

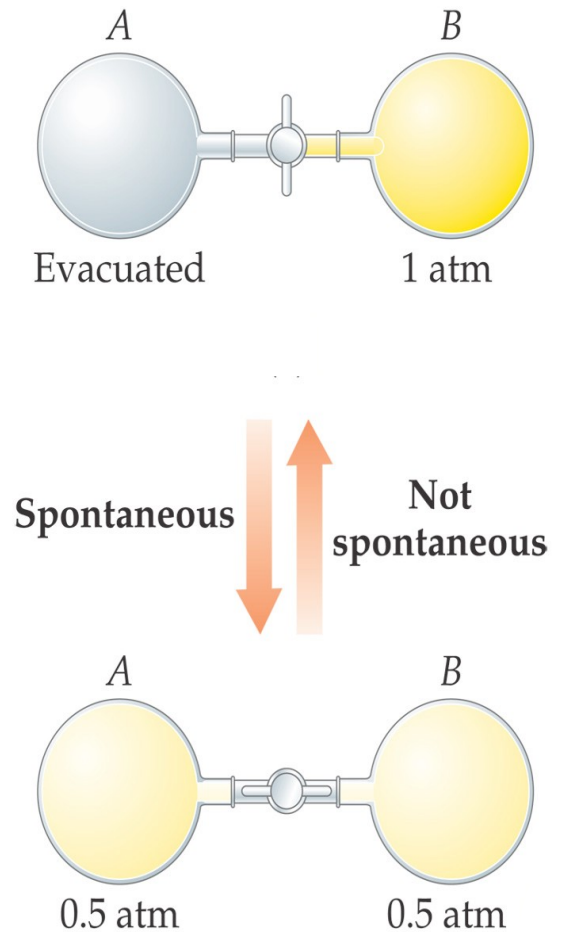
# Sjálfgeng efnahvörf

## 1. Kafli Efn203

- Heilarorka í heiminum er konstant
- Orka getur hins vegar skipt um form
- Raforka, efnaorka, varmaorka....
- Sumt í þessari veröld gerist sjálfkrafa....  
Aðrir hlutir gerast eftir að þeim hefur verið hjálpað af stað.
- Sumt gerist ekki....

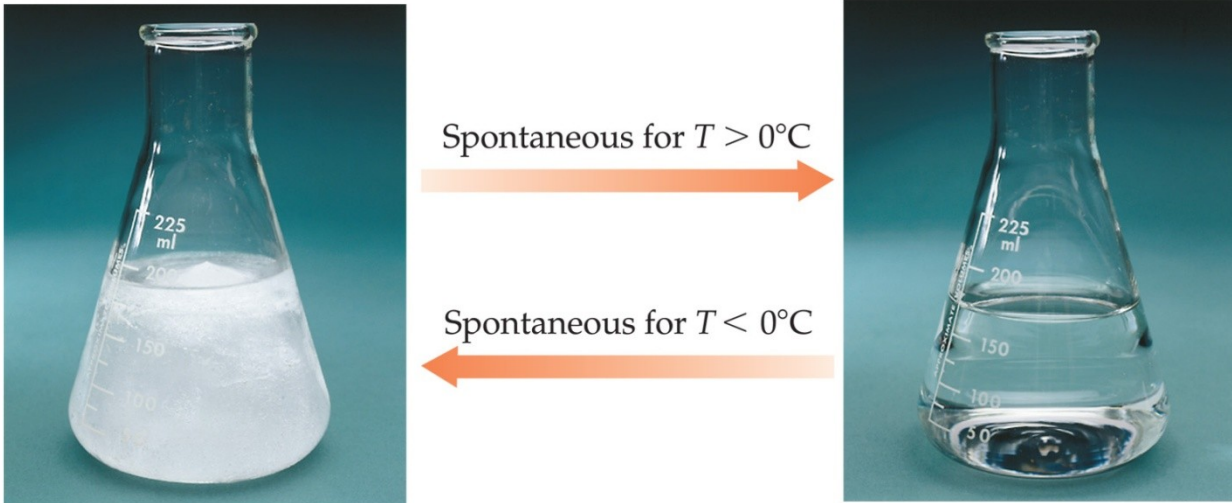
# Sjálfgengt - spontaneous

- Spontaneous processes are those that can proceed without any outside intervention.
- The gas in vessel *B* will spontaneously effuse into vessel *A*, but once the gas is in both vessels, it will *not* spontaneously

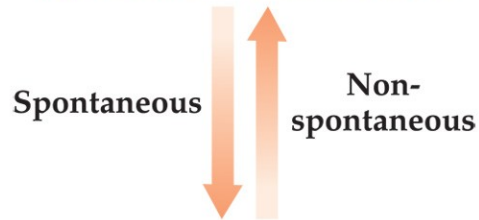


# Spontaneous Processes

- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.
- Above  $0^{\circ}\text{C}$  it is spontaneous for ice to melt.
- Below  $0^{\circ}\text{C}$  the reverse process is spontaneous.



