Lecture Notes E: Entropy and Free Energy

1) Discussion of Laboratory 1

2) Criteria for spontaneous reactions

ΔH_f^o ($H_2O_{(l)}$) = -285.83 kJ/mol ; ΔH_f^o ($CO_2(g)$) = -393.51 kJ/mol; ΔH_f^o (MgO(s)) = -601.70 kJ/mol

$Mg + \frac{1}{2} O_2 \rightarrow MgO$ ΔH= -601.7 kJ/mole

$Mg + \frac{1}{2} CO_2 \rightarrow MgO + C$ ΔH= -404.94 kJ/mole

$Ba(OH)_2 \cdot 8H_2O_{(s)} + 2NH_4Cl_{(s)} \rightarrow 2\ NH_{3\ (aq)} + 10\ H_2O_{(l)} + BaCl_{2\ (aq)}$ $\Delta H > 0$

3) Gibbs Free Energy

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

A process is spontaneous if $\Delta G < 0$

Two driving forces for reactions:

Enthalpy driven: $\Delta H < 0$

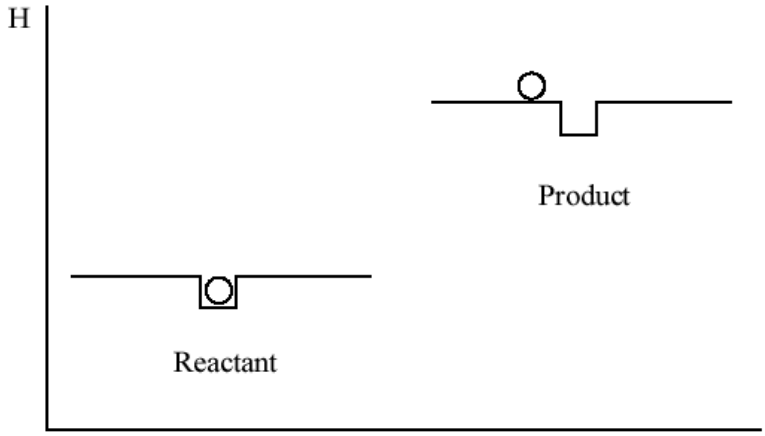
Entropy driven: $\Delta S > 0$

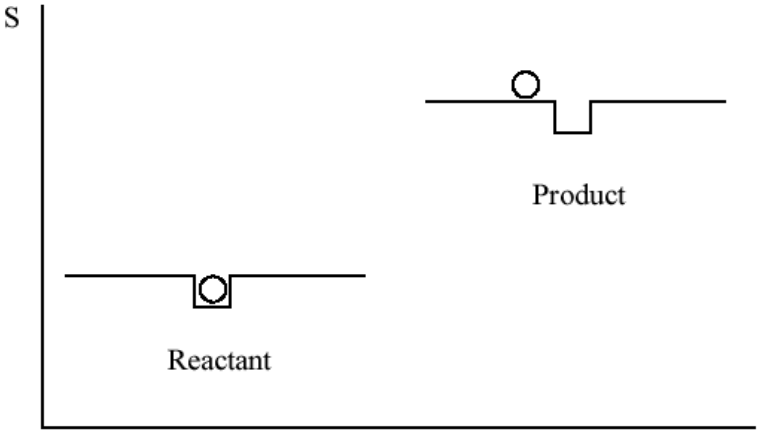
4) Entropy

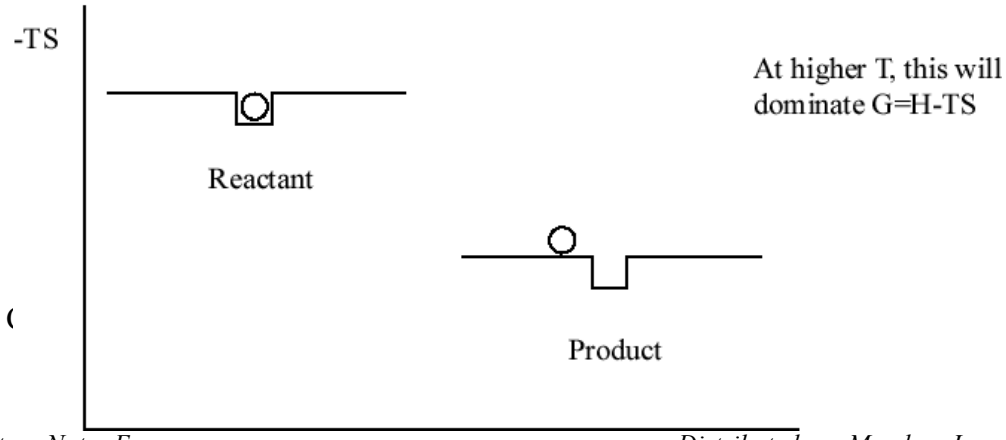
Takes into account the "amount of space" available to a system.

