Entropy: a thermodynamic property, can be used as a measure of **disorder**, is measure of **randomness**.

We define entropy, **S**, as an additional thermodynamic state function.

For a system, $\Delta S = S_f - S_i$

If $\Delta S > 0$ the randomness increases,

If $\Delta S < 0$ the order increases.

The infinitesimal change in entropy, dS, is defined as

$$dS = \frac{dq_{rev}}{T}$$

Where "rev" is reversible process, Integrating equation

$$dS = \int \frac{dq_{rev}}{T} = \frac{q_{rev}}{T}$$

Equation demonstrates that entropy has units of J/K

The Second Law uses the entropy to identify the *spontaneous changes* among those permissible changes. This direction of heat flow is one of the ways of expressing the second law. One property common to spontaneous processes is that the **final state** is more **disordered** or **random** than the **original**.

Spontaneity is related to an **increase** in **randomness**.

We can break down entropy change as resulting from changes in specific properties of our system. There are changes in five things that will lead to a change in the entropy of the system.

1. Mixing
2. Temperature
3. Phase
4. Composition (chemistry)
5. System parameters (T, P, V, n)

Mathematical expression of entropy

The value of ΔS *of the system* is **independent** of the path between the initial and final states, so this expression applies the change of state occurs reversibly

The infinitesimal change in entropy is

$$dS = \frac{dq_{rev}}{T} \Rightarrow dq_{rev} = TdS \qquad \text{------(1)}$$

from first thermodynamic law expression, we get

$$dq_{rev} = dU - dw \qquad \text{------(2)}$$

for the reversibly change, $\Delta U = C_V\, dT$ and $w = -nRT\,\frac{dV}{V}$

$$dq_{rev} = C_V\, dT + nRT\,\frac{dV}{V} \qquad \text{------(3)}$$

sub eq.(1) in eq. (3)

$$TdS = C_V\, dT + nRT\,\frac{dV}{V} \qquad \text{------(4)} \ \div T$$

$$dS = C_V\,\frac{dT}{T} + nR\,\frac{dV}{V} \qquad \text{------(5)}$$

and then integrate:

$$\int_i^f dS = C_V \int_i^f \frac{dT}{T} + nR \int_i^f \frac{dV}{V} \qquad \text{-----(6)}$$

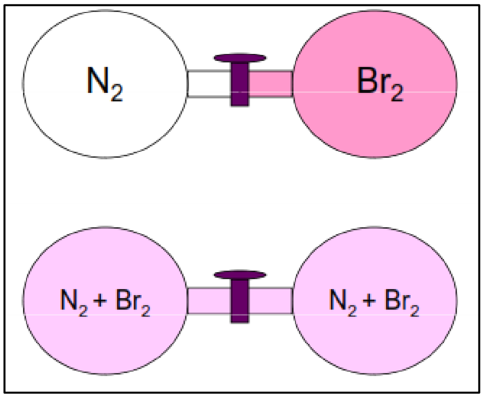
$$\Delta S = C_V\, \ln\frac{T_2}{T_1} + nR\, \ln\frac{V_2}{V_1} \qquad \text{-----(7)}$$

acorrding to boyle 's law $\frac{V_2}{V_1} = \frac{P_1}{P_2}$, we can calculate entropy in terms of pressure

$$\Delta S = C_V\, \ln\frac{T_2}{T_1} + nR\, \ln\frac{P_1}{P_2} \qquad \text{-----(8)}$$

1- Change in entropy for **mixing** gas

Mixing of gases (eg. by diffusion), always results in increase in entropy. Mixing is spontaneous.



We can also calculate the entropy of mixing for an ideal gas. Both gas A and gas B are expand reversible at constant Temperature (isothermal T_2=T_1). Thus we have:

$$\Delta S = C_V \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2} \qquad \text{-----(8)}$$ T_2=T_1 and ln1 =0. Thus we get:

$$\Delta S_i = n_i R\ln\frac{P_1}{P_2} \qquad \text{-----(9)}$$

$$\Delta S_A = n_A R\ln\frac{P_T}{P_A} = -n_A R\ln\frac{P_A}{P_T} \qquad \text{-----(10)}$$ Entropy for gas A

$$\Delta S_B = n_B R\ln\frac{P_T}{P_B} = -n_B R\ln\frac{P_B}{P_T} \qquad \text{-----(11)}$$ Entropy for gas A

$$\Delta S_{mixing} = \Delta S_A + \Delta S_B = -n_A R\ln\frac{P_A}{P_T} + (-n_B R\ln\frac{P_B}{P_T}) \qquad \text{-----(12)}$$

$$\Delta S_{mixing} = -nR(\frac{n_A}{n}\ln\frac{P_A}{P_T} + \frac{n_B}{n}\ln\frac{P_B}{P_T}) \qquad \text{-----(13)} \quad X_i = \frac{n_i}{n} = \frac{P_i}{P}$$

$$\Delta S_{mixing} = -nR(X_A \ln X_A + X_B \ln X_B) \qquad \text{-----(14)}$$

X= is mole fraction

Q) A mixture of 40% N_2O and 60% O_2 may be used in a dentist office as an anesthetic. Assuming that the gases behave ideally, determine the entropy of mixing to produce 1 mole of the mixture.

$$n_{N_2O} = \frac{40}{100} \times 1mol = 0.4mol$$

$$X_{N_2O} = \frac{n_{N_2O}}{n_T} = \frac{0.4}{1} = 0.4$$

$$n_{O_2} = \frac{60}{100} \times 1mol = 0.6mol$$

$$X_{O_2} = \frac{n_{O_2}}{n_T} = \frac{0.6}{1} = 0.6$$

$$\Delta S_{mixing} = -nR\,(X_{N_2O} \ln X_{N_2O} + X_{O_2} \ln X_{O_2})$$

$$\Delta S_{mixing} = -1mol \times 8.314(0.4 \ln 0.4 + 0.6 \ln 0.6)$$

$$\Delta S_{mixing} = 5.6J\ /\ K$$

H.W) determine the entropy of mixing 8g of O_2 gas and 7g of N_2 gas Assuming that the gases behave ideally.

