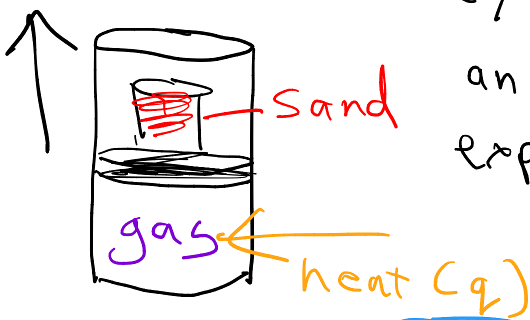
6/15/20

Entropy



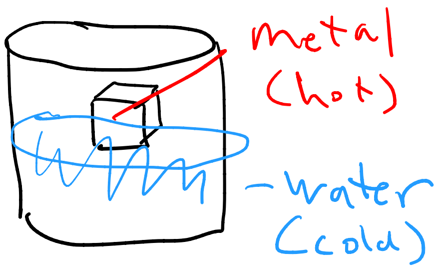
In this example, a cylinder is undergoing an infinitesimal expansion ("perfect reversible expansion").

$$\Delta S_{sys} = \frac{q_{rev}}{T}$$

q_{rev} — heat that is absorbed under these ideal expansion conditions.

A change in entropy alone has an impact on energy

1st law: $\Delta E = 0 = \Delta H_{rxn_1} + \Delta H_{rxn_2}$



$$q_T = 0 = q_{metal} + q_{H_2O}$$

(assuming isolated system)

$$\Delta E = 0 = q_{system} + q_{surroundings}$$

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T}$$

Does not depend on the process in the system.

2nd law of thermodynamics

$(\Delta S_{system} + \Delta S_{surroundings}) > 0$

in any spontaneous process.

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surround}$$

system and surroundings

$$\Delta S_{surround} = \frac{-\Delta H_{sys}}{T}$$

$$(-T)\ \Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}\ (-T)$$

$$-T\Delta S_{univ} = -T\Delta S_{sys} + \Delta H_{sys}$$

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

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the amount of free energy available to a system depends on the enthalpy changes of the system adjusted for the effects of entropy

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

$$\Delta G = RT \ln \frac{Q}{K}$$

The amount of energy available for a reaction depends on how far away the reaction is from equilibrium.

At equilibrium, $Q = K$

$\Delta G = RT \ln 1 = 0$ (definition of equilibrium)

$Q > K$ $\quad Q/K > 1$ $\quad \Delta G > 0$

non-spontaneous

$Q < K$ $\quad Q/K < 1$ $\quad \Delta G < 0$

spontaneous

$$\Delta G = RT \ln Q - RT \ln K$$

Standard state

25°C, 1 bar, 1 M concentration

Q at the standard state always equals 1.

$\Delta G^{\circ} = RT \ln 1 - RT \ln K = -RT \ln K$

(° = standard state)

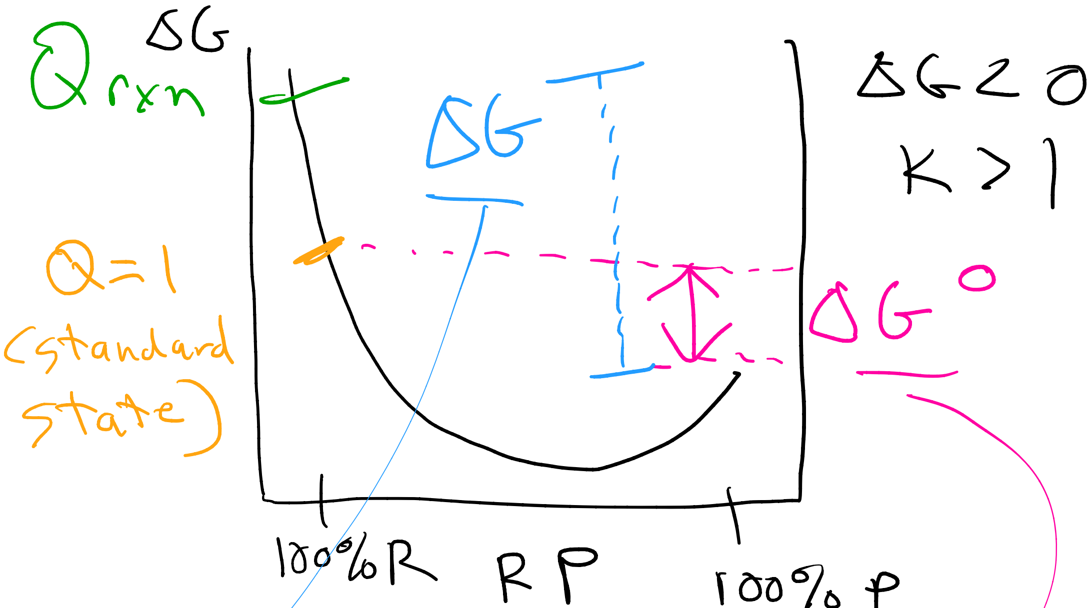
$$\Delta G^{\circ} = -RT \ln K$$

$$\Delta G = RT \ln Q - RT \ln K$$

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

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

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



true amount of energy available for the rxn

the amount of energy available at the standard state.