$S = R \ln \Omega$ R = gas constant

Ω = number of different ways a system can arrange itself and still have the same Energy and Volume.







5) Calculating ΔS for chemical reactions

S^o = Standard Molar Entropy (use like heat of formation)

$$CO_{2\,(g)} \rightarrow CO_{(g)} + \tfrac{1}{2} O_{2\,(g)}$$

From Appendix D, $S^o(CO_{2\,(g)})$ = 197.56 J/(K mol)
$S^o(CO_{(g)})$ = 213.63 J/(K mol)
$S^o(O_{2\,(g)})$ = 205.03 J/(K mol)

Problem

Is the following reaction spontaneous at room temperature. If so, is it enthalpy driven, entropy driven or both?

	$Mg_{(s)}$ +	$\frac{1}{2} CO_{2(g)}$ →	$MgO_{(s)}$ +	$C_{(graphite)}$
ΔH^o_f (kJ/mol)	0	-393.51	-601.7	0
S^o (J/(K mol))	32.68	213.63	26.94	5.74

6) Sign of ΔS for some common processes

Concept

What is the sign of ΔS for the following processes

a) $\Delta S > 0$, S increases b) $\Delta S < 0$, S decreases

Solid → Liquid

Liquid → Gas

N reactants → M products

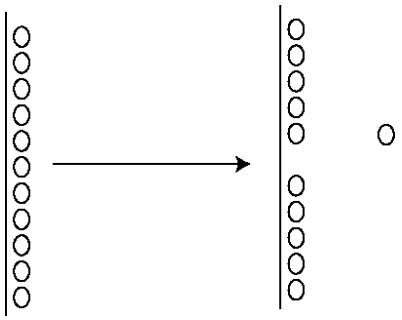
N < M $CO_{2\,(g)} \rightarrow CO_{(g)} + \frac{1}{2} O_{2\,(g)}$

N > M $H_2C{=}CH_{2\,(aq)} + Br_{2\,(aq)} \rightarrow H_2BrC\text{-}CBrH_{2\,(aq)}$

Break a bond

$NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$

Desorption from a surface



Elongate a polymer molecule

7) Calculating ΔS for physical processes

$\Delta S = q_{rev}/T$ q_{rev} = heat absorbed from or given to the surroundings in a reversible process

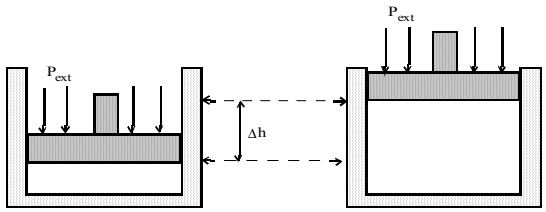
Phase transitions

Solid → Liquid

Liquid → Solid

Heat a system at constant V or P

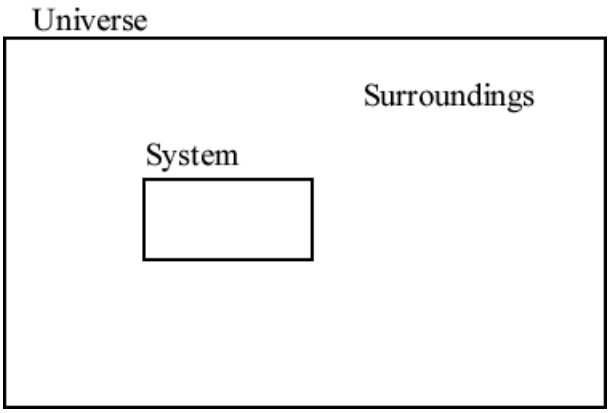
Reversible, isothermal expansion of an ideal gas



8) ΔG_{system} versus $\Delta S_{universe}$

A process taking place at constant T and P is spontaneous if $\Delta G_{system} < 0$

A process taking place in an isolated system is spontaneous if $\Delta S_{universe} > 0$



The system is at constant Pressure and Temperature.

To maintain constant T, the system must be able to exchange heat with the surroundings. We also assume the universe is big enough that no matter how much heat we give it, its temperature remains constant (it is a heat bath).

To maintain a constant P, the system must be able to change its volume (i.e. exchange volume with the surroundings).