Q) why the entropy sign of mixing always positive?

Mixing is a spontaneous process that is **entropically** driven.

$$\Delta S_{mixing} = -nR\,(X_A \ln X_A + X_B \ln X_B) \qquad \text{-----(14)}$$

From the definition of mole fraction $x < 1$ (always),

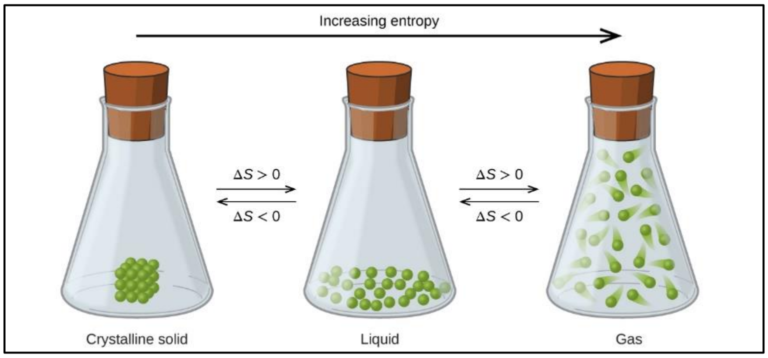
It follows that $\ln x < 0$ And thus ΔS_m is always positive.

H.W) Calculate **ΔS** and **q** at **STP (25°C, 1mol)** for a mixture of 15% N_2, 55% H_2 and 30% NH_3.

H.W.) Calculate the entropy of mixing 10.0 L of N_2 with 3.50 L of N_2O at 300.0 K and 0.550 atm. Assume that the volumes are additive; that is, $V_{tot.}$ 13.5L.

2-The entropy of a substance (dependent on temperature)

From entropy expression $dS = \frac{dq_{rev}}{T}$, the entropy of a substance increases (ΔS > 0) as it transforms from a relatively **ordered solid** to a **less**-ordered **liquid**, and then to a **still** less-ordered **gas**. The entropy decreases (ΔS < 0) as the substance transforms from a **gas** to a **liquid** and then to a **solid**.



Now consider the vapor or **gas** phase, the atoms or molecules occupy a *much* greater **volume** than in the liquid phase; therefore each atom or molecule can be found in many **more locations** than in the liquid (or solid) phase. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of **vaporization** and **sublimation** likewise involve increases in entropy, $\Delta S > 0$. According to **kinetic-molecular theory**,

1- The **temperature** of a substance is **proportional** to the average **kinetic energy** of its particles.

2- Raising the temperature of a substance will result in more extensive **vibrations** of the particles in **solids** and more rapid **translations** of the particles in liquids and gases.

3-At **higher** temperatures, the **distribution** of kinetic energies among the atoms or molecules of the substance is also **broader** (more **dispersed**) than at lower temperatures.

EX) For a phase change, H_2O (liq) ---> $H_2O(g)$ $\Delta H = q = +40{,}700$ J/mol, calculate the entropy change.

$$\Delta S = \frac{\Delta H}{T} = \frac{40{,}700 \text{ J/mol}}{373.15 \text{ K}} = +109 \text{ J/K·mol}$$

3- Entropy Changes for Phase Changes

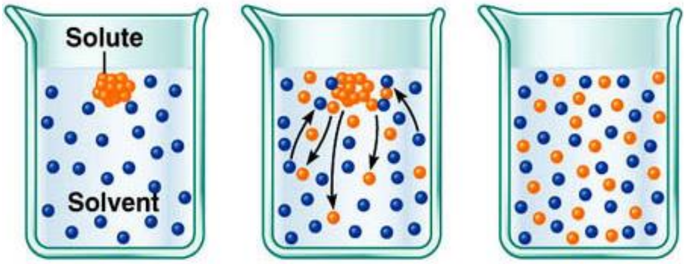
The entropy can change as the result of chemistry. Different molecules have different entropies. Thus it can be difficult to look at a reaction if the entropy is going up or going down.

However, in general if the products have a larger number of mole (molecules) than the reactants then the entropy is likely to increase. Additionally, if products are in phases of higher entropy than the reactants than the reaction is likely to have a higher entropy. For example

$$2Fe(s)+3O_2(g)\rightarrow 2Fe_2O_3(s) \qquad \Delta Sr<0$$

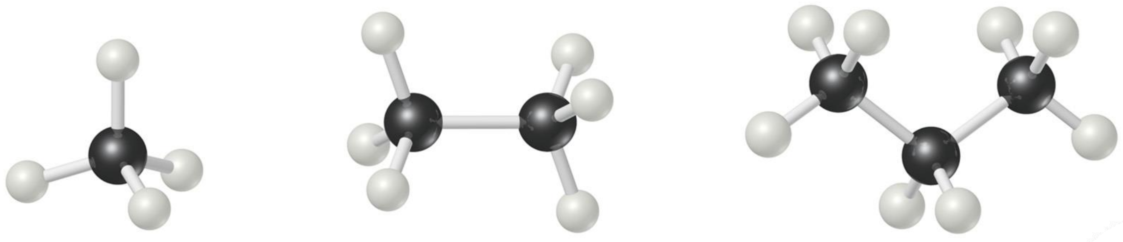
The change in entropy for this reaction will be negative. This because the reactants have both a solid and a gaseous species while the product is simply a solid compound.

Entropy usually increases when a pure liquid or solid dissolves in a solvent. Substances dissolve with either gain or loss of enthalpy



4- Composition (chemistry)

Larger, more complex molecules have higher standard molar entropy values than smaller or simpler molecules. There are more possible arrangements of atoms in space for larger, more complex molecules, increasing the number of possible microstates.



