Lecture 11

Combined First and Second Law equations

First law for a closed system in the differential form for an internally reversible process

$$(đQ)_{\substack{int \\ rev}} - (đW)_{\substack{int \\ rev}} = dU$$

But

$$(đQ)_{\substack{int \\ rev}} = TdS$$

$$(đW)_{\substack{int \\ rev}} = pdV$$

Therefore

$$TdS = dU + pdV \ \ kJ$$

Or

$$Tds = du + pdv \ \ kJ/kg \ \text{.......................(1)}$$

$h = u + pv$

$dh = du + pdv + vdp$

but

$du + pdv = Tds$ according to eq (1)

$Tds = dh - vdp$ $\ \ kJ/kg$.....................................(2)

Eq (1) and (2) are known as combined first and second law equations.

Relations for differential changes in entropy

Expressions for ds can be obtained by dividing eq 1 and 2 by T

$$ds = \frac{du}{T} + \frac{pdv}{T} \text{................................(3)}$$

And

$$ds = \frac{dh}{T} + \frac{vdp}{T} \text{................................(4)}$$

Entropy changes for solids and liquids

Solids and liquids can be approximated as incompressible substances since their specific volume remains nearly a constant during a process. Therfore dv≈0 for solids and liquids.

Eq (3) now becomes

$$ds = \frac{du}{T} = \frac{cdT}{T}$$

Integrating for a process 1-2

$$s_2 - s_1 = c \ ln\frac{T_2}{T_1} \quad kJ/kg$$

Where c is the average specific heat.

$$S_2 - S_1 = mc \, ln\frac{T_2}{T_1} \quad \text{kJ}$$

Entropy changes for ideal gas

For ideal gases du = c_vdT and pv = RT

Or p/T = R/v

Substituting these relations in eq (3) we get

$$ds = \frac{c_v dT}{T} + R\frac{dv}{V}$$

Integrating for a process 1 – 2 assuming constant specific heats

$$s_2 - s_1 = c_v \, ln\frac{T_2}{T_1} + R \, ln\frac{v_2}{v_1} \quad \text{kJ/kg}$$

$$\boldsymbol{S_2 - S_1 = m \left(c_v \, ln\frac{T_2}{T_1} + R \, ln\frac{v_2}{v_1} \right) \quad \text{kJ}}$$

Now dh = c_pdT and and v/T = R/p

Substituting the above relations in eq (4) we get

$$ds = \frac{c_p dT}{T} - R\frac{dp}{p}$$

Integrating for a process 1 – 2 assuming constant specific heats

$$s_2 - s_1 = c_p \, ln\frac{T_2}{T_1} - R \, ln\frac{p_2}{p_1} \quad \text{kJ/kg}$$

$$S_2 - S_1 = m \left(c_p \, ln\frac{T_2}{T_1} - R \, ln\frac{p_2}{p_1} \right) \text{kJ}$$

Statistical Interpretation of Entropy

Even though a system is in macroscopic equilibrium, microscopically the particles making up the matter are in continuous motion. For any macroscopic equilibrium state of a system there will be a large number of possible microscopic states. The total number of possible microscopic states available to a system is called the thermodynamic probability, ω. The entropy of a system is related to ω by Boltzmann relation

S = k ln ω

Where k is the Boltzmann constant k = 1.3806 x 10^{-23} J/K

k = Universal gas constant / Avogadro number

Any process that increases the number of possible microscopic states of a system increases its entropy. As the number of microscopic states increases the randomness or the disorder of the system increases. Entropy is therefore a measure of randomness or disorder of the system.

Third Law of Thermodynamics

The molecules of a substance in solid phase continually oscillate, creating an uncertainty about their position. These oscillations fade as the temperature is decreased, and the molecules become motionless at absolute zero. This represents a state of ultimate molecular order (and minimum energy).

Therefore, the entropy of a pure crystalline substance at absolute zero temperature is zero since there is no uncertainty about the state of the molecules at that instant. This statement is known as Nernst-Simon statement of the **third law of thermodynamics**.

The third law of thermodynamics provides an absolute reference point for the determination of entropy.

Fowler-Guggenheim statement of Third Law

It is impossible by any procedure, no matter how idealized, to reduce any condensed system to the absolute zero of temperature in a finite number of operations.