Thermodynamics:

Study of energy changes that accompany physical and chemical changes.

First Law of Thermodynamics:
Energy is niether created nor destroyed but simply converted from one form to another.

E: internal energy of a system. State function.

ΔE: change in internal energy.

ΔE: change in internal energy. Energy enters a system as heat(q) and/or work(w).

Consider a system with an initial amount of energy E_i. If it absorbs some heat and then has work done on it.

$$E_f = E_i + q + w$$

$$\Delta E = E_f - E_i$$

$$\Delta E = q + w$$

q = heat   w = work

$\Delta E = q + w$

$\Delta E = E_f - E_i$ q = heat   w = work

q   +# heat absorbed by system
     -# heat given off by system

w   +# work done on the system
     -# work done by the system

ΔE +# energy enters the system
     -# energy leaves the system

Ex:

A gas while expanding absorbs 25 J of heat and does 243 J of work. Calculate ΔE.

Pressure-Volume Work:

$$W = -P\Delta V \qquad 1 \text{ L·atm} = 101.3 \text{ J}$$

Ex:

A gas expands from 1.00 L to 5.00 L against a constant pressure of 1.00 atm, calculate the work done by the gas.

Constant Volume Process
$\Delta E = q_v$ q_v: heat evolved or absorbed during a constant volume process.

Constant Pressure Process
$\Delta H = q_p$ q_p: heat evolved or absorbed during a constant pressure process.

For reactions involving gases, changes in volume are significant.

$$\Delta H = \Delta E + (\Delta n)RT$$

Δn = moles gas product - moles gas react
R: 8.314 J/K·mole
T: temperature in Kelvins

Ex:

A sample of quinone, $C_6H_4O_2$(s), is combusted in a bomb calorimeter(constant volume) with a heat capacity of 7.45 kJ/°C and produced a temperature increase of 4.00 °C. What is q, ΔH, & ΔE(at 25°C)?

$$C_6H_4O_2(s) + 6O_2(g) \rightarrow 6CO_2\ (g)\ + 2H_2O(g)$$

Thermodynamics continued:
First Law of Thermodynamics:
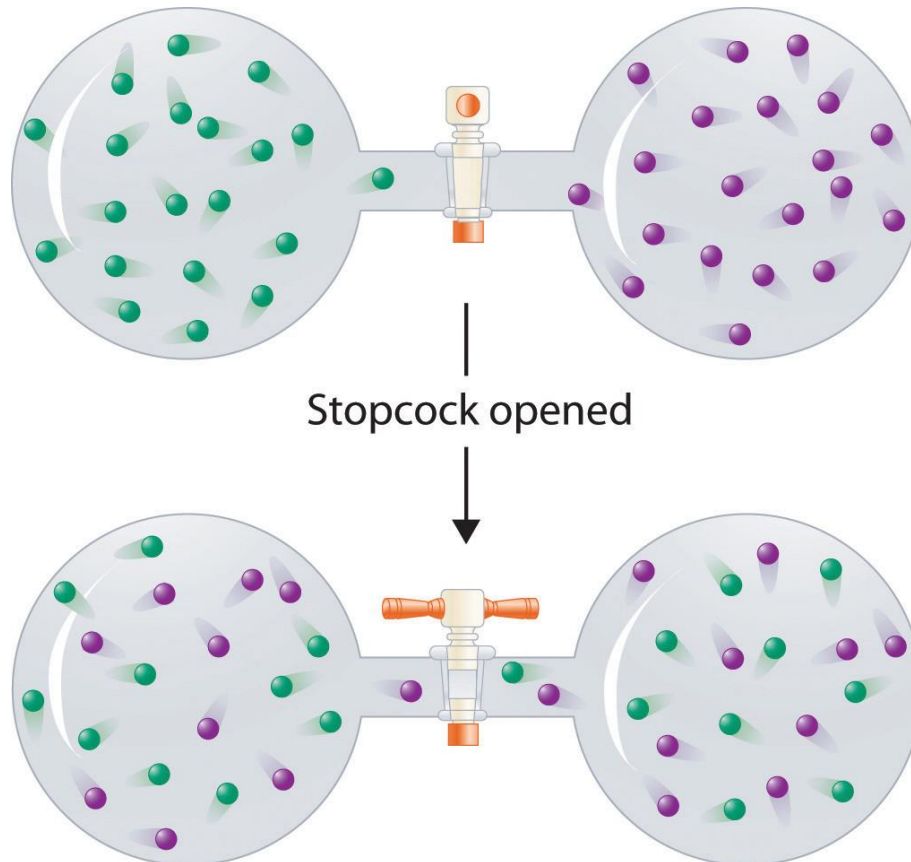
Total energy of the universe is constant.