Methane, CH_4 $S° = 186.3\ \text{J mol}^{-1}\ \text{K}^{-1}$ Ethane, C_2H_6 $S° = 229.6\ \text{J mol}^{-1}\ \text{K}^{-1}$ Propane, C_3H_8 $S° = 270.3\ \text{J mol}^{-1}\ \text{K}^{-1}$

5- The calculating of ΔS by depended on thermodynamic process

Now consider gas-phase processes. What if the temperature were constant but the pressure or the volume changed reversibly?

1) Non-specific process

$$\Delta S = C_V \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1} \qquad \text{-----(1)}$$

2) Isothermal process (a thermodynamic process at constant Temperature)

$$\Delta S = R \ln\frac{V_2}{V_1} \qquad \text{...........(1)}$$

$$\Delta S = R \ln\frac{P_2}{P_1} \qquad \text{...........(2)}$$

3) Isochoric process (a thermodynamic process at constant volume)

$$\Delta S = C_V \ln\frac{T_2}{T_1} \qquad \text{.................(1)}$$

$$C_V = nC_{V,m} \qquad \text{....................(2)}$$

$$\Delta S = nC_{V,m} \ln\frac{T_2}{T_1} \qquad \text{...........(3)}$$

4) Isobaric process (a thermodynamic process at constant pressure)

$$\Delta S = C_p \ln\frac{T_2}{T_1} \quad ....(1)$$

$$C_P = nC_{p,m} \quad ....(2)$$

$$\Delta S = nC_{p,m} \ln\frac{T_2}{T_1} \quad ....(3)$$

note/ ($C_{p,m} = C_{v,m} + R$)

4- Reversible and adiabatic process (at constant heat)

$$\Delta S = \frac{q}{T} \quad ....(1)$$

$$when \quad q = 0 \quad ....(2)$$

$$So \quad \Delta S = 0 \quad ....(3)$$

Q) Calculate Δ*S* (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{v,m}$ =5/2 *R*, is changed from 25°C and 1.5 atm to 135°C and 7 atm. How do you rationalize the sign of Δ*S*?

$$\Delta S = C_V \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

$$\Delta S = nC_{V,m} \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

$$\Delta S = 2mol \times \frac{5}{2} \times 8.314\ln\frac{(135+273)K}{(25+273)K} + 2mol \times 8.314\ln\frac{1.5atm}{7atm}$$

$$\Delta S = -12.55J$$

If ΔS < 0 the order increases.

EX// Consider a Sample of ideal gas initially in volume V at temperature T and pressure p. does ΔS_{sys} **increase**, **decrease**, or **stay** the same in the following process? Explain.

(a) The gas expands isothermally

(b) The pressure increased at constant temperature

(c) The gas is heated at constant pressure

EX) which system has the higher absolute entropy? Explain.

(a) 1g **solid** Au at 1064K or 1 g **liquid** Au At 1064K?

The liquid will always have higher absolute entropy than the solid at the same temperature.

(b) 1 mole **CO** at 25°C and 1 atm or 1mole of **CO_2** at 25°C and 1 atm.

1 mole CO_2 – at the same temperature and pressure, the trimolecular has more energy states available to it; therefore gaseous CO_2 has higher than gaseous CO.

(c) 1mole Ar at 25°C and **1 atm** or 1 mole Ar at 25°C and **0.01 atm**

1 mole Ar at 25°C and 0.01 atm- both samples at the same temperature, So the gas with lower pressure will have the larger volume and hence the larger entropy.

<u>H.W/</u> Which the substance in each following pairs would have the greater entropy? Explain.

(**a**) At 75°C and 1 bar: 1mol H_2O (l) or 1 mol H_2O (g)

(**b**) At 5°C and 1 bar: 50g Cl_2 or 0.8 mol Cl_2 (g)

(**c**) 1 mol Br_2 (l, 1 bar, 8°C) or 1 mol Br_2 (s, 1 bar, -8°C)

(**d**) 0.312 mol SO_2 (g, 0.110 bar, 32.5 °C) or 0.284 mol (g, 15 bar, 22.3°C).

EX// predict whether the entropy change is positive or negative for each the following reaction at 298 K:

$(a)\quad O_{(g)} + O_{2(g)} \longrightarrow O_{3(g)}$

(b) $\mathrm{NH_4}Cl_{(S)} \longrightarrow NH_{3(g)} + HCl_{(g)}$

$(c)\quad \mathrm{H}_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$

S^0[(H-H) = 131, (Cl-Cl) = 223, (H-Cl) =223] J/K.mol

Sol//

$$(a)\quad O_{(g)} + O_{2(g)} \longrightarrow O_{3(g)}$$

The products have a lesser number of mole (molecules) than the reactants then the entropy is likely to decrease.

$$\text{(b)}\quad \mathrm{NH_4}Cl_{(S)} \longrightarrow NH_{3(g)} + HCl_{(g)}$$

The products have a larger number of mole (molecules) than the reactants then the entropy is likely to increase. Additionally, the products are in phase (gas) of higher entropy than the reactants (solid) than the reaction is likely to have a higher entropy.

$$(c)\quad \mathrm{H}_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$$

The products and reactants in a same phase (gas) and have a same number of moles. So the sign of change in entropy can be calculate form molar bonding entropy as the following:

$$\Delta_r S^{\Theta} = \sum n_p S_m^{\Theta}(products) - \sum n_r S_m^{\Theta}(\text{reactans})$$

$$\Delta_r S^{\Theta} = 2\ mol\ \ (186.79)\ -\left[1\ mol\ \ (131)\ +\ 1\ mol\ \ (223)\right]$$

$$\Delta_r S^{\Theta} = 19.58\text{J/K}$$

Entropy of system, surrounding and universe

To generalize:

The total entropy of the universe **increases** whenever an irreversible process occurs. The total entropy of the universe is **unchanged** whenever a reversible process occurs.

Since all real processes are **irreversible**, the entropy of the universe **continually increases**. If entropy **decreases** in a system due to work being done on it, a greater **increase** in entropy occurs outside the system.