# Spontaneous Processes



Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.

# Sjálfgengt efnahvarf

- Er hvarf sem gengur sjálfkrafa, annað hvort strax eða eftir að því hefur verið komið af stað.
- Dæmi:
  - Gas dreifist jafnt um rými
  - Salt leysist upp í vatni
  - Kerti brennur (kveikt á því)

- Flest sjálfgeng efnahvörf eru útvermin
  - Eins og allur bruni
- Nokkur eru innvermin eins og
  - Þegar saltpétur er leystur í vatni lækkar hitinn
  - Þegar salt er sett í snjó lækkar hitinn – en snjórinn bráðnar samt
  - Vatnsdropi gufar upp við stofuhita...

# Sjálfgengni ræðst af 3 þáttum

- Hitastigi mælt í Kelvin
- Enthalpi breytingu eða hvarfvarmanum  $\Delta H$
- Entrópi eða óreiðubreytingunni  $\Delta S$ 
  - Það er meiri óreiða í vökva en í föstu efni,
  - það er meiri óreiða sameinda í gasi en í vökva
  - og það er meiri óreiða í uppleystu jónefni (salti) en í föstu salti.

# Fríorka Gibbs

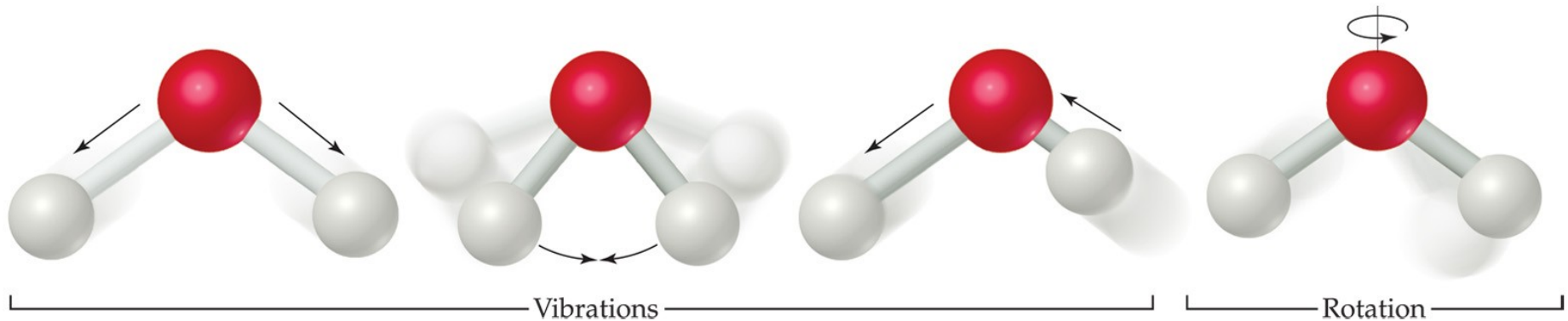
- Gibbs tókst að taka þetta saman svona
- $\Delta G = \Delta H - T^* \Delta S$
- $\Delta G$  kallast fríorkubreyting efnahvarfs
- $\Delta G$  hvarfs er hámark nýtanlegrar orku úr sjálfgengu efnahvarfi.

- $\Delta H < 0$  þá er hvarf útvermið – og öfugt
- $\Delta S > 0$  þá er óreiða að aukast – og öfugt
- Hækki hitastig, eykur það óreiðupáttinn.
- $\Delta G < 0 \rightarrow$  hvarfið er sjálfgengt

- Dæmi:
  - Ef hvarf er útvermið er H þátturinn mínustala
  - Ef óreiða er að aukast er S þátturinn plústala margfölduð með T
  - Mínustala – plústala er stærri mínus.
  - $5 - (6) = -11$

