

Lecture 6

Uses of Entropy

Entropy – How to get that?

$$dU = dq + dw \text{ First law}$$

$$= dq_{\text{rev}} + dw_{\text{rev}}$$

$$dw_{\text{rev}} = -PdV$$

$$TdS = dq_{\text{rev}}$$

$$dU = TdS - PdV$$

For an ideal gas,

$$dU = nC_v dT$$

$$P = nRT/V$$

$$nC_v dT = TdS - (nRT/V) dV$$

$$dS = nC_v dT/T + nR dV/V$$

If C_v is constant for the temperature range,

$$\int_{1}^{2} dS = n C_v \int_{1}^{2} dT/T + nR \int_{1}^{2} dV/V$$

$$\Delta S = n C_v \ln T_2/T_1 + nR \ln V_2/V_1$$

In terms of P and T,

$$V_2 = RT_2/P_2; V_1 = RT_1/P_1$$

$$V_2/V_1 = RT_2/P_2 \cdot P_1/RT_1 = T_2 P_1/T_1 P_2$$

$$\Delta S = n C_v \ln T_2/T_1 + nR \ln T_2/T_1 - nR \ln P_2/P_1$$

$$\text{Since } V_2/V_1 = T_2 P_1/P_2 T_1$$

$$= n (C_v + R) \ln T_2/T_1 - nR \ln P_2/P_1$$

$$= n C_p \ln T_2/T_1 - nR \ln P_2/P_1$$

Entropy has units cal/deg which is referred as the entropy unit.

For an isothermal process,

$$\Delta S_T = nR \ln V_2/V_1 = -nR \ln P_2/P_1$$

For isochoric process,

$$\Delta S_V = nC_V \ln T_2/T_1$$

For isobaric process

$$\Delta S_p = nC_p \ln T_2/T_1$$

A relation can be obtained in terms of P and V also.

$$\Delta S = nC_v \ln T_2/T_1 + nR \ln V_2/V_1$$

$$T_2/T_1 = P_2V_2/P_1V_1$$

$$\begin{aligned} &= nC_v \ln P_2/P_1 + nC_v \ln V_2/V_1 + nR \ln V_2/V_1 \\ &= nC_v \ln P_2/P_1 + nC_p \ln V_2/V_1 \end{aligned}$$

Entropy change for a phase change

$$TdS = dU + PdV$$

At constant pressure,

$$TdS = d(U + PV) = dH$$

$$dS = dH/T$$

$$\Delta S = \Delta H/T$$

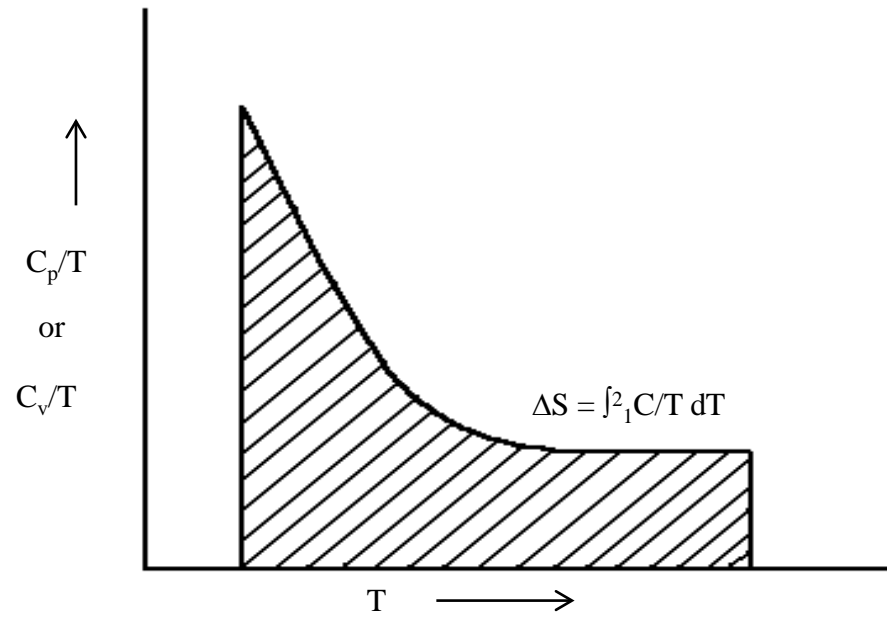
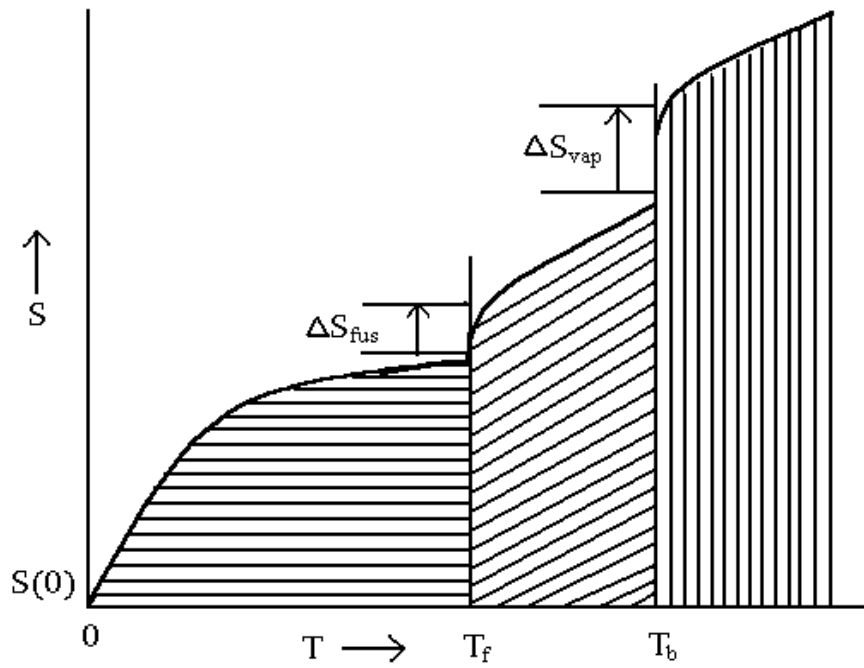
Depending on the process, $\Delta H = L_v, L_f$, etc.

