as the standard enthalpy of formation of substance X,

$$\Delta H°_f(X) \equiv \Delta H°_{rxn} \text{ for the formation of one mole of X from its elements}$$

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Standard enthalpy of formation, $\Delta H°_f$

The enthalpy change of reaction of the formation reaction of substance X is
defined as the standard enthalpy of formation of substance X,

$$\Delta H°_f(X) \equiv \Delta H°_{rxn} \text{ for the formation of one mole of X from its elements}$$

A consequence of this definition is that for each element in its standard state,

$$\Delta H°_f(\text{element in its standard state}) = 0$$

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What is the standard state at 25℃?

For example,

$$O_2(g) \rightarrow O_2(g), \Delta H°_{rxn} = 0 = \Delta H°_f(O_2, g)$$

This means we can use tabulations of standard enthalpies of formation to
determine the standard state of an element.

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Slide 27

What is the standard state at 25°C?

ΔH°_f / kJ/mol

In tables of enthalpies of formation, such as http://goo.gl/aljmi, ...

Dinitrogen pentoxide	Gas	N_2O_5	11.3
Oxygen			
Monatomic oxygen	Gas	O	249
Oxygen	Gas	O_2	0
Ozone	Gas	O_3	143
Phosphorus			
White phosphorus	Solid	P_4	0

the standard state will have value $\Delta H^\circ_f = 0$.

$\frac{1}{2} O_2(g) \rightarrow O(g)$ $\Delta H_{rxn} \equiv \Delta H^\circ_f (O, g) = +249 \text{ kJ/mol}$

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ΔH°_f of fructose, $C_6H_{12}O_6(s)$

The standard enthalpy of formation of fructose is defined as ...

the enthalpy change when one mole of fructose is formed ...

from its elements, each in their standard states.

$6 C(g) + 6 H_2(g) + 3 O_2(g) \rightarrow C_6H_{12}O_6(s)$ $\Delta H_{rxn} \equiv \Delta H^\circ_f (C_6H_{12}O_6, s)$

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ΔH°_f of fructose, $C_6H_{12}O_6(s)$

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

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ΔH°_f of fructose, $C_6H_{12}O_6(s)$

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

The enthalpy change, ΔH_{rxn}, 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, $\Delta H^\circ_f[C_6H_{12}O_6, s]$.

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Slide 31

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

$Na_2(g) + Br_2(g) \rightarrow 2\,NaBr(g)$. ΔH_{rxn}

$Na_2(g) \rightarrow 2\,Na(g)$
$Br_2(g) \rightarrow 2\,Br(g)$

The uppermost horizontal line corresponds to the species …

$2\,Na(g) + 2\,Br(g)$

38% ① $2\,Na(s) + Br_2(l)$
15% ② $2\,Na(g) + 2\,Br(g)$ $Na_2(g) + Br_2(g)$
31% ③ $Na_2(g) + Br_2(g)$
15% ④ something else

$R \rightarrow P$ ΔH

$2\,Na(s) + Br_2(l)$ ΔH_{rxn}

$+2\Delta H^\circ_f[NaBr, g]$

$2\,NaBr(g)$

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$Na(s) + \tfrac{1}{2} Br_2(l) \rightarrow NaBr(g)$ $\Delta H_{rxn} = \Delta H^\circ_f$

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Slide 32

Using ΔH°_f to compute ΔH°_{rxn}

$$4\,NH_3(g) + 5\,O_2(g) \rightarrow 4\,NO(g) + 6\,H_2O(g)$$

$$\Delta H^\circ_f = 4\,\Delta H^\circ_f(NO, g) + 6\Delta H^\circ_f(H_2O, g) - 4\Delta H^\circ_f(NH_3, g) - 5\Delta H^\circ_f(O_2, g)$$

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Using ΔH°_f to compute ΔH°_{rxn}

$$4\,NH_3(g) + 5\,O_2(g) \rightarrow 4\,NO(g) + 6\,H_2O(g)$$

$4\,NH_3(g) \rightarrow 2\,N_2(g) + 6\,H_2(g)$	$\Delta H_1 = -4\Delta H^\circ_f[NH_3, g]$
$5\,O_2(g) \rightarrow 5\,O_2(g)$	$\Delta H_2 = 0$
$2\,O_2(g) + 2\,N_2(g) \rightarrow 4\,NO(g)$	$\Delta H_3 = +4\Delta H^\circ_f[NO, g]$
$6\,H_2(g) + 3\,O_2(g) \rightarrow 6\,H_2O(g)$	$\Delta H_4 = +6\Delta H^\circ_f[H_2O, g]$

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Slide 34

Using ΔH°_f to compute ΔH°_{rxn}

$$4\,NH_3(g) + 5\,O_2(g) \rightarrow 4\,NO(g) + 6\,H_2O(g)$$

$4\,NH_3(g) \rightarrow 2\,N_2(g) + 6\,H_2(g)$	$\Delta H_1 = -4\Delta H^\circ_f[NH_3, g]$
$5\,O_2(g) \rightarrow 5\,O_2(g)$	$\Delta H_2 = 0$
$2\,O_2(g) + 2\,N_2(g) \rightarrow 4\,NO(g)$	$\Delta H_3 = +4\Delta H^\circ_f[NO, g]$
$6\,H_2(g) + 3\,O_2(g) \rightarrow 6\,H_2O(g)$	$\Delta H_4 = +6\Delta H^\circ_f[H_2O, g]$

