

# **Lecture 3**

## **Evaluation of Entropy**

If we wish to designate  $S$  by a proper name we can say of it that it is the *transformation content* of the body, in the same way that we say of the quantity  $U$  that it is the *heat and work content* of the body. However, since I think it is better to take the names of such quantities as these, which are important for science, from the ancient languages, so that they can be introduced without change into all the modern languages, I proposed to name the magnitude  $S$  the *entropy* of the body, from the Greek word  $\eta$  τροπή, a transformation. I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*, since both these quantities, which are to be known by these names, are so nearly related to each other in their physical significance that a certain similarity in their names seemed to me advantageous.

**Rudolf Clausius** 1865, *Annalen der Physik und Chemie*, **125**, 353-  
(1865).

Earlier paper: *Annalen der Physik und Chemie*, **79**, 368-97, 500-24 (1850)

What controls the direction of spontaneous change?

According to first law, energy is conserved in the process. Therefore, energy of an isolated system is not reduced (or changed) during a process. It can be considered that energy of the system under consideration alone is undergoing change.

However, there are also processes such as the expansion of ideal gas into vacuum, where energy is constant. While the energy is constant, the process may redistribute it in several packets. It can be seen that in all processes energy is partitioned and distributed into several smaller quantities.

In second law, we introduce a new state function called "Entropy" which characterises spontaneous changes. The redistribution may be understood in terms of entropy.

In the case of surroundings, the temperature does not change during heat transfer. The internal energy changes during the energy transfer,

$$dS_{\text{sur}} = dq_{\text{sur,rev}}/T_{\text{sur}} = dq_{\text{sur}}/T_{\text{sur}}$$

In adiabatic change,  $dq_{\text{sur}} = 0$  and  $\Delta S_{\text{sur}} = 0$

This breaking of processes into several sub processes means that we can write,

$$\Delta S = \sum q_{\text{rev}}/T$$

The summation extends over all the sub-processes. Thus, it is possible for entropy to reduce in some processes and increase in some others so as to increase the overall entropy.

**Thus, partitioning of energy into various units while keeping the total energy constant is the key to spontaneity.**

## Evaluation of entropy

$$dU = dq - dw$$

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

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

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

$$dU = TdS - PdV$$

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,

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

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

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

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

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

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

Enthalpy has units cal/deg which is referred as the enthalpy 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

$$TdS = dU + PdV$$

A 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 of enthalpy with temperature

