Second Law

- There exists a function (S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

- Another way of looking at it:
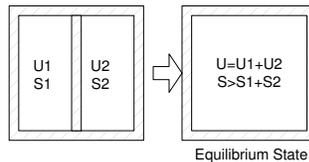
Figure 1: Second Law

- Entropy is additive. And...

$$\left(\frac{\partial S}{\partial U}\right)_{V,N...} > 0$$

- S is an extensive property: It is a homogeneous, first order function of extensive parameters:

$$S\left(\lambda U, \lambda V, \lambda N\right) = \lambda S\left(U, V, N\right)$$

- S is not conserved.

$$dS_{Sys} \geq \frac{\delta Q}{T_{Sys}}$$

For an Isolated System, (i.e. Universe)
$\triangle S > 0$
Locally, the entropy of the system can decrease. However, this must be compensated by a *total* increase in the entropy of the universe. (See 2)

$$\Delta S_1 = -\frac{Q}{T_1} \quad \Delta S_2 = +\frac{Q}{T_2}$$
$$\Delta S_{Total} = Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right) > 0$$

Quasi-Static Processes

A *Quasi-static* thermodynamic process is defined as the trajectory, in thermodynamic space, along an infinite number of contiguous equilibrium states that connect to equilibrium states, A and B.
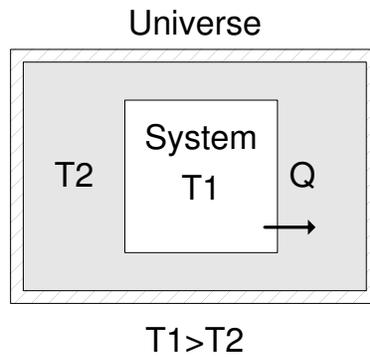
Figure 2: Local vs. Total Change in Energy

Irreversible Process

Consider a closed system that can go from state A to state B. The system is induced to go from A to B through the removal of some internal constraint (e.g. removal of adiabatic wall). The systems moves to state B only if B has a maximum entropy with respect to all the other accessible states. $S_B > S_A$. This kind of process is irreversible.

Reversible Process

In the limit, when a quasi-static process is such that the entropy increase is vanishingly small, this process can be considered reversible. The initial and final entropies of the process are the same.$\triangle S = 0$.

Entropy and Reversible Processes

An example of a reversible process is the heat exchange among two systems, in diathermal contact, that are at the same temperature, T. For the first system, the change in entropy would be given by (first law), $-\delta Q/T$. While the second system would increase its entropy by an amount $\delta Q/T$.

For a reversible process, thus,

$$dS = \frac{\delta Q_{rev}}{T}$$

Entropy for irreversible Processes???

According to the second law, for irreversible processes,

$$dS > \frac{\delta Q}{T}$$

When two thermodynamic states are connected through an irreversible path, we still can calculate the entropy change in the system, since S is a state function and is path independent. What we need to do is to find a sequence of reversible processes that have the same end result.

Maximum Work Theorem

For all processes leading from a specified initial state to a specified final state, the delivery of work is maximum for a reversible system. Consider a process that goes from state 1 to state 2. Consider two possible trajectories, a reversible and an irreversible one.

Write the first law for the process.

$$dU_R = dU_I$$
$$\delta Q_R + \delta W_R = \delta Q_I + \delta W_I$$

The second law states that:

$$dS = \tfrac{\delta Q_R}{T} \quad dS > \tfrac{\delta Q_I}{T}$$

Therefore,

$$TdS + \delta W_R < TdS + \delta W_I$$

If you want to produce work, $W_R < 0$, therefore, $|W_R| > |W_I|$. The Maximum work theorem has been proved.

Limits of Q and W

In a cyclic process, at one temperature, T:

$$\Delta S = \oint \frac{\delta Q}{T} = \frac{Q}{T} = 0$$

Since it is a cyclic process, with initial and final states being the same, $\triangle U - 0$. Since $Q = 0$, $W = 0$. This proves the Kelvin-Planck Statement of the Second Law.

How do we produce work then?

We make the process operate at two distinct temperatures.

The fact that

$$\Delta S = \oint \frac{\delta Q}{T} = \frac{Q}{T} = 0$$

Does not mean that Q_H and Q_L have to be zero. The only condition that has to hold is:

$$\Delta S = \frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0$$

Combined First and Second Laws:

$$dU = \delta Q + \delta W$$
$$dU = TdS - PdV$$
$$dU = TdS + \sum_i Y_i dX_i$$
$$dS = \tfrac{1}{T}dU + \sum_i \tfrac{Y_i}{T} dX_i$$

Problem 1

An ideal monoatomic gas undergoes a constant pressure, reversible expansion. During this expansion, it absorbs $6236\,J$ of heat and its entropy changes by $\triangle S = 14.41\,J/K$. Calculate the initial and final temperatures of the gas.

Problem 2

When an ideal gas undergoes a Joule-Thompson expansion its temperature remains constant. Show that this expansion is irreversible by showing that entropy of the universe (system + environment) increases. The Joule-Thompson expansion is an adiabatic flow through an insulated valve, i.e. the gas comes out a lower pressure than it goes in. For an ideal gas the temperature of the gas going out is identical to the temperature of the incoming gas, i.e. $T_i = T_o$