Irreversible Processes examples

1. A battery discharges through a resistor, releasing energy. The reverse process will not occur.
2. Two gases, initially in separated adjoining chambers, will mix uniformly.
3. A free expansion of gas (in Gay-Lussac-Joule experiment)
4. Heat flows from a high temperature body to a low temperature reservoir in the absence of other effect

Entropy of universal ΔS_{univ}

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \quad ....(1)$$

At irreversible and isothermal process:

$$\Delta S_{univ} \geq 0 \quad ....(2)$$

But at reversible and isothermal process:

$$\Delta S_{univ} = 0 \quad ....(3)$$

$$\Delta S_{sys} = -\Delta S_{surr} \quad ....(4)$$

When $\Delta S_{sys} = \dfrac{q}{T}$ ....(5)

Therefore

$$\Delta S_{surr} = -\frac{q}{T} \quad ....(6)$$

Calculate ΔS_{sys}, ΔS_{surr}, and ΔS_{univ}, when the volume of a sample of argon gas (39.95 g/mol) of mass 21 g at 298 K and 1.5 bar increase from 2.3 dm^3 to 4.60 dm^3 in (a) an isothermal reversible expansion (b) an is isothermal irreversible expansion against $P_{ex} = 0$, and (c) an adiabatic reversible expansion.

(a) $$\Delta S_{sys} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{sys} = \frac{21g}{39.95g\ /\ mol} \times 8.314 mol \ln \frac{4.6}{2.3} = 3.029 J\ /\ K$$

$$\Delta S_{univ} = 0 \quad \text{(reversible process)}$$

$$\Delta S_{surr} = -\Delta S_{sys} = -3.029 J\ /\ K$$

(b) $$\Delta S_{sys} = 3.029 J\ /\ K \quad \text{(S is state function)}$$

$$\Delta S_{surr} = -\frac{q_{surr}}{T} = -\frac{w_{surr}}{T} = -\left(\frac{-P\,\Delta V}{T}\right) = 0 \quad \text{(external pressure = 0)}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 3.029 + 0 = 3.029 J\ /\ K$$

(c) $$\Delta S_{sys} = 0 \quad \text{(reverisble adiabatic process)}$$

$$\Delta S_{surr} = 0$$

$$\Delta S_{univ} = 0$$

H.W// 1.00 mol of perfect gas molecules at 27°C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in two ways: (a) reversibly, and (b) against a constant external pressure of 1.00 atm. Calculate ΔS_{sys}, ΔS_{surr}, and ΔS_{univ}.

H.W// 2 mol helium is expanded adiabatically and irreversibly at a constant external pressure of 1 atm from a volume of 5 L and temperature of 273.15 K to 25 L. Calculate ΔS_{sys}, ΔS_{surr}, and ΔS_{univ}.

EX// one mole of an ideal gas at 298 K expands isothermally from 1.0 to 2.0 L (a) reversibly and (b) against a constant external pressure of 12.2 atm. calculate ΔS_{sys}, ΔS_{surr}, and ΔS_{univ} in both cases.

$$\text{(a)}\quad \Delta S_{sys} = nR\ln\frac{V_2}{V_1}$$

$$\Delta S_{sys} = 1mol \times 8.314mol\ln\frac{2}{1} = 5.76J/K$$

$$\Delta S_{univ} = 0 \quad \text{(reversible process)}$$

$$\Delta S_{surr} = -\Delta S_{sys} = -5.76J/K$$

$$\text{(b)}\quad \Delta S_{sys} = 5.76J/K \quad \text{(S is state function)}$$

$$\Delta S_{surr} = -\frac{q_{surr}}{T} = -\frac{w_{surr}}{T} = -\left(\frac{-P\Delta V}{T}\right)$$

$$\Delta S_{surr} = \frac{12.2atm \times \frac{101325pa}{1atm}(2-1)L \times \frac{1m^3}{1000L}}{298K} = 4.148J/K$$

$$\Delta S_{univ} = \Delta S_{sys} - \Delta S_{surr} = -5.76 + 4.148 = -1.612J/K$$

EX// 1 g sample of water (g) at 100°C has a volume of 1.7L. It is isothermally compressed by an external pressure of 2.00 atm until it reaches a volume of 0.85L. Calculate ΔS_{sys}, ΔS_{surr}, and $\Delta S_{univ.}$

$$\Delta S_{sys} = nR\ln\frac{V_2}{V_1}$$

$$\Delta S_{sys} = \frac{1g}{18g/mol} \times 8.314mol\ln\frac{0.85}{1.7} = -0.32J/K$$

$$\Delta S_{surr} = -\frac{q_{surr}}{T} = -\frac{w_{surr}}{T} = -\left(\frac{-P\Delta V}{T}\right)$$

$$\Delta S_{surr} = \frac{2atm \times \frac{101325pa}{1atm}(0.85-1.7)L \times \frac{1m^3}{1000L}}{(100°C + 273)K} = -0.46J/K$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = -0.32 + (-0.46) = -0.76J/K$$

Consider the following reaction

$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(liq)$

$\Delta S^o_{sys} = -326.9$ J/K

$\Delta S^o_{surr} = +1917$ J/K

$\Delta S^o_{universe} = \Delta S^o_{sys} + \Delta S^o_{surr} = +1590.$ J/K

The entropy of the universe is increasing, so the reaction is product-favored.