$$dS = dq_{\text{rev}}/T = dH/T = C_p dT/T$$

constant pressure

$$dS = dq_{\text{rev}}/T = dU/T = C_v dT/T$$

constant volume

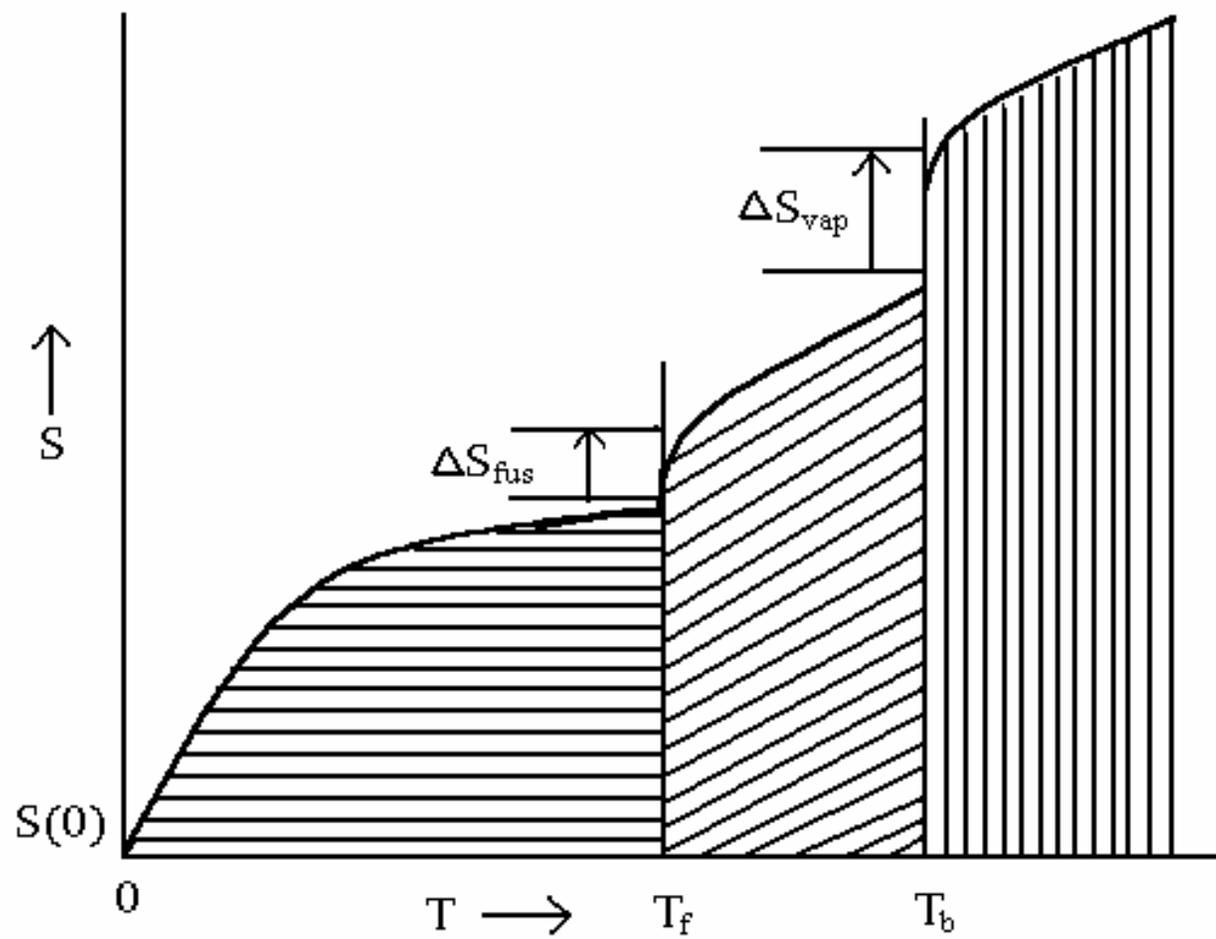
These equations can be integrated to get variation in entropy. If heat capacities are expressed as a function of temperature,  $\Delta S$  can be evaluated accurately.