Energy is neither created or destroyed.

E constant for an isolated system.

Spontaneous Processes and Entropy:

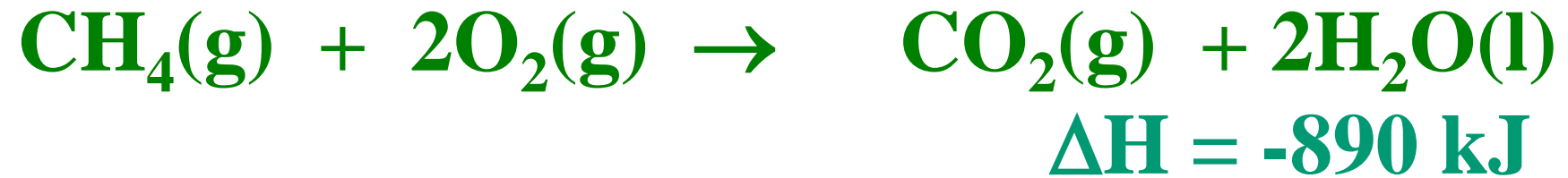**Spontaneous process is a process which has a tendency to occur without external influence. Ex: Mixing of gas molecules.**

Stopcock opened

Spontaneous processes were originally thought to be exothermic processes.

Not so!

Ex: Combustion of natural gas.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
$$\Delta H = -890 \text{ kJ}$$

Endothermic process are also spontaneous:

$$H_2O(s) \rightarrow H_2O(l) \quad \Delta H = +6.0 \text{ kJ}$$

Spontaneous reactions occur because matter and energy tend to become more disordered.

Entropy:

Entropy(S) – Thermodynamic property related to the degree of disorder.

Can not measure S directly. Can measure ΔS.

$$\Delta S = S_{FINAL} - S_{INITIAL}$$

$+\Delta S$: system becoming more disordered.

$-\Delta S$: system becoming less disordered or more organized.

Ex:

Solid $\rightarrow$ Liquid $\qquad \Delta S = +$

System is becoming less ordered.

Entropy cont…

Second Law of Thermodynamics – In any spontaneous process there is always an increase in the entropy of the universe.

