

Thermodynamics:

Study of energy changes that accompany physical and chemical changes.

First Law of Thermodynamics:

Energy is neither 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.

$$E_f = E_i + q + w$$

$$\Delta E = E_f - E_i$$

$$\Delta E = q + w$$

$q = \text{heat}$

$w = \text{work}$

$$\Delta E = q + w$$

$$\Delta E = E_f - E_i$$

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:

$$W = -P\Delta V$$

$$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$$

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 $7.45 \text{ kJ}/^\circ\text{C}$ and produced a temperature increase of $4.00 \text{ }^\circ\text{C}$. What is q , ΔH , & ΔE (at 25°C)?



Thermodynamics continued:

First Law of Thermodynamics:

Total energy of the universe is constant.

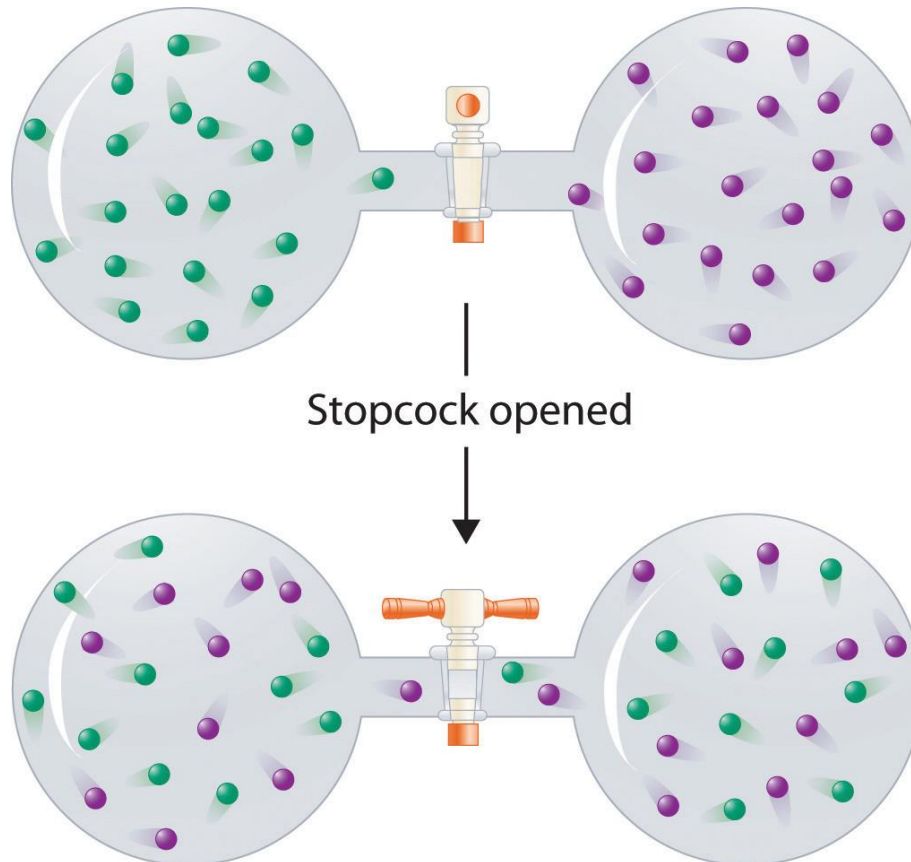
Energy is neither created or destroyed.

E constant for an isolated system.

Spontaneous Processes and Entropy:

Spontaneous process is a process which has a tendency to occur without external influence.

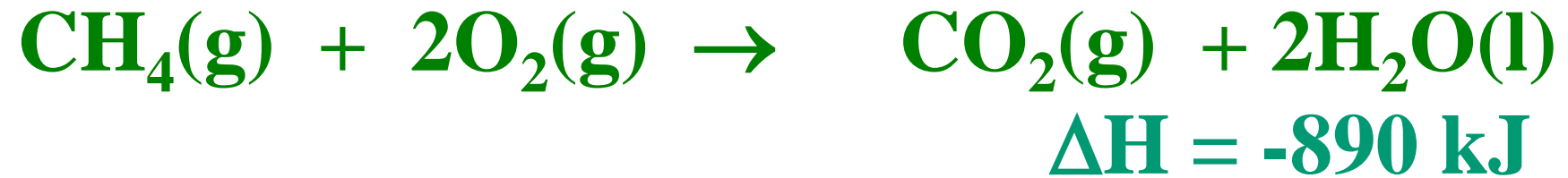
Ex: Mixing of gas molecules.



Spontaneous processes were originally thought to be exothermic processes.

Not so!

Ex: Combustion of natural gas.



Endothermic process are also spontaneous:



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 .

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

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

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

Ex:

Solid \rightarrow Liquid $\Delta S = +$

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

$\Delta S_{\text{universe}} > 0$. Where

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

ΔS_{SYS} : entropy change for the system.