Hess's law:

$$\Delta H^\circ_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$
$$= +4\Delta H^\circ_f[NO, g] + 6\Delta H^\circ_f[H_2O, g] - 4\Delta H^\circ_f[NH_3, g]$$

Note: Elements in standard states are absent

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Using $\Delta H°_f$ to compute $\Delta H°_{rxn}$

The key feature of standard enthalpies of formation is that,
the enthalpy change of any reaction, $\Delta H°_{rxn}$, can be computed using them,
as …

$\Delta H°_{rxn} = Sum[\Delta H°_f(products)] - Sum[\Delta H°_f(reactants)]$

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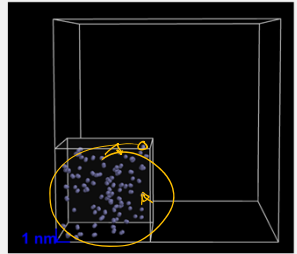
"things happen simply because they can happen
and because they are statistically
most likely to happen."

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

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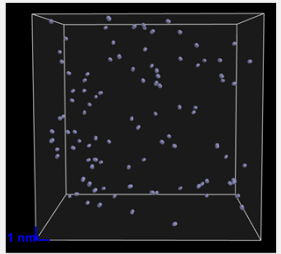
66

66

A gas fills its container

1 nm
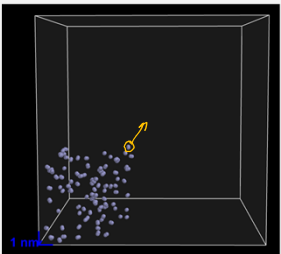
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A gas fills its container
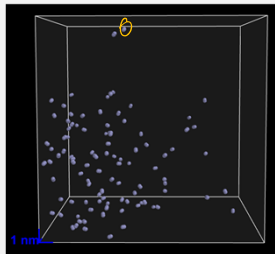
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A gas fills its container

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A gas fills its container

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A gas fills its container

lattice gas

Gas all on left of container

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A gas fills its container

Gas evenly distributed throughout container

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Pressure in a gas is uniform

moveable barrier

$$\frac{P_i}{RT} = \frac{n}{V} = \frac{2}{8} = \frac{1}{4}$$

$$\frac{3}{4} = \frac{6}{8} = \frac{P_R}{RT}$$

$$W_{iL} \neq W_{iR} = W_i$$

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

73

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Pressure in a gas is uniform

moveable barrier

$$\frac{2}{4} = \frac{1}{2}$$

$$\frac{6}{12} = \frac{1}{12} \Big\}$$

$$W_{fL} \neq W_{fR} = W_f$$

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

$$W_i < W_f$$

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Gases mix evenly

permeable barrier

One gas on left, another on right
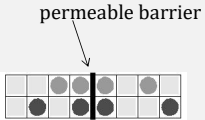
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Gases mix evenly

permeable barrier

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;

…

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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:

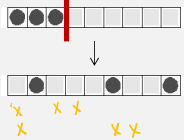$$W_i \rightarrow W_f = W_{\max}$$

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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 .

$W_i = 1$

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

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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

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

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

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Arrangements → entropy

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

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

S = k log W

LVDWIG BOLTZMANN
1844 · 1906

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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:

$$W \longrightarrow W \times W = W^2$$

$$S \to k_B \ln(W^2) = 2 k_B \ln(W) = 2S, \text{ so } \dots$$

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

S scales with size of system

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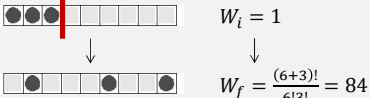
82

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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**] Using $S = k_B \ln(W)$, what is the value of $\frac{\Delta S}{k_B}$ for $W_i = 1 \rightarrow W_f = 84$?

- 0%   1.   1
- 100%   2.   4.4
- 0%   3.   83
- 0%   4.   84
- 0%   5.   Something else
- 0%   6.   Note sure

(handwritten)
$$\Delta S = S_f - S_i$$
$$= k_B \ln(W_f) - k_B \ln(W_i)$$
$$= k_B \left(\ln(W_f) - \ln(W_i) \right)$$
$$= k_B \ln\left(\frac{W_f}{W_i} \right)$$

If $W_i < W_f,\ \frac{W_f}{W_i} > 1,\ \Delta S \propto \ln\left(\frac{W_f}{W_i}\right) > 0$

$$\frac{\Delta S}{k_B} = \ln\left(\frac{W_f}{W_i} \right) = \ln\left(\frac{84}{1} \right)$$

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If $W_i > W_f,\ \frac{W_f}{W_i} < 1,\ \Delta S \le 0$

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The essence of spontaneous change

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

$W_i = 1$

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

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

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Heat (energy) flow → entropy change

We can quantify the energy added to a system in terms of the number of small units (quanta, to analogous photons) of energy.

