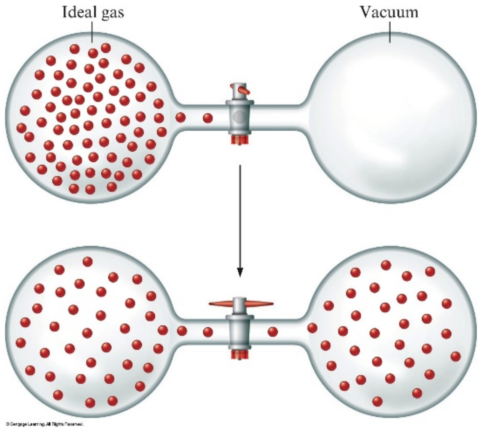
Spontaneous processes and entropy

EX: Ice melting at RT

EX: Salt dissociation

- A spontaneous process is one that occurs without outside intervention.



- The driving force for a spontaneous process is an **increase** in the **entropy of the universe**.

- A measure of molecular randomness or disorder.

Amplitude of the S_{system}

$2C_{(s)} + 1O_{2(g)} \rightarrow 2CO_{2(g)}$

$CO_{2(g)}$, T = 300K $CO_{2(g)}$,T = 400K

$2SO_{2(g)} + 1O_{2(g)} \rightarrow 2SO_{3(g)}$

$CaO_{(s)}$ $H_2O_{(l)}$ $SeO_{2(g)}$ $SeO_{3(g)}$

$2MgO_{(s)} + 1CO_{2(g)} \rightarrow 2MgCO_{3(s)}$

A measure of molecular randomness or disorder.

What is the measurable quantity ??

S =

Calculate the ΔS^0 of the system:

$2H_{2(g)} + 1O_{2(g)} \rightarrow 2H_2O_{(g)}$

S^0 of $H_{2(g)}$ = 131 J/molK
S^0 of $O_{2(g)}$ = 205 J/molK
S^0 of $H_2O_{(g)}$ = 189 J/molK