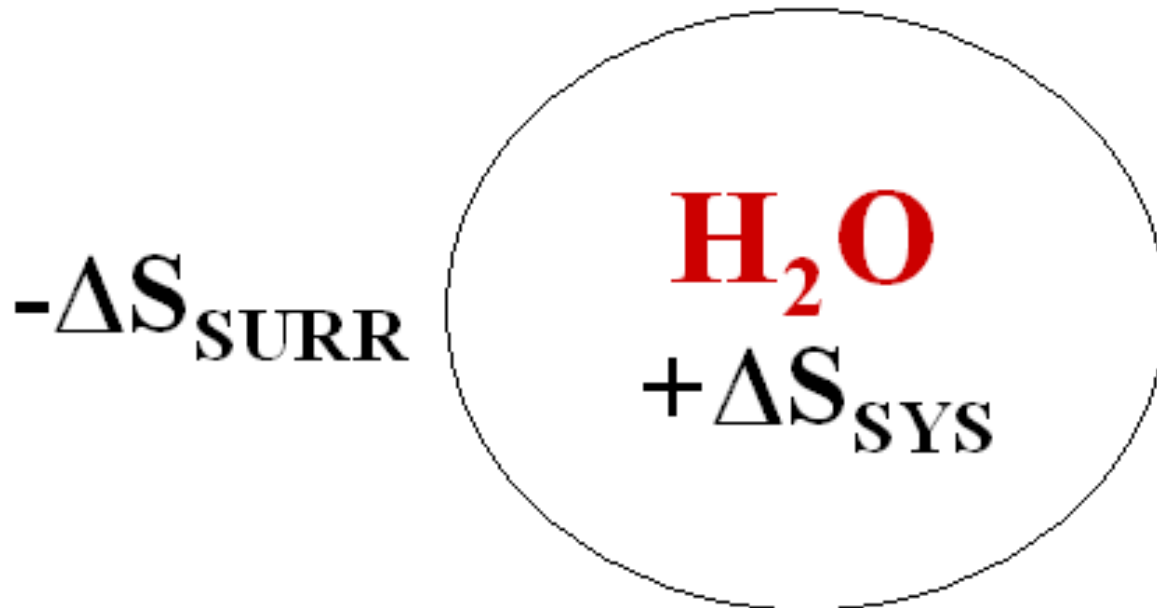
ΔS_{SUR} : entropy change for the surroundings

Spontaneity is Temperature Dependent:

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

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

Consider a system of Liquid Water:



Quantifying ΔS

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

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. $\Delta H = q$

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

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(0 K).

Ex:

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



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

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

Multiply by T.

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

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

Since

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

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

Gibbs Free Energy(G):

$$G = H - TS$$

since we measure change

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

$\Delta G < 0$: process is spontaneous

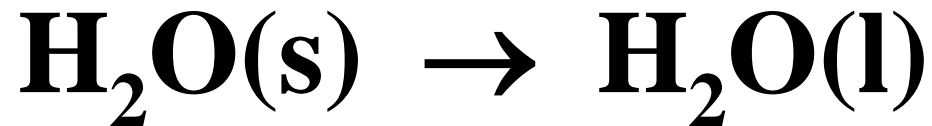
$\Delta G > 0$: process is not spontaneous

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

Gibbs Free Energy(G):

Ex:

Calculate the change in Gibbs free energy for the melting of ice if $\Delta H = +6.0$ kJ and $\Delta S = +22$. J/K at 0.0°C .



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



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°):

''^o'' Indicates standard conditions
(1 atm and 25°C)

Can determine ΔG° from ΔH° and ΔS° .

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

Standard Entropies:

Similar method used for ΔS° .

$$\Delta S^\circ = \Sigma \Delta S^\circ(\text{prods}) - \Sigma \Delta S^\circ(\text{reacts})$$

Ex: Calculate ΔS° for the following:

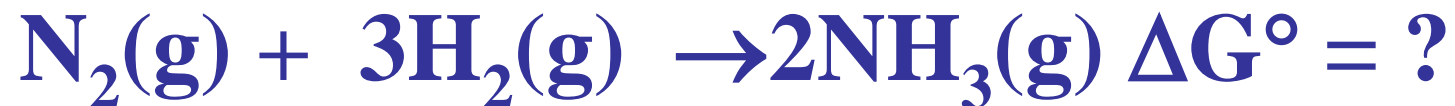


Given:

<u>Compound</u>	$\Delta S^\circ(\text{J/K}\cdot\text{mole})$
$\text{N}_2\text{O}_4(\text{g})$	+304.2
$\text{NO}_2(\text{g})$	+240.0

Calculating ΔG° :

Ex: Calculate ΔG° for the following:



Given:

<u>Reagent</u>	ΔH_f° (kJ/mole)	ΔS° (J/K·mole)
$\text{N}_2(\text{g})$	0	+191.5
$\text{H}_2(\text{g})$	0	+130.68
$\text{NH}_3(\text{g})$	-46.11	+192.3

Standard Free Energies of Formation:

Similar method can be used for ΔG° .

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

Relationship between ΔG and ΔG° :

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

R: Gas Constant(8.314 J/K·mole)

T: temperature in Kelvin

Q: reaction quotient

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

ΔG° cont...

Ex:

Calculate ΔG for the following



at 25 °C if $\Delta G^\circ = -29.0$ kJ and $p(\text{CO})$ is 5.0 atm and $p(\text{H}_2)$ is 3.0 atm.

ΔG and Equilibrium:

For systems at equilibrium

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

Can now determine the equilibrium constant from ΔG° .