This means that adding energy increases the units of energy in the system.

And so, adding energy increases the ways, W_e, the energy can be stored in the system.

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Slide 87

Heat (energy) flow → entropy change

Just as spontaneous change corresponds to an increase in the number of arrangement of particles, W_p, spontaneous change also corresponds to an increase the ways energy is stored, W_e.

This means that added energy contributes to the entropy, $S_e = k_B \ln(W_e)$.

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Heat (energy) flow → entropy change

How does the entropy increase depend on how much energy is already present?

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Slide 89

[TP] Temperature is a measure of how much (kinetic) energy is in the system. Which is larger?

ΔS_1 for adding 10 J to 1 mol at 300 K

ΔS_2 for adding 10 J to 1 mol at 600 K?

- 0%   1. $\Delta S_1 < \Delta S_2$
- 0%   2. $\Delta S_1 = \Delta S_2$
- 100% 3. $\Delta S_1 > \Delta S_2$
- 0%   4.   Not sure

quiet library reading room

noisy hockey game

two friends chatting.

$$\ln\left(\frac{W_{ef}}{W_{ei}}\right) \text{ for } 10\,J \text{ added at } 300K > \ln\left(\frac{W_{ef}}{W_{ei}}\right) \text{ for } 10\,J \text{ added at } 600K.$$

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0

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Slide 90

Heat (energy) flow → entropy change

ΔS is larger the less energy already present

Temperature is a measure of how much (kinetic) energy is in the system.

This means that ΔS is larger the lower T at which the energy is added and so that …

$$\Delta S \sim \frac{1}{T}$$

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Slide 91

Heat (energy) flow → entropy change

How does the entropy increase depend on how much energy is added?

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[TP] The more energy added, the more quanta of energy there are in the system. Which is larger?

ΔS_1 for adding 10 J to 1 mol at 400 K

ΔS_2 for adding 20 J to 1 mol at 400 K

- 100% 1. $\Delta S_1 < \Delta S_2$
- 0%   2. $\Delta S_1 = \Delta S_2$
- 0%   3. $\Delta S_1 > \Delta S_2$
- 0%   4. Not sure

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Heat (energy) flow → entropy change

The more energy added, the more quanta of energy there are in the system and so the larger the number arrangements, W_e.

This means ΔS is larger the more energy added and so that …

$$\Delta S \sim \Delta H$$

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Heat (energy) flow → entropy change

ΔS is larger the more energy added

$$\Delta S \sim \Delta H$$

ΔS is larger the lower T at which the energy is added.

$$\Delta S \sim \frac{1}{T}$$

Amazingly, these results combine into the fundamental relation for entropy change due to energy flow,

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

$$\frac{W_P}{W_e}$$

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Spontaneity = increase in total entropy

Spontaneity means that what happens is always associated with an increase in entropy, $\Delta S > 0$.

We will see that it is useful to partition entropy change as that due to the chemical or physical system (what we are interested in) and the surroundings (everything else).

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Spontaneity = increase in total entropy

Therefore, the spontaneity condition can be written as

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur} > 0$$

Note that this requirement does not require separately that ...

$$\Delta S_{sys} > 0 \text{ or } \Delta S_{sur} > 0$$

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Spontaneity = increase in total entropy

A neat illustration of the roles of ΔS_{sys} and ΔS_{sur} is understanding why steam condenses and water boils.

Water spontaneously ($\Delta S_{tot} > 0$) vaporizes when $T > 100°C$

Water and steam are in equilibrium ($\Delta S_{tot} = 0$) when $T = 100°C$

Steam spontaneously ($\Delta S_{tot} > 0$) condenses when $T < 100°C$

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[TP] For steam → liquid, the system is the water (liquid and steam), and the surroundings is everything else. For steam → liquid, which of the following must always be true, independently of temperature?

0%   1. $\Delta S_{sys} < 0$ and $\Delta S_{sur} < 0$
0%   2. $\Delta S_{sys} < 0$ and $\Delta S_{sur} = 0$
100% 3. $\Delta S_{sys} < 0$ and $\Delta S_{sur} > 0$
0%   4. $\Delta S_{tot} < 0$
0%   5. $\Delta S_{tot} = 0$
0%   6. $\Delta S_{tot} > 0$
0%   7.   None of the above
0%   8.   Not sure

$H_2O(g) \rightarrow H_2O(\ell)$

$\ln\left(\frac{W_\ell}{W_g}\right) < 0$

$\Delta S_{sys} < 0$

$\frac{W_\ell}{W_g} \ll 1$

$\Delta S_{sur} = \frac{\Delta H_{sur}}{T}$

$\Delta H_{sur} > 0$

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steam → liquid water at 94°C

Since $\Delta S_{sys} < 0$ and $\Delta S_{sur} > 0$, their contributions to

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur}$$

oppose one another.

$H_2O(g) \rightarrow H_2O(\ell)$

$\Delta S_{sys} < 0$

$\Delta H_{sur} > 0, \quad \Delta S_{sur} = \frac{\Delta H_{sur}}{T} > 0$

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