Foundations of Physics 2B/3C 2019-2020

Thermodynamics – Lecture 6 Recap

- Finished looking at real engine refrigeration cycles, including the Stirling Cycle.
- Considered the Clausius Inequality, and what it means from a thermodynamic perspective: $Q_L < 0$

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \qquad \boxed{\oint \frac{\delta Q}{T} \leq 0.}$$

- Were introduced to the concept of entropy as a thermodynamic function of state:

$$\boxed{dS = \frac{\delta Q_{Rev}}{T} \quad ; \quad \Delta S_{AB} = S_B - S_A = \int_A^B dS = \int_A^B \frac{\delta Q_{rev}}{T}.}$$

- Saw how to calculate entropy changes in standard thermodynamic processes.

Thermodynamics – Lecture 7 Aims

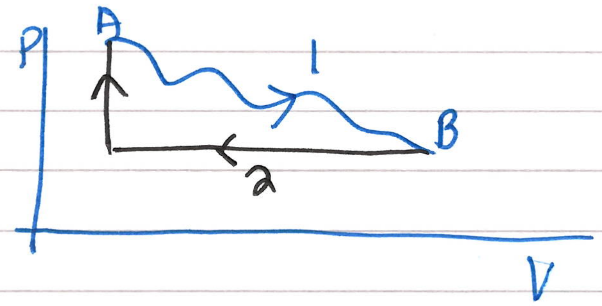
- To finish looking at entropy, including entropy change in various processes and see how entropy relates to the arrow of time.
- To look at temperature-entropy diagrams and their uses.
- To look at the thermodynamic identity:

$$\boxed{dU = TdS - pdV.}$$

- To be introduced to the thermodynamic potentials.

Example 13.2 Entropy change in any process.

Consider irreversible process between two thermo states. Always possible to a construct a complementary reversible process between them



1: Irreversible
2: Reversible (isobaric → isochoric)

Clausius on cycle $\oint \frac{\delta Q}{T} \leq 0$

heat added/removed reversibly on 2

$$\therefore \int_A^B \frac{\delta Q}{T} + \int_B^A \frac{\delta Q_{rev}}{T} \leq 0$$

$$\int_A^B \frac{\delta Q}{T} \leq \int_A^B \frac{\delta Q_{rev}}{T}$$ dS by definition

Holds no matter what separation of states A + B

$$\Delta S_{AB} = \int_A^B \frac{\delta Q_{rev}}{T} \geq \int_A^B \frac{\delta Q}{T}$$

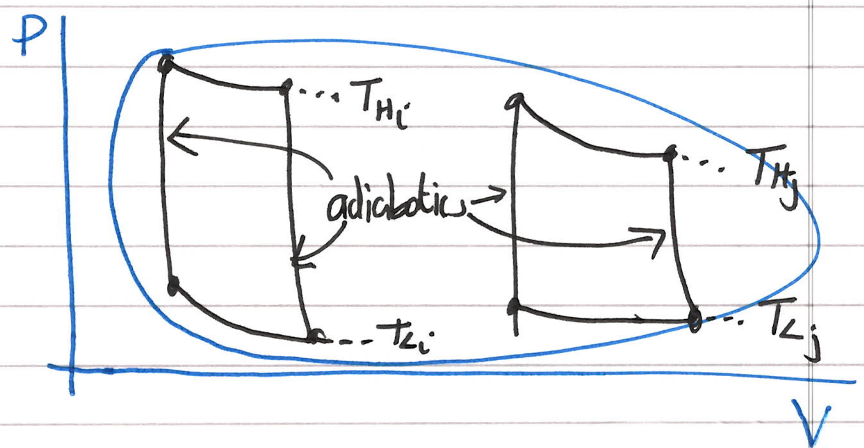
Always possible to arrange for irreversible process to be thermally isolated $\delta Q = 0$

$$\Delta S_{AB} = \int_A^B \frac{\delta Q_{rev}}{T} \geq 0$$

Clausius 'Universe entropy tends to a maximum; Universe energy is constant'

Example 13.3 Entropy change for any cycle is zero (exact)

Split an arbitrary cycle into # Carnot cycles. Each Carnot cycle interacts at T_{H_i}, T_{L_i}



Carnot cycles

Each Carnot has $\oint \frac{\delta Q_{rev}}{T} = 0$

Adiabatic parts (steep) of each successive Carnot cycle are equal + opposite if isotherms T_{H_i}, T_{H_j} are separated by dT.

Carnot cycles taken in limit $\longrightarrow$ Zero size

$$\Delta S_{carnot} = 0 \Longrightarrow \Delta S_{cycle} = \sum \Delta S_{carnot} = 0$$

Principle of Entropy increase: For every process taking place in a system, the entropy change of the system increases or remains constant.

Nett entropy increases — can always have some part of the system where entropy decreases BUT will always be a corresponding entropy increase, which is greater than decrease elsewhere.

Another of the 2nd Law 'Entropy increases in a thermo process'

In nature things, left to their own devices, tend to a more disordered state. Restoring original, requires input of energy. Entropy is related to our decreasing knowledge with time.

Processes in the real world are irreversible. Can always find a combination of (infinitesmal) reversible, quasi-static processes to return to the original configuration. Provide lower bound on the entropy increase.

In any real process, always find more ways exist to convert internal energy of a system to heat. This 'waste' heat can be rejected to environment at low temperature, heat tends to thermal equilibrium with environment.

Heat in at 'low' temperature corresponds to entropy increase

Lost heat has become unavailable for 'work'

Overall entropy increase is the arrow of time.

Thermodynamics – Handout 7