For a spontaneous process $\Delta S_{universe} > 0$. Where

$$\Delta S_{universe} = \Delta S_{SYS} + \Delta S_{SUR}$$

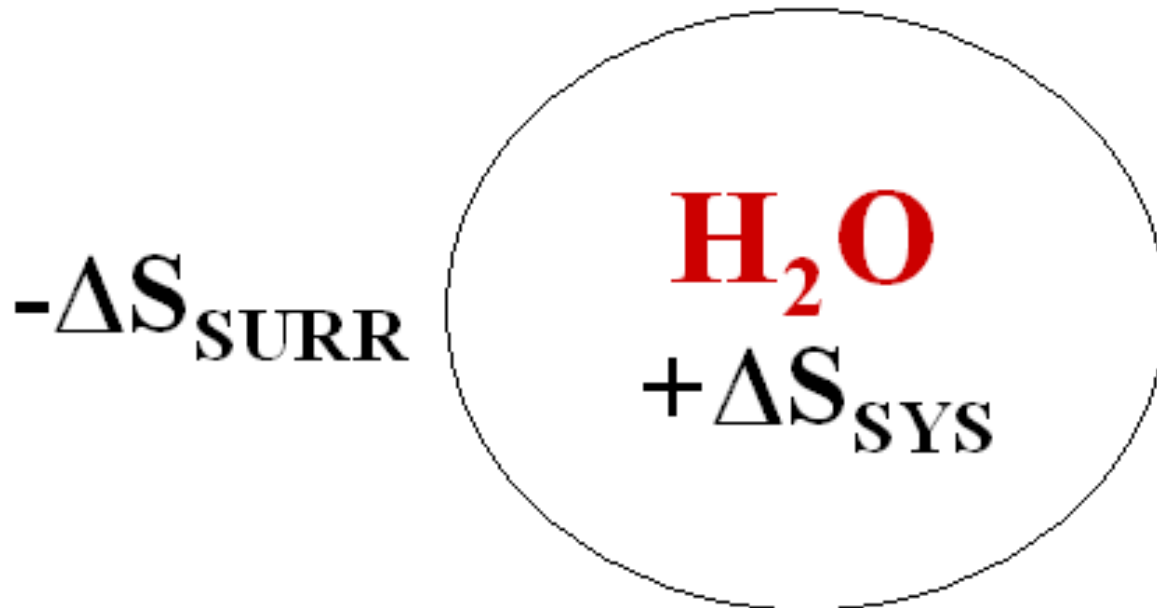**ΔS_{SYS}: entropy change for the system.**
ΔS_{SUR}: entropy change for the surroundings

Spontaneity is Temperature Dependant:

For a spontaneous process $\Delta S_{universe} > 0$.

$$\Delta S_{universe} = \Delta S_{SYS} + \Delta S_{SUR}$$

Consider a system of Liquid Water:

$$H_2O(l) \rightarrow H_2O(g)$$

$-\Delta S_{SURR}$

H_2O
$+\Delta S_{SYS}$

Quantifying ΔS

$$\Delta S = \frac{q_{rev}}{T}$$

q_{rev}: Heat changes for a reversible process. Process that can be reversed in direction by a small change in a system property.

T: temperature in Kelvin

Entropy:

Assuming a constant pressure. $\Delta H = q$

$$\Delta S \equiv \frac{q_{rev}}{T}$$

T: temperature in Kelvin

ΔS has units of kJ/K or J/K.

Entropy cont…

Third Law of Thermodynamics – The entropy for a pure perfect crystal is zero at absolute zero(O K).

Ex:
Calculate the change in entropy for the melting of ice at 0 °C.

$$H_2O(s) \rightarrow H_2O(l) \quad \Delta H = +6.0 \text{ kJ}$$

To determine if a process is spontaneous, can not measure $\Delta S_{universe}$ and ΔS_{SUR}.

$$\Delta S_{universe} = \Delta S_{SUR} + \Delta S_{SYS}$$

Multiply by T.

$$T \cdot \Delta S_{universe} = T \cdot \Delta S_{SUR} + T \cdot \Delta S_{SYS}$$

$$T \cdot \Delta S_{universe} = \Delta H_{SUR} + T \cdot \Delta S_{SYS}$$

Since

$$\Delta S = \frac{\Delta H}{T} \qquad \text{Then } \Delta H_{SUR} = T \cdot \Delta S_{SUR}$$

Since $\Delta H_{SUR} = - \Delta H_{SYS}$

Gibbs Free Energy(G):

$$G = H - TS$$

since we measure change

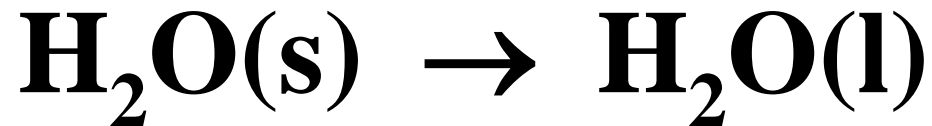$$\Delta G = \Delta H - T\Delta S$$

$\Delta G < 0$: process is spontaneous

$\Delta G > 0$: process is not spontaneous

$\Delta G = 0$: process is at equilibrium

Gibbs Free Energy(G):