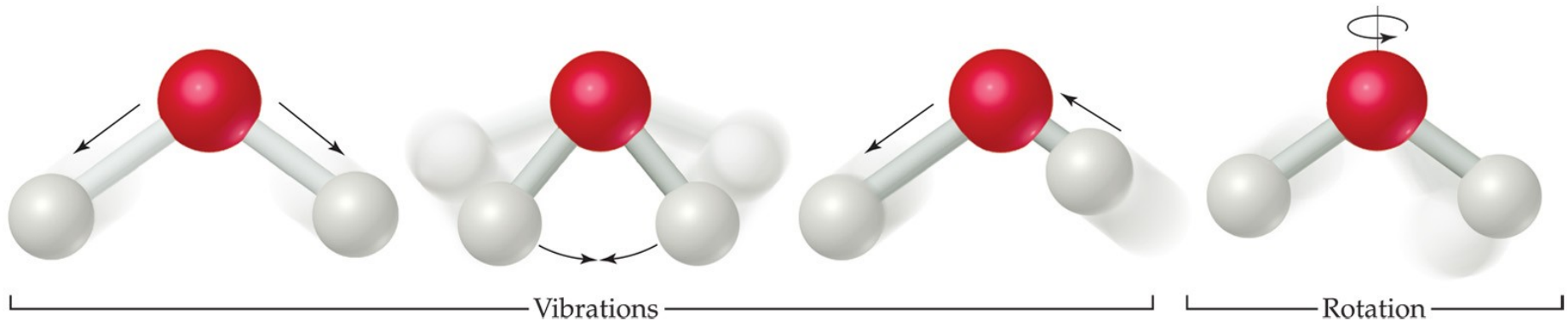
# ÓREIÐA SAMEINDA

- Ludwig Boltzmann described the concept of entropy on the molecular level.
- Hitastig mælir meðalhreyfiorku sameinda.



# Óreiða í sameindum

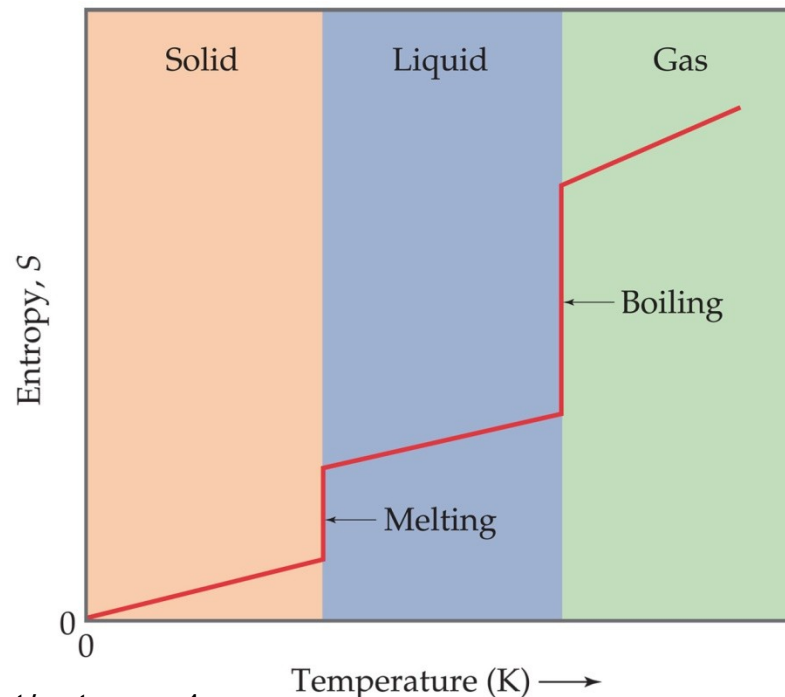
- Molecules exhibit several types of motion:
  - **Hreyfing**: Movement of the entire molecule from one place to another.
  - **Titringur**: Periodic motion of atoms within a molecule.
  - **Snúningur**: Rotation of the molecule on about an axis or rotation about  $\sigma$  bonds.



# Third Law of Thermodynamics

The entropy of a pure crystalline substance at absolute zero is 0.

$$S = k \ln W = k \ln 1 = 0$$



**No stereotypes, labels, or genres can rationalize this. Fueled by the decay of the world, order and chaos unite, Entropy is born...**

# Standard Entropies

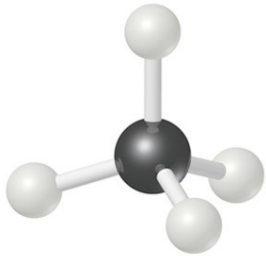
- These are molar entropy(óreiðu) values of substances in their standard states.
- Standard óreiða eykst almennt með hækkandi mólmassa.

TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

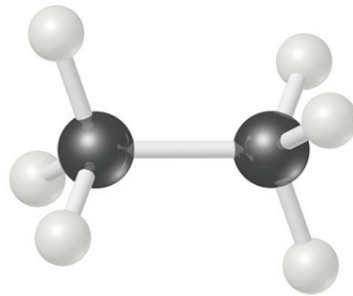
Substance	$S^\circ$ , J/mol-K
<b>Gases</b>	
H <sub>2</sub> (g)	130.6
N <sub>2</sub> (g)	191.5
O <sub>2</sub> (g)	205.0
H <sub>2</sub> O(g)	188.8
NH <sub>3</sub> (g)	192.5
CH <sub>3</sub> OH(g)	237.6
C <sub>6</sub> H <sub>6</sub> (g)	269.2
<b>Liquids</b>	
H <sub>2</sub> O(l)	69.9
CH <sub>3</sub> OH(l)	126.8
C <sub>6</sub> H <sub>6</sub> (l)	172.8
<b>Solids</b>	
Li(s)	29.1
Na(s)	51.4
K(s)	64.7
Fe(s)	27.23
FeCl <sub>3</sub> (s)	142.3
NaCl(s)	72.3

# Standard Entropies

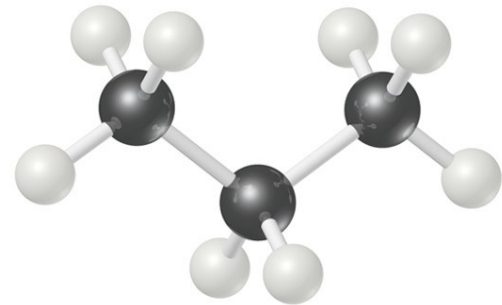
→ Stórar og flóknar sameindir hafa hærra entropí.



Methane, CH<sub>4</sub>  
 $S^\circ = 186.3 \text{ J mol}^{-1} \text{ K}^{-1}$



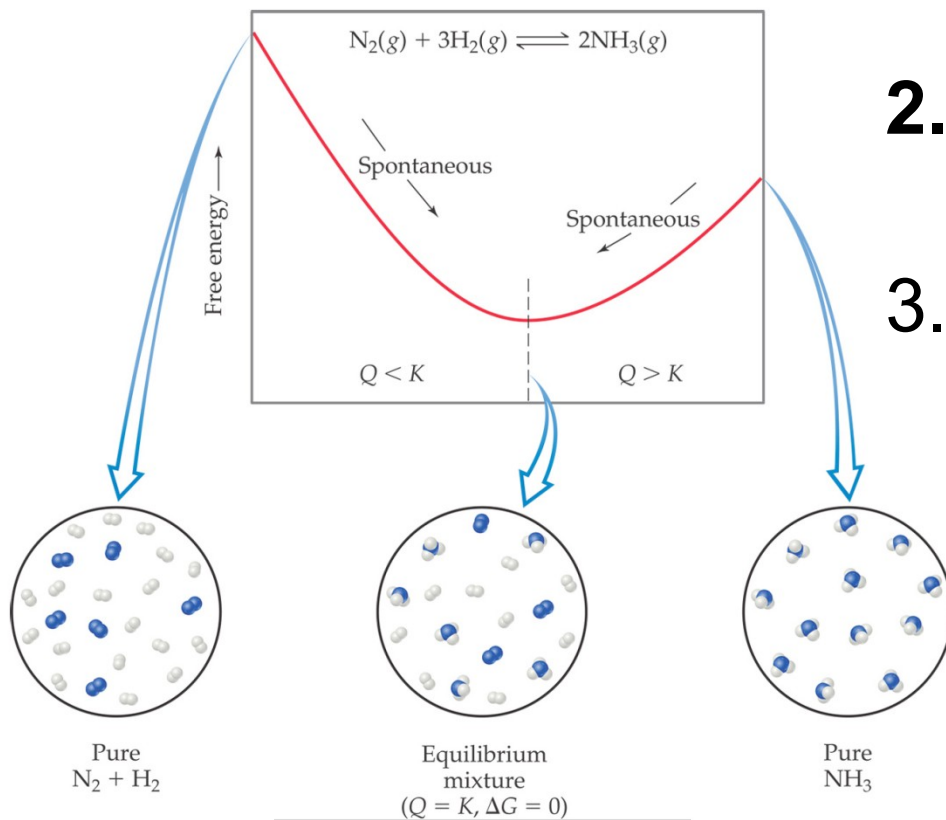
Ethane, C<sub>2</sub>H<sub>6</sub>  
 $S^\circ = 229.6 \text{ J mol}^{-1} \text{ K}^{-1}$



Propane, C<sub>3</sub>H<sub>8</sub>  
 $S^\circ = 270.3 \text{ J mol}^{-1} \text{ K}^{-1}$

# Gibbs Free Energy

1. If  $\Delta G$  is negative, the forward reaction is spontaneous.
2. If  $\Delta G$  is 0, the system is at equilibrium.
3. If  $\Delta G$  is positive, the reaction is spontaneous in the reverse direction.