Variation with temperature

Example

Let us say a solid is heated to melt and the liquid is made to boil.

$$S(T) = \boxed{S(0)} + \int_0^{T_0} (C_p(s) dT/T) + (\Delta_{fus} H/T_f) + \int_{T_b}^{T_f} (C_p(l) dT/T) + (\Delta_{eva} H/T_b) + \int_{T_b}^{T_f} C_p(g) dT/T$$



Entropy changes with specific processes

$\Delta S = \Delta H/T$. When ΔH is positive such as melting, ΔS is positive.

Standard molar entropy of vaporization of liquids is a constant of value, 85 J/K/mol. This is called the Trouton's rule.

With this rule, enthalpy of vaporization of liquids at their normal boiling points can be calculated. When liquids are associated, the entropies are generally larger.

Entropies of phase transitions (Table)

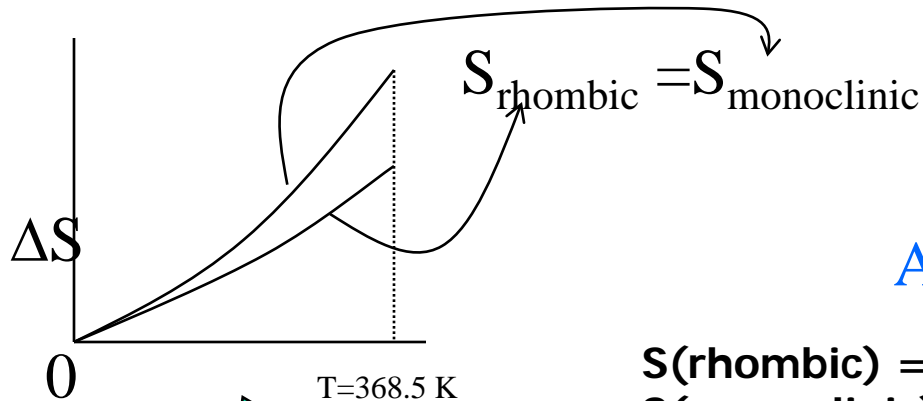
Entropies of phase transitions at 1 atm ($\Delta S_m/\text{JK}^{-1}\text{mol}^{-1}$)

System	Fusion	Evaporation
He	6.3	19.7
Ar	14.2	71.7
H ₂	8.4	44.4
N ₂	11.42	73.16
H ₂ O	22.0	109.0
NH ₃	28.9	97.21
CH ₃ OH	18.1	104
CH ₃ COOH	40.4	61.9

The Third Law of Thermodynamics

Orthorhombic to monoclinic

$$\Delta_{tr}S = \frac{401 \text{ J / mol}}{368.5 \text{ K}} = 1.09 \text{ J / K mol}$$