Tracking Entropy

$H_2O_{(l)} \leftrightarrow H_2O_{(g)}$

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

Standard state: 1M, 1atm

G^0 (product) < G^0 (reactant)
ΔG^0

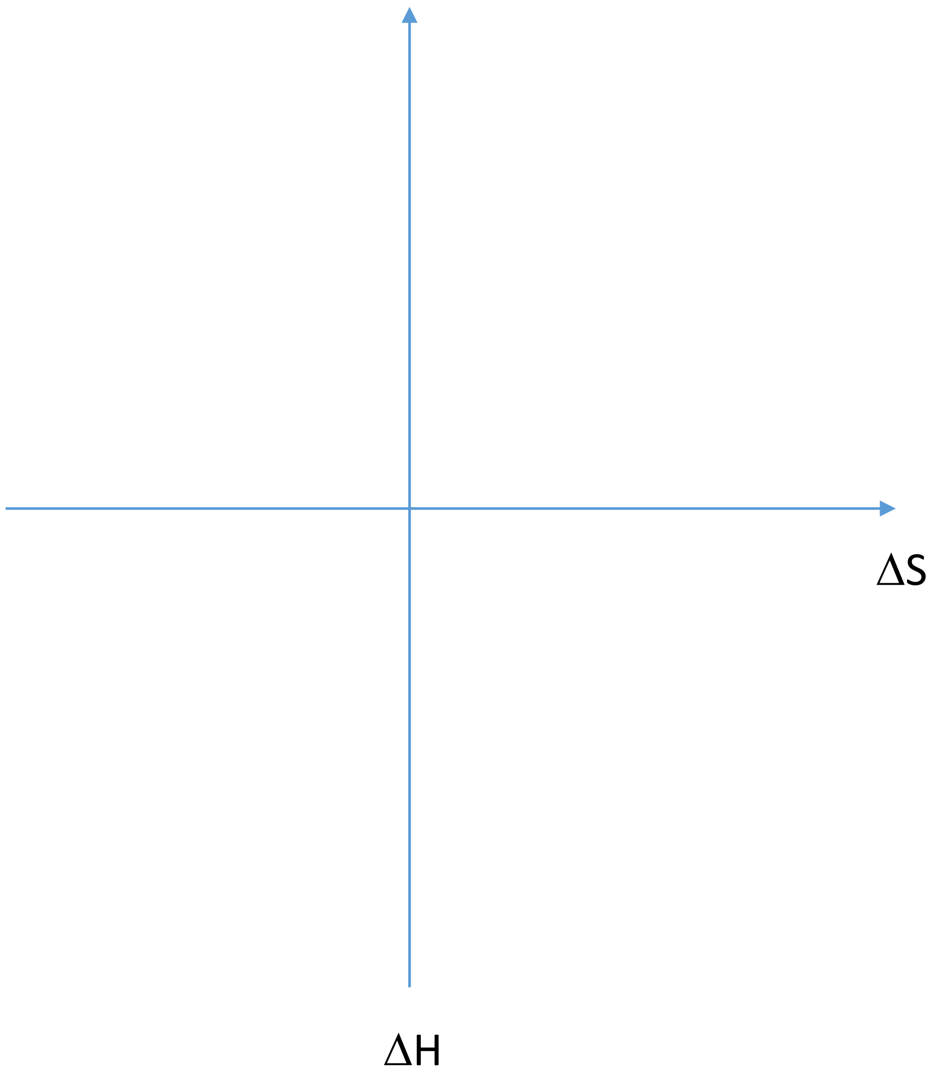
G^0 (product) > G^0 (reactant)
ΔG^0

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

spontaneity of this reaction
changes at $\Delta G = 0$

Free Energy Space

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



Free Energy and Reactions

	ΔH	ΔS	ΔG
$K_{(s)} + H_2O_{(l)} \rightarrow K^+_{(aq)} + OH^-_{(aq)} + 1/2\ H_{2(g)}$, exothermic			
$H_2O_{(l)} + 1/2\ O_{2(g)} \rightarrow H_2O_{2\ (l)}$, endothermic			
$AlBr_{3(s)} \rightarrow Al_{(s)} + 3/2\ Br_{2\ (l)}$, endothermic			
$2Mg_{(s)} + CO_{2(s)} \rightarrow 2MgO_{(s)} + C_{(s)}$, exothermic			

Free Energy and equilibrium

$$aA \quad + \quad bB \quad \leftrightarrow \quad cC \quad + \quad dD$$

ΔG^o , K

ΔG^o
K

ΔG^o
K

ΔG^o
K

Not spontaneous

spontaneous

$$\Delta G^o = - RT \ln K$$

$$K = \exp\left(\frac{-\Delta G^o}{RT}\right)$$

A particular reaction has a ΔH^o value of -10 kJ and ΔS^o of -500 J/mol K at 298 K. Assuming that ΔH^o and ΔS^o hardly change with temperature, determine the temperature in ^oC at which the spontaneity of this reaction changes.

Free Energy and Reaction Quotient

$\Delta G = G(P) - G(R)$

$\Delta G < 0 \Leftrightarrow Q<K$

$\Delta G = 0 \Leftrightarrow Q=K$

$\Delta G > 0 \Leftrightarrow Q>K$

$\Delta G = \Delta G^0 + RT \ln Q$

What are ΔG and K at equilibrium at 25C for $H_2O_{(l)} \leftrightarrow H_2O_{(g)}$

(A) $\Delta G<0$ (B) $\Delta G = 0$ (C) $\Delta G>0$

What is ΔG for the following reaction under the given conditions at 400K?
Will the reaction go toward products, reactants or is it at equilibrium?
P_{N2} = 4.2 bar, P_{H2} = 1.8 bar, P_{NH3} = 21 bar, K(400K) = 41
$N_2 + 3H_2 \leftarrow \rightarrow 2NH_3$