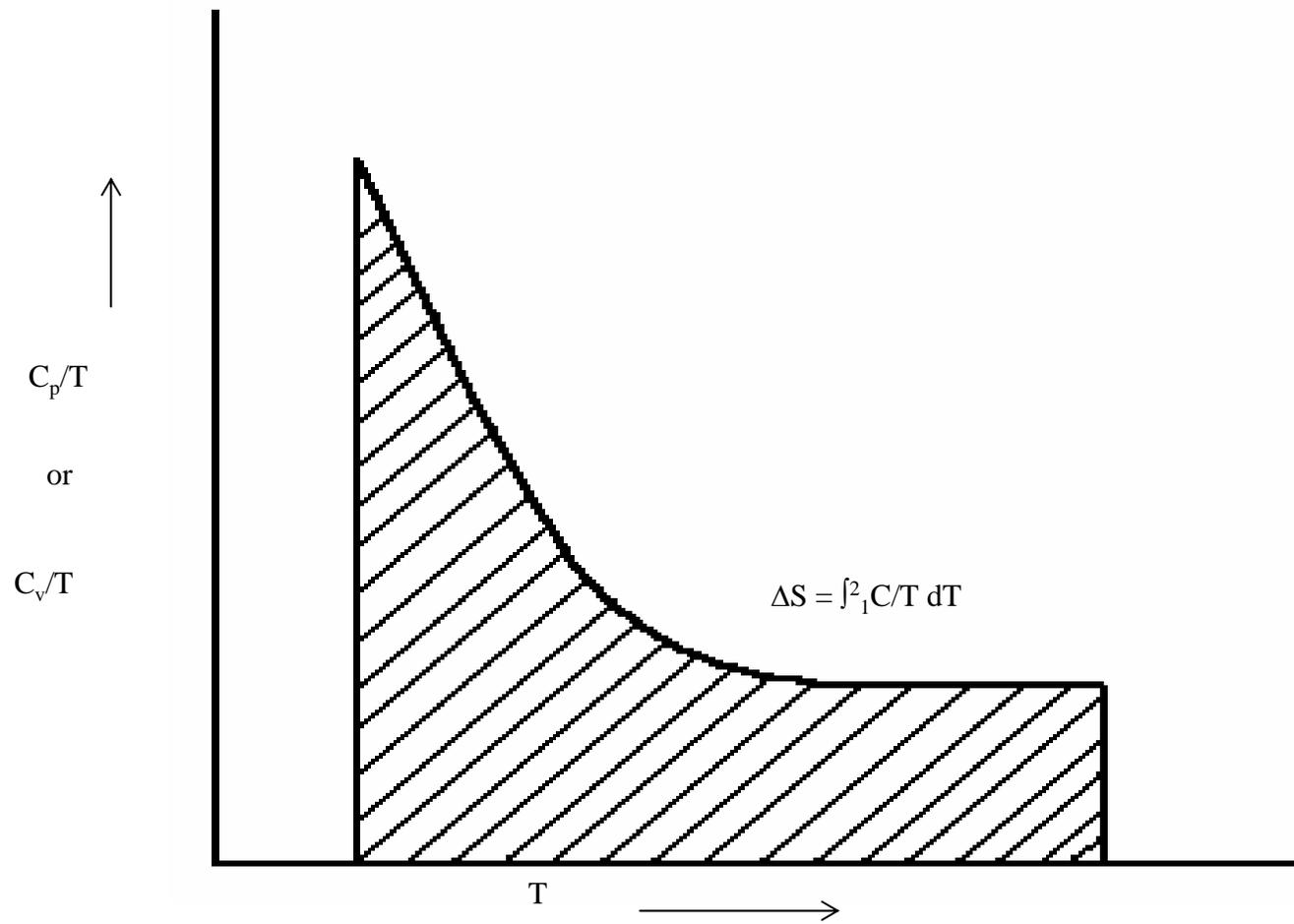
## Variation with temperature

### Example

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

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





## Entropy changes with specific processes

Heat change associated with a process such as phase transition is  $q = \Delta H$ , Therefore  $\Delta S = \Delta H/T$ . When  $\Delta H$  is positive such as melting,  $\Delta S$  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.