Calculating ΔS for a Reaction

For a given reaction, the overall entropy change is equal to the difference between the algebraic sum of molar entropies of products and the algebraic sum of enthalpies of formation of reactants.

$$\Delta_r S^{\Theta} = \sum n_p S_m^{\Theta}(products) - \sum n_r S_m^{\Theta}(\text{reactans})$$

Where $\mathbf{n_p}$ and $\mathbf{n_r}$ are stoichiometric numbers

EX/ Consider the following reaction

$H_2(g) \quad + \quad 1/2O_2(g) \longrightarrow H_2O\ (l)$

S^o [(H_2O) = 69.9, (H_2) = 130.7, and (O_2) = 205.3] J/K•mol. Calculate $\Delta_r S^o$

Sol/

$$\Delta_r S^{\Theta} = \sum n_p S_m^{\Theta}(products) - \sum n_r S_m^{\Theta}(\text{reactans})$$

$$\Delta_r S^{\Theta} = 1\ mol\ \ (69.9)\ - \left[1\ mol\ \ (130.7)\ +\ \frac{1}{2}\ mol\ \ (205.3)\right]$$

ΔS^o = -163.45 J/K

Note that there is a decrease in S because **1.5 mol** of **gas** give **1 mol** of **liquid**.

Standard or absolute entropies:

The degree of dispersal of matter and energy changes when a substance **freezes** or **boils** as a result of changes in the **order** with which the molecules pack together and the extent to which the energy is **localized** or **dispersed**. Therefore, we should expect the transition to be accompanied by a change in **entropy**.

1- At heating from 0 K to T_m (**melting** temperature)

$$\Delta S^{\Theta}_{fus} = \int_0^{T_m} \frac{C_{P(solid)}}{T} dT = C_{p(solid)} \ln \frac{T_2}{T_1}$$

2- at melting at T_m

$$\Delta S^{\Theta}_{fus} = \frac{\Delta H_{fus}}{T_m}$$

3-at heating from T_m to T_b

$$\Delta S^{\Theta}_{vap} = \int_0^{T_m} \frac{C_{P(liquid)}}{T} dT = C_{p(liquid)} \ln \frac{T_2}{T_1}$$

4- at vaporization at T_m

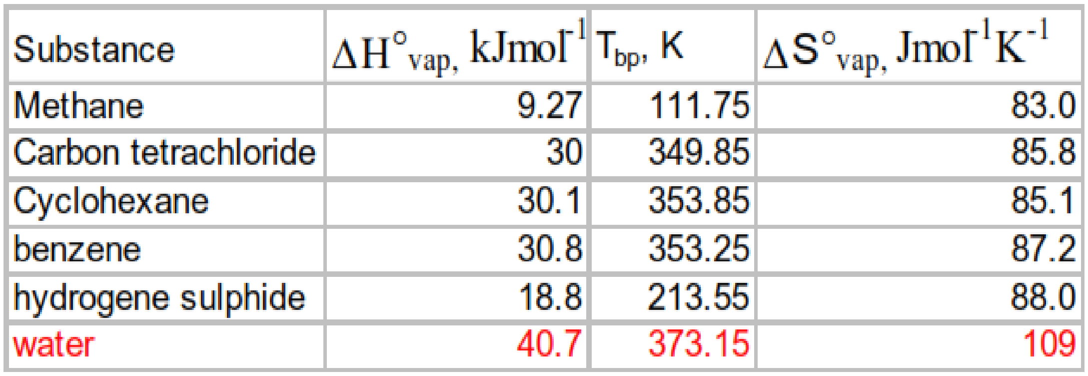
$$\Delta S^{\Theta}_{vap} = \frac{\Delta H_{vap}}{T_m}$$

Trouton’s rule

At their **boiling points**, most **organic** compounds have a **similar** entropy of vaporization: ΔS_{vap} (T_b) = **85 – 90** J/molK

These rule in applied on the liquid which don’t have **a hydrogen bond** that caused the **deviation** about the 85 J $K^{-1}mol^{-1}$ (exception: **strongly polar** or **H-bonding** compounds such as water, ethanol, etc.).

An example is **water**, where the large entropy of vaporization reflects the presence of structure arising from hydrogen-bonding in the liquid. Hydrogen bonds **tend to organize** the molecules in the liquid.



Substance	ΔH^{o}_{vap}, $kJmol^{-1}$	T_{bp}, K	ΔS^{o}_{vap}, $Jmol^{-1}K^{-1}$
Methane	9.27	111.75	83.0
Carbon tetrachloride	30	349.85	85.8
Cyclohexane	30.1	353.85	85.1
benzene	30.8	353.25	87.2
hydrogene sulphide	18.8	213.55	88.0
water	40.7	373.15	109

Nonassociated (ideal) liquids, $\Delta H_{vap}/T_{b.p.} \sim 88$ J/mol

Carbon tetrachloride, Benzene, Cyclohexane

Associated liquids, $\Delta H_{vap}/T_{b.p.} > 88$ J/mol

Water (109), Methanol (112), Ammonia (97)

Association in the vapor state, $DH_{vap}/T_{b.p.} < 88$ J/mol

Acetic acid (62)

Hydrogen fluoride (26)

5- **Heating** or **cooling** of matter

$$\Delta S^{\Theta} = m.C \ln \frac{T_2}{T_1}$$

Where **m** is the matter mass (g, Kg), and C is the **specific heat** (J/g.K, kJ/kg. K)

EX// Calculate entropy change if 500g of water at 30^0 C is heated to 80^0C at 1 bar pressure. The specific heat of water is 4.2kJ/kg-K.

$$\Delta S^{\Theta} = m.C \ln \frac{T_2}{T_1}$$

$$\Delta S^{\Theta} = 500g \times \frac{1kg}{1000g} \times 4.18 \frac{kJ}{kg.K} \ln \frac{(80℃ + 273)K}{(30℃ + 273)K}$$

$$\Delta S^{\Theta} = 0.076 kJ/K = 76 J/K$$

EX/ Calculate the entropy change for the following constant pressure process

H_2O (ice, 100g, -10°C, 1 bar) → H_2O (liquid, 100g, 10°C, 1 bar)

The enthalpy of fusion for ice is $\Delta_{fus}H° = 6.01$ kJ mol^{-1} at 0°C, and heat capacities as C_P (ice) = 37.12 J mol^{-1} K^{-1} and C_p (liquid) = 75.3 J mol^{-1} K^{-1}.