Assuming $\bar{S}_0^0 = 0$ $\bar{S}_T^0 - \bar{S}_0^0 = \int_0^T \frac{\bar{C}_P^0}{T} dT$

$S(\text{rhombic}) = S(0), \text{ rhombic} + 37 \text{ J/K mol}$
 $S(\text{monoclinic}) = S(0), \text{ monoclinic} + 38 \text{ J/K mol}$
 Difference is 1 J/K mol

$\Delta_{tr}S \rightarrow 0 \text{ as } T \rightarrow 0$

W. Nernst $\lim_{T \rightarrow 0} \Delta_r S = 0$

Max Planck

Entropy of pure element in perfect crystalline state is zero, at **Absolute zero**

$$dU = TdS - PdV \quad (1) \quad \textit{Fundamental equation}$$

Applicable to both reversible and irreversible.

$$U = f(S, V) \quad \text{why only these two?}$$

$$dU = (\partial U / \partial S)_V dS + (\partial U / \partial V)_S dV \quad (2)$$

Compare (1) and (2)

$$(\partial U / \partial S)_V = T \quad (3)$$

$$(\partial U / \partial V)_S = -P \quad (4)$$

Thermodynamics give unusual relations!

**Using
thermodynamic
equations**

$$\text{From (3), } (\partial U / \partial V \partial S) = (\partial T / \partial V)_S$$

$$\text{From (4), } (\partial U / \partial S \partial V) = -(\partial P / \partial S)_V$$

As dU is an exact differential,

$$(\partial T / \partial V)_S = -(\partial P / \partial S)_V$$

Maxwell's relation (1)

Examples of manipulations

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

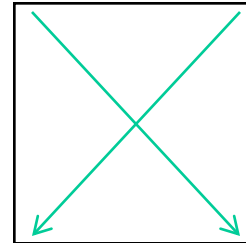
$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

$$\begin{aligned} H &= U + PV \\ A &= U - TS \\ G &= H - TS \end{aligned}$$

$U(S, V)$

$H(S, P)$



$G(T, P)$

$A(T, V)$

These are four fundamental relations of thermodynamics.

These are actually several ways of looking at the same relation,
 $dU = TdS - PdV$.

Each relation relates one thermodynamic function to two variables.

S and V are said to be natural variables of U ;

S and P for H ; T and V for A as well as T and P for G .

Maxwell's relations

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Function,

$df = g dx + h dy$ is exact if,
 $(\partial g / \partial y)_x = (\partial h / \partial x)_y$

$$(\partial T / \partial V)_S = -(\partial P / \partial S)_V$$

$$(\partial T / \partial P)_S = (\partial V / \partial S)_P$$

$$(\partial S / \partial V)_T = (\partial P / \partial T)_V$$

$$-(\partial S / \partial P)_T = (\partial V / \partial T)_P$$

The first two relations are for constant entropy, ie. adiabatic processes. Rate of change of temperature with volume and pressure are the quantities discussed. The latter two relations are for constant temperature, ie. isothermal processes. Entropy change as a function of volume and pressure can be related to changes in pressure and volume.

How can such relations be tested?

Thermodynamic equation of state

The ideal gas law and van der Waals equation are relations between P , V and T . These are based on some data and extrapolations and speculations on the molecular dimensions and interactions between molecules.

Is there a more generalised law describing equilibrium?

Thermodynamics gives one.

$dU = TdS - PdV$ is the condition of equilibrium.

Let us write,

$$(\partial U)_{\text{T}} = T(\partial S)_{\text{T}} - P(\partial V)_{\text{T}}$$

Divide by $(\partial V)_{\text{T}}$

$$(\partial U/\partial V)_{\text{T}} = T(\partial S/\partial V)_{\text{T}} - P$$

U and S are functions of T and V.

Thus, the above relation relates P with functions of T and V.

Therefore, this is an equation of state.

Using value of $(\partial S/\partial V)_T$ from Maxwell's relation $(\partial S/\partial V)_T = (\partial P/\partial T)_V$,

$$P = T(\partial P/\partial T)_V - (\partial U/\partial V)_T$$

Taking,

$$dH = TdS + VdP$$

$$(\partial H/\partial P)_T = T(\partial S/\partial P)_T + V$$

Using Maxwell relation, $-(\partial S/\partial P)_T = (\partial V/\partial T)_P$

$$V = T(\partial V/\partial T)_P + (\partial H/\partial P)_T$$

This equation expresses volume as a function of temperature and pressure.

These relations are applicable to any substance.