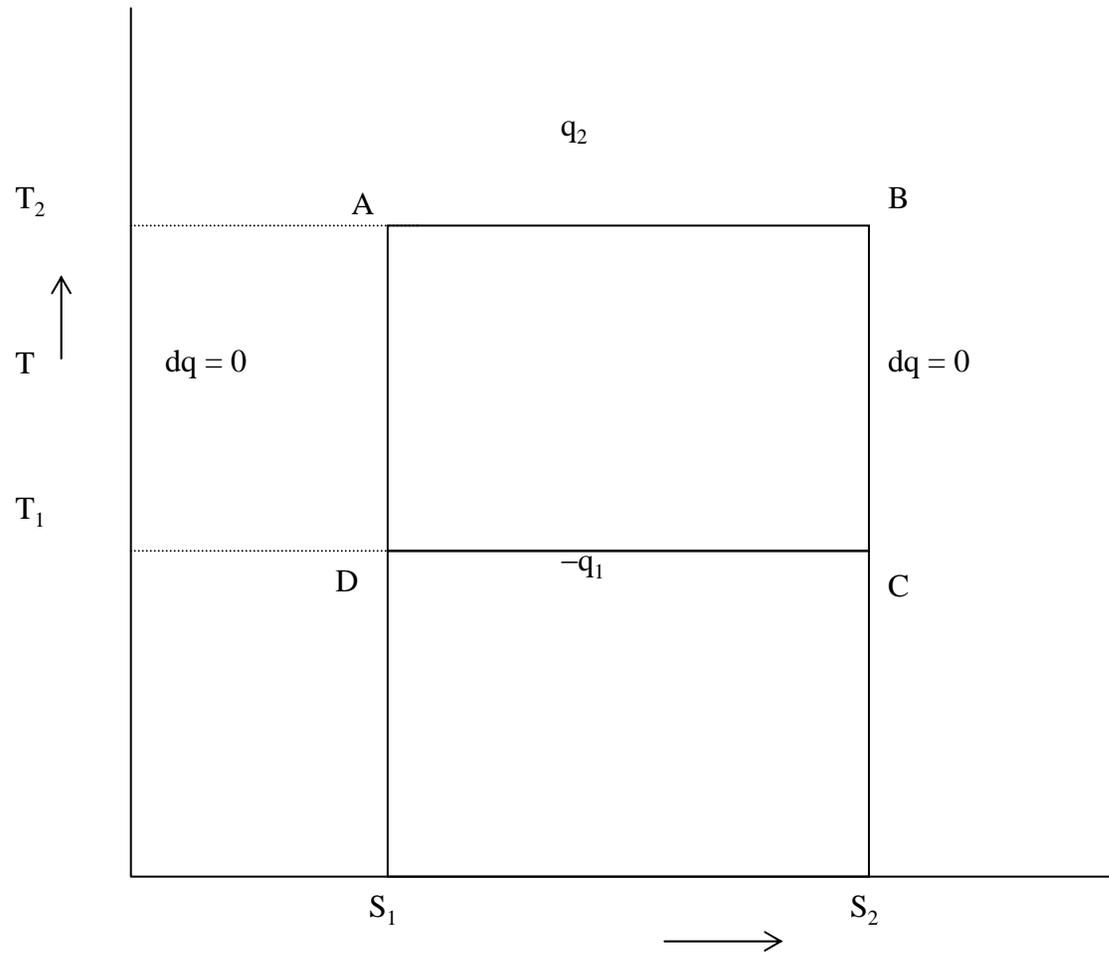
With this rule, enthalpy of vaporization of liquids at their normal boiling points can be calculated. When liquids are associated, the entropies are generally larger.

## 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 <sub>2</sub>	8.4	44.4
N <sub>2</sub>	11.42	73.16
H <sub>2</sub> O	22.0	109.0
NH <sub>3</sub>	28.9	97.21
CH <sub>3</sub> OH	18.1	104
CH <sub>3</sub> COOH	40.4	61.9

# Entropy temperature diagram



Heat absorbed  $q_2 = T_2 (S_2 - S_1)$

Heat evolved during isothermal compression

$$-q_1 = T_1 (S_1 - S_2)$$

$$= -T_1 (S_2 - S_1)$$

This value of energy is the energy unavailable for work.