Solve

1- Heating of ice from -10°C to 0°C

$$\Delta S_1 = C_{p(ice)} \ln\frac{T_2}{T_1} = nC_{p,m} \ln\frac{T_2}{T_1}$$

$$= \frac{100g}{18g.mol^{-1}} \times 37.12 \ln\frac{273+0℃}{273+(-10℃)} = 7.69 J.K^{-1}$$

2- Fusion of ice at 0°C

$$\Delta S_2 = \frac{\Delta H_{fus}}{T_m}$$

$$= \frac{100g}{18g.mol^{-1}} \times \frac{6.01\times1000J.mol^{-1}}{273K} = 122.18 J.K^{-1}$$

3- Heating of ice from 0°C to 10°C

$$\Delta S_3 = C_{p(liquid)} \ln\frac{T_2}{T_1} = nC_{p,m(liquid)} \ln\frac{T_2}{T_1}$$

$$= \frac{100g}{18g.mol^{-1}} \times 75.3 \ln\frac{273+10℃}{273+0℃} = 15.03 J.K^{-1}$$

The total entropy change the sum of the individual steps:

$$\Delta S_{total} = \Delta S_1 + \Delta S_2 + \Delta S_3 = 7.69 + 122.18 + 15.03 = 144.9 JK^{-1}$$

H.W// suppose 2.00 moles of supercooled water turning into ice

H_2O (liquid, 10°C, 1 bar) → H_2O (ice, -10°C, 1 bar)

The enthalpy of freezing for water is $\Delta_{fre}H° = -6.01$ kJ mol^{-1} at 0°C, and heat capacities as C_P (ice) = 37.12 J mol^{-1} K^{-1} and C_p (liquid) = 75.3 J mol^{-1} K^{-1}.

(Sol. -41.2 J K^{-1})

Entropy change with variation in temperature

The entropy values vary with variation in temperature. From the Kirchhoff's Law we can calculate the entropy change at any temperature if its value at a specific temperature is known. We can derive the Kirchhoff's equation as

$$\Delta S^{\Theta}_{heating} = \int_{T_1}^{T_2} \frac{n\bar{C}_{P,m}}{T} dT$$

$$\bar{C}_{P,m} = \alpha + \beta T + \gamma T^2$$

$$\Delta S^{\Theta}_{heating} = \int_{T_1}^{T_2} \frac{n\bar{C}_{P,m}}{T} dT$$

$$\Delta S^{\Theta}_{heating} = \int_{T_1}^{T_2} n\left(\frac{\alpha + \beta T + \gamma T^2}{T}\right) dT$$

$$\Delta S^{\Theta}_{heating} = \int_{T_1}^{T_2} n\left(\frac{\alpha}{T} + \beta + \gamma T\right) dT$$

$$\Delta S^{\Theta}_{heating} = n\left[\alpha \ln\frac{T_2}{T_1} + \beta(T_2 - T_1) + \gamma\left(\frac{T_2^2}{2} - \frac{T_1^2}{2}\right)\right]$$

And the heating of reaction can calculate from the relation

$$\Delta C_p = \sum \upsilon\, C_p(\text{products}) - \sum \upsilon\, C_p(\text{reactants})$$

υ is the stoichiometric coefficients of chemical reaction
Where α, β, and γ are numerical value.

Heating for reaction, we can use Kirchhoff's Law

$$\Delta S_{T_2} = \Delta S_{T_1} + \int_{T_1}^{T_2} \left[\frac{\Delta C_p}{T}\right] dT$$

EX// the molar capacity of solid gold is given by the relation

$$\bar{C}_{P,m} = (25.69 + 7.32\times10^{-4}T + 4.58\times10^{-6}T^{2} / k)JK^{-1}mol^{-1}$$

Calculate the entropy change for heating 2.50 moles of gold from 22.0°C to 1000°C at constant pressure.

T_1 = 22°C +273= 295 K, T_2 = 1000°C + 273 = 373 K

When $\bar{C}_{P,m} = \alpha + \beta T + \gamma T^{2}$

So α = 25.69, β = 7.32 × 10^{-4}, and γ = 4.58 × 10^{-6}

$$\Delta S^{\Theta}_{heating} = \int_{T_1}^{T_2} \frac{n\bar{C}_{P,m}}{T}dT$$

$$= \int_{T_1}^{T_2} n(\frac{\alpha - \beta T + \gamma T^{2}}{T})dT$$

$$= \int_{T_1}^{T_2} n(\frac{\alpha}{T} - \beta + \gamma T)dT$$

$$= n[\alpha \ln\frac{T_2}{T_1} - \beta(T_2 - T_1) + \gamma(\frac{T_2^{2}}{2} - \frac{T_1^{2}}{2})]$$

$$= [\alpha \ln\frac{1273}{295} - \beta(1273 - 295) + \gamma(\frac{(1273)^{2}}{2} - \frac{(295)^{2}}{2})]$$

$$= 2.5mol[1.46\alpha - 978\beta + 723239.5\gamma]$$

$$= 2.5mol[1.462(25.69) - 978(7.32\times10^{-4}) + 723239.5(4.58\times10^{-6})]$$

$$= 2.5mol[37.558 - 0.715 + 3.312]$$

$$\Delta S^{\Theta}_{heating} = 100.387 J/K$$

H.W// the molar heat capacity of water is represented by

$$\bar{C}_{P,m} = (30.54 + 0.01029T / k)JK^{-1}mol^{-1}$$

a) Find ΔS for heating 2 moles of water vapor at a constant pressure from 100°C to 500°C. b) Find q at 500°C