Ex:

Calculate the change in Gibbs free energy for the melting of ice if ΔH= +6.0 kJ and ΔS = +22. J/K at 0.0°C.

$$H_2O(s) \rightarrow H_2O(l)$$
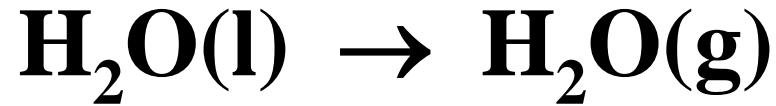
ΔG Temperature Dependant:

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

ΔG	ΔH	ΔS	Spontaneous
-	-	+	All temps.
- or +	-	-	Low temps.
+	+	-	Not sponts.
- or +	+	+	High temps.

ΔG cont…:

Ex:

Consider the following process

$$H_2O(l) \rightarrow H_2O(g)$$

where $\Delta H = +44.0$ kJ and $\Delta S = +118$ J/K

Calculate ΔG at 90 °C, 100 °C, and 110 °C.

Standard Gibbs Free Energy Change(ΔG°):

"°" Indicates standard conditions
   (1 atm and 25°C)

Can determine ΔG° from ΔH° and ΔS°.

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

Standard Entropies:

Similar method used for $\Delta S°$.

$$\Delta S° = \Sigma\Delta S°(prods) - \Sigma\Delta S°(reacts)$$

Ex: Calculate $\Delta S°$ for the following:

$$N_2O_4(g) \rightarrow 2NO_2(g) \qquad \Delta S° = ?$$

Given:

Compound	$\Delta S°(J/K \cdot mole)$
$N_2O_4(g)$	+304.2
$NO_2(g)$	+240.0

Calculating $\Delta G°$:

Ex: Calculate $\Delta G°$ for the following:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta G° = ?$$
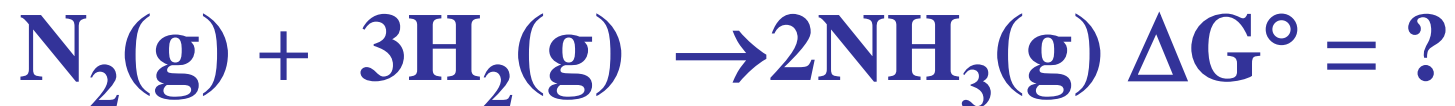
Given:

Reagent	$\Delta H_f°$ (kJ/mole)	$\Delta S°$ (J/K·mole)
$N_2(g)$	0	+191.5
$H_2(g)$	0	+130.68
$NH_3(g)$	-46.11	+192.3

Standard Free Energies of Formation:

Similar method can be used for $\Delta G°$.

$$\Delta G° = \Sigma \Delta G_f°(\text{prod}) - \Sigma \Delta G_f°(\text{reacts})$$

Relationship between ΔG and ΔG°:

$$\Delta G = \Delta G° + RTlnQ$$

R: Gas Constant(8.314 J/K·mole)

T: temperature in Kelvin

Q: reaction quotient

$$Q = \frac{[products]}{[reactants\ ]}$$

ΔG° cont…

Ex:

Calculate ΔG for the following

$$CO(g) \ + \ 2H_2(g) \ \rightarrow \ CH_3OH(l)$$

at 25 °C if ΔG° = -29.0 kJ and p(CO) is 5.0 atm and p(H$_2$) is 3.0 atm.

ΔG and Equilibrium:

For systems at equilibrium

$$\Delta G° = -RT \ln K$$

Can now determine the equilibrium constant from ΔG°.