Heat absorbed = work done

$$= q_2 - q_1$$

$$= (T_2 - T_1) (S_2 - S_1)$$

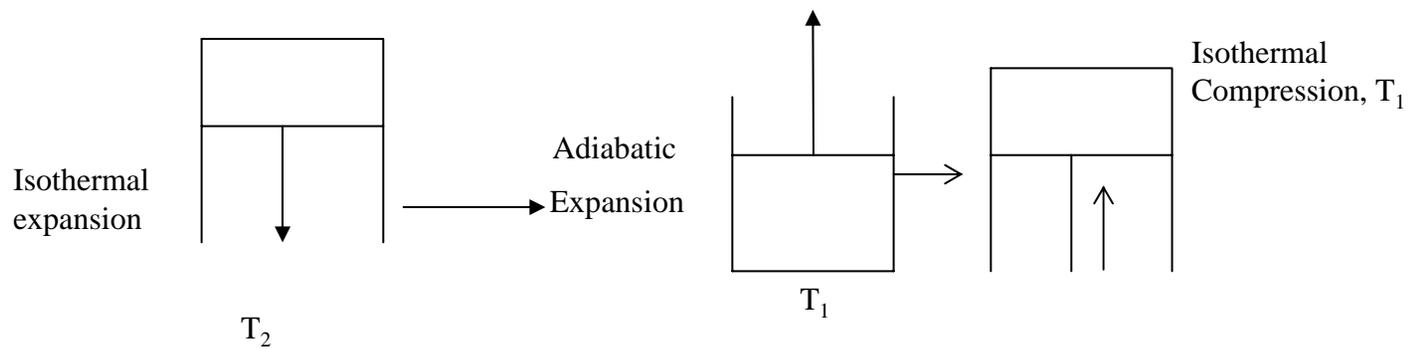
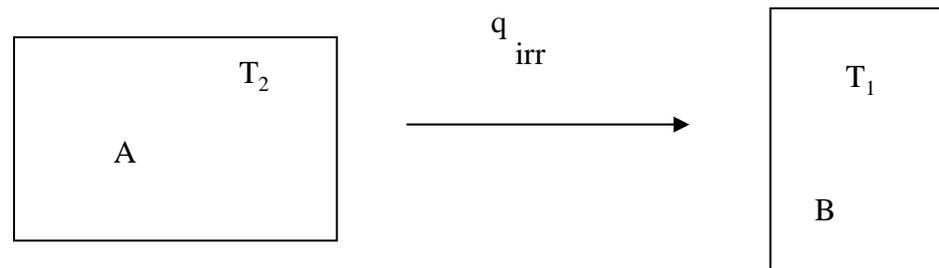
This product is the area **ABCD**

The heat energy transferred cannot be completely used for work. **Energy unavailable for work is proportional to  $\Delta S$ .**

## Maximum work

$$\begin{aligned}W_{\max} &= \text{Efficiency} \times \text{heat absorbed} \\&= ((T_2 - T_1) / T_2) \times q_2 \\&= q_2 (1 - T_1 / T_2) = q_2 - T_1 q_2 / T_2 \\&= \mathbf{q_2 - T_1 \Delta S}\end{aligned}$$

# Entropy change in irreversible processes



Three reversible steps, which are shown in the picture.

1. Isothermal expansion at  $T_2$  till heat  $q$  is absorbed (at A).
2. Additional expansion till temperature reaches  $T_1$
3. Isothermal compression till  $q$  is transferred to B.

At the reservoirs,

At A, heat lost =  $-q$  at  $T_2$

At B, heat gained =  $q$  at  $T_1$

## Total entropy change

$$\Delta S_{\text{net}} = q/T_1 - q/T_2$$

Since  $T_2 > T_1$ ,  $\Delta S_{\text{net}} > 0$

Entropy change in a reversible process is zero.

$$\Delta S_{\text{system}} = Q_{\text{rev}}/T$$

$$\Delta S_{\text{surrounding}} = -Q_{\text{rev}}/T$$

$$\Delta S_{\text{total}} = Q_{\text{uni}} = Q_{\text{rev}}/T - Q_{\text{rev}}/T = 0$$

$$nR \ln V_2/V_1 - nR \ln V_2/V_1 = 0$$

Entropy of the final state is higher for irreversible processes.  
Irreversible processes are spontaneous.

**For spontaneous process  $\Delta S > 0$**