# Free Energy Changes

$$\Delta G = \Delta H_{sys}^{\circ} - T\Delta S_{system}$$

This equation shows how  $\Delta G^{\circ}$  changes with temperature.

(We assume  $S^{\circ}$  &  $\Delta H^{\circ}$  are independent of T.)

# Free Energy and Temperature

TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions

$\Delta H$	$\Delta S$	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
-	+	-	-	Spontaneous at all temperatures	$2 \text{O}_3(g) \longrightarrow 3 \text{O}_2(g)$
+	-	+	+	Nonspontaneous at all temperatures	$3 \text{O}_2(g) \longrightarrow 2 \text{O}_3(g)$
-	-	+	+ or -	Spontaneous at low $T$ ; nonspontaneous at high $T$	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(s)$
+	+	-	+ or -	Spontaneous at high $T$ ; nonspontaneous at low $T$	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$

By knowing the sign (+ or -) of  $\Delta S$  and  $\Delta H$ , we can get the sign of  $\Delta G$  and determine if a reaction is spontaneous.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

Gibbs free energy breyting =

Heildarorkubreyting kerfis - orka töpuð til óreiðu

If Efnahvarf is

- exothermic (negative  $\Delta H^{\circ}$ ) (útvermið)
- and entropy increases (positive  $\Delta S^{\circ}$ )  
(óreiða eykst)
- þá verður  $\Delta G^{\circ}$  að vera **NEGATIVE**
- og efnahvarfið þá sjálfgengt (gengur t.h.)

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

If reaction is

- Innvermin - endothermic (positive  $\Delta H^{\circ}$ )
- og óreiða minnkar (negative  $\Delta S^{\circ}$ )
- þá verður  $\Delta G^{\circ}$  **POSITIVE**
- Efnahvarfið er ekki sjálfgengt (vill t.v.).

# Gibbs Free Energy, G

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$\Delta H^{\circ}$	$\Delta S^{\circ}$		$\Delta G^{\circ}$ Reaction
út(-)	increase(+)	-	sjálfgengt
Inn(+)	decrease(-)	+	Ekki sjálfgengt
út(-)	decrease(-)	?	T dependent
Inn(+)	increase(+)	?	T dependent

# Calculating $\Delta G^\circ$

Bruni acetylen við 25°C



Fundið í töflu  $\Delta H^\circ = -1238 \text{ kJ}$

S fundið í töflu

$$\Delta S^\circ = -97.4 \text{ J/K or } -0.0974 \text{ kJ/K}$$

$$\begin{aligned}\Delta G^\circ &= -1238 \text{ kJ} - (298 \text{ K})(-0.0974 \text{ J/K}) \\ &= \underline{-1209 \text{ kJ}}\end{aligned}$$

Reaction is **sjálfgengt** þrátt fyrir minnkandi óreiðu  $\Delta S$ .

**Efnahvarf er entalpí(hvarfvarma) drifið**

# Calculating $\Delta G^\circ$



Leysist ammoniumnítat í vatni? (sjálfgengt)

EF svo er, er það á óreiðu eða hvarfvarmadrifið?

# Calculating $\Delta G^\circ$



Fundið í töflu  $\Delta H^\circ = +25.7 \text{ kJ}$

$\Delta S^\circ = +108.7 \text{ J/K}$  or  $+0.1087 \text{ kJ/K}$

$\Delta G^\circ = +25.7 \text{ kJ} - (298 \text{ K})(+0.1087 \text{ J/K})$

$= -6.7 \text{ kJ}$

Efnahvarfið er sjálfgengt þrátt fyrir að það er innvermið.

Hvarfið er óreiðudrifið

## Við hvaða hitastig verður hvarf sjálfgengt



$$\Delta H^\circ = +467.9 \text{ kJ} \quad \Delta S^\circ = +560.3 \text{ J/K}$$

$$\Delta G^\circ = +300.8 \text{ kJ}$$

Hvarfið er ekki sjálfgengt við 298 K  
við hvaða hita, T, breytist G úr(+) í að vera(-) semsagt  
verður sjálfgengt?

$$\text{Þegar } \Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H_{\text{rxn}}}{\Delta S_{\text{rxn}}} = \frac{467.9 \text{ kJ}}{0.5603 \text{ kJ/K}} = 835.1 \text{ K}$$