EX// Calculate ΔS for the following reaction at 1450K and 1 bar;

$$\tfrac{1}{2}\,H_2(g) + \tfrac{1}{2}\,Cl_2(g) \rightarrow HCl(g)$$

Given that ΔH° = (HCl,g) = -92.3 kJ/mol at 298.15K and that;

$$C^0_{p,m}(\mathrm{H}_2, g) = \left(29.064 - 0.8363 \text{ x } 10^{-3}\,\frac{T}{\mathrm{K}} + 20.111 \text{ x } 10^{-7}\,\frac{T^2}{\mathrm{K}^2}\right)\ \mathrm{JK^{-1}mol^{-1}}$$

$$C^0_{p,m}(\mathrm{Cl}_2, g) = \left(31.695 + 10.143 \text{ x } 10^{-3}\,\frac{T}{\mathrm{K}} - 40.373 \text{ x } 10^{-7}\,\frac{T^2}{\mathrm{K}^2}\right)\ \mathrm{JK^{-1}mol^{-1}}$$

$$C^0_{p,m}(\mathrm{HCl}, g) = \left(28.165 + 1.809 \text{ x } 10^{-3}\,\frac{T}{\mathrm{K}} + 15.464 \text{ x } 10^{-7}\,\frac{T^2}{\mathrm{K}^2}\right)\ \mathrm{JK^{-1}mol^{-1}}$$

Solution

$$\Delta S_{T_2} = \Delta S_{T_1} + \int_{T_1}^{T_2} \left[\frac{\Delta C_p}{T}\right] dT$$

$$\Delta S_{T_1} = \frac{\Delta H^\circ}{T} = \frac{-92.3 \times 1000 J.mol^{-1}}{298K} = -309.7 J.mol^{-1}K^{-1}$$

$$\Delta_r C^0_{p,m}(T) = \begin{bmatrix} \left(28.165 + 1.809 \text{ x } 10^{-3}\,\frac{T}{\mathrm{K}} + 15.464 \text{ x } 10^{-7}\,\frac{T^2}{\mathrm{K}^2}\right) \\ -\frac{1}{2}\left(29.064 - 0.8363 \text{ x } 10^{-3}\,\frac{T}{\mathrm{K}} + 20.111 \text{ x } 10^{-7}\,\frac{T^2}{\mathrm{K}^2}\right) \\ -\frac{1}{2}\left(31.695 + 10.143 \text{ x } 10^{-3}\,\frac{T}{\mathrm{K}} - 40.373 \text{ x } 10^{-7}\,\frac{T^2}{\mathrm{K}^2}\right) \end{bmatrix}$$

$$\Delta_r C^0_{p,m}(T) = \left[\left(-2.215 - 2.844 \text{ x } 10^{-3}\,\frac{T}{\mathrm{K}} + 25.595 \text{ x } 10^{-7}\,\frac{T^2}{\mathrm{K}^2}\right)\right]\ \mathrm{J\ K^{-1}mol^{-1}}$$

$$\Delta S_{T_2} = \Delta S_{T_1} + \int_{298.15}^{1450} \left(-\frac{\alpha}{T} - \beta + \gamma T\right) \mathrm{d}T$$

$$= \Delta S_{T_1} + [\alpha \ln\frac{T_2}{T_1} - \beta(T_2 - T_1) + \gamma(\frac{T_2^{\ 2}}{2} - \frac{T_1^{\ 2}}{2})]$$

$$= \Delta S_{T_1} + [\alpha \ln\frac{1450}{298} - \beta(1450 - 298) + \gamma(\frac{(1450)^2}{2} - \frac{(298)^2}{2})]$$

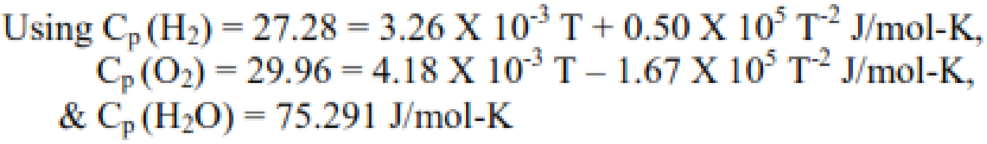
$$=\Delta S_{T_1}+[0.458\alpha-1152\beta+1006848\gamma]$$

$$=-309.7+[0.458(-2.215)-1152(2.844\times10^{-3})+1006848(25.595\times10^{-7})]$$

$$=-309.7+(-1.703)=311.4J.mol^{-1}K^{-1}$$

H.W// for reaction 2 $H_{2\,(g)}$ + $O_{2\,(g)}$ → $2H_2O_{(g)}$ $\Delta_rH°$= -484 kJ mol^{-1} at 298K

Calculate ΔS for heating at 1000 K



Using $C_p(H_2) = 27.28 = 3.26 \text{ X } 10^{-3}\text{ T} + 0.50 \text{ X } 10^{5}\text{ T}^{-2}$ J/mol-K,

$C_p(O_2) = 29.96 = 4.18 \text{ X } 10^{-3}\text{ T} - 1.67 \text{ X } 10^{5}\text{ T}^{-2}$ J/mol-K,

& $C_p(H_2O) = 75.291$ J/mol-K

Combined the first and second's law of thermodynamics

In **thermodynamics**, the combined law of thermodynamics, also called the **Gibbs fundamental equation**, is a mathematical summation of the first law of thermodynamics and the second law of thermodynamics subsumed into a single concise mathematical statement

Four quantities called "**thermodynamic potentials**" are useful in the chemical thermodynamics of reactions and non-cyclic processes. They are

(**1**) Internal energy (**U**), (**2**) the enthalpy (**H**), (**3**) the Helmholtz free energy (**A**) and (**4**) the Gibbs free energy (**G**).

1- The internal energy

$\because dU = dq + dw$ -----(1) 1st thermodynamics law

$^{and} \because TdS \geq dq$ -----(2) 2nd thermodynamics law

by subsituting eq. (2) in eq. (1)

$\therefore dU = TdS + dw$ -----(3)

$\because dw = -PdV$ -----(4)

$dU = TdS - PdV$ -----(5)

2-the enthalpy

the enthalpy was defined by

$H = U + PV$ ------(1)

by differential:

$dH = dU + PdV + VdP$ ------(2)

and $dU = TdS - PdV$ ------(3)

$\therefore dH = TdS - PdV + PdV + VdP$ ------(4)

$\therefore dH = TdS + VdP$ ------(5)

3- Helmholtz Energy (A)

The concept of Helmholtz free energy was developed by Hermann von Helmholtz, a in a lecture called "On the thermodynamics of chemical processes". It is usually denoted by the letter A (from the German "Arbeit" or work).

the **Helmholtz free energy** is a thermodynamic potential that measures the "useful" work obtainable from a closed thermodynamic system at a constant temperature and volume.

While Gibbs free energy is most commonly used as a measure of thermodynamic potential, especially in the field of chemistry, it is inconvenient for some applications that do not occur at constant pressure. For example, in explosives research.

the Helmholtz free energy was defined by

$A = U - TS$ ------(1)

by differential:

$dA = dU - TdS - SdT$ ------(2)

and $dU = TdS - PdV$ ------(3)

$\therefore dA = TdS - PdV - TdS - SdT$ ------(4)

$\therefore dA = -SdT - PdV$ ------(5)

(4) The Gibbs free energy (G).

In thermodynamics, the Gibbs free energy (IUPAC recommended name: Gibbs energy or Gibbs function; also known as free enthalpy.

To distinguish it from Helmholtz free energy is a thermodynamic potential that can be used to calculate the maximum of reversible work that may be performed by a thermodynamic system at a constant temperature and pressure (isothermal, isobaric).

It is a thermodynamic property that was defined in 1876 by Josiah Willard Gibbs to predict whether a process will occur spontaneously at constant temperature and pressure.

ΔG is negative for spontaneous processes, positive for nonspontaneous processes and zero for processes at equilibrium.

the Gibbs Free Energy was defined by

$$G = H - TS \qquad \text{------}(1)$$

by differential:

$$dG = dH - TdS - SdT \qquad \text{------}(2)$$

and $dH = TdS + VdP \qquad \text{------}(3)$

$$\therefore dG = TdS + VdP - TdS - SdT \qquad \text{------}(4)$$

$$\therefore dG = -SdT + VdP \qquad \text{------}(5)$$

Natural Variable Equations and Partial Derivatives

Now that we have defined all independent energy quantities in terms of p, V, T, and S, we summarize them in terms of their natural variables:

$dU = TdS - PdV$ Internal energy U(S,V)

$dH = TdS + VdP$ Enthalpy H(S,P)

$dA = -SdT - PdV$ Helmholtz Energy A(T,V)

$dG = -SdT + VdP$ Gibbs free energy G(T,P)

For example, consider (2) **the internal energy**, U. Its natural variables are **S** and **V**; that is, the internal energy is a function of S and V:

$$U = U(S,V) \quad \text{------}(1)$$

$$dU = \left(\frac{dU}{dS}\right)_V dS + \left(\frac{dU}{dV}\right)_S dV \quad \text{------}(2)$$

from the natural variable equation, we know that

$$dU = TdS - PdV \quad \text{-------}(3)$$

compare two equation (2) and (3)

$$\left(\frac{dU}{dS}\right)_V dS = TdS \qquad \text{------}(4)$$

$$\left(\frac{dU}{dV}\right)_S dV = -PdV \quad \text{------}(5)$$

Then the partial derivatives in terms of U are equal to:

$$\left(\frac{dU}{dS}\right)_V = T \qquad \text{------}(6)$$

$$\left(\frac{dU}{dV}\right)_S = -P \quad \text{------}(7)$$

Finally, in many derivations, partial derivatives like these will show up. Equations like 6 and 7 allow us to substitute simple state variables for more complicated partial derivatives.

EX) The partial derivatives of enthalpy (H)

The partial derivatives of Helmholtz free energy (A)

$A = A(T, V)$ ------(1)

$dA = \left(\frac{dA}{dT}\right)_V dT + \left(\frac{dA}{dV}\right)_T dV$ ------(2)

from the natural variable equation, we know that

$dA = -SdT - PdV$ -------(3)

compare two equation (2) and (3)

$\left(\frac{dA}{dT}\right)_V dT = -SdT$ ------(4)

$\left(\frac{dA}{dV}\right)_T dV = -PdV$ ------(5)

$Then$ the partial derivatives in terms of U are equal to:

$\left(\frac{dA}{dT}\right)_V = -S$ ------(6)

$\left(\frac{dA}{dV}\right)_T = -P$ ------(7)

The partial derivatives of Gibbs free energy (G)

$G = G(T, P)$ ------(1)

$$dG = \left(\frac{dG}{dT}\right)_P dT + \left(\frac{dG}{dP}\right)_T dP \quad \text{------(2)}$$

from the natural variable equation, we know that

$dG = -SdT + VdP$ -------(3)

compare two equation (2) and (3)

$$\left(\frac{dG}{dT}\right)_p dT = -SdT \quad \text{------(4)}$$

$$\left(\frac{dG}{dP}\right)_T dP = VdP \quad \text{------(5)}$$

Then the partial derivatives in terms of U are equal to:

$$\left(\frac{dG}{dT}\right)_P = -S \quad \text{------(6)}$$

$$\left(\frac{dG}{dP}\right)_T = V \quad \text{------(7)}$$

Summary of partial derivatives

Internal Energy (U)	Enthalpy (H)	Helmholtz Free Energy (A)	Gibbs Free Energy (G)
$\left(\frac{dU}{dS}\right)_V = T$ $\left(\frac{dU}{dV}\right)_S = -P$	$\left(\frac{dH}{dT}\right)_P = T$ $\left(\frac{dH}{dP}\right)_S = V$	$\left(\frac{dA}{dT}\right)_V = -S$ $\left(\frac{dA}{dV}\right)_T = -P$	$\left(\frac{dG}{dT}\right)_P = -S$ $\left(\frac{dG}{dP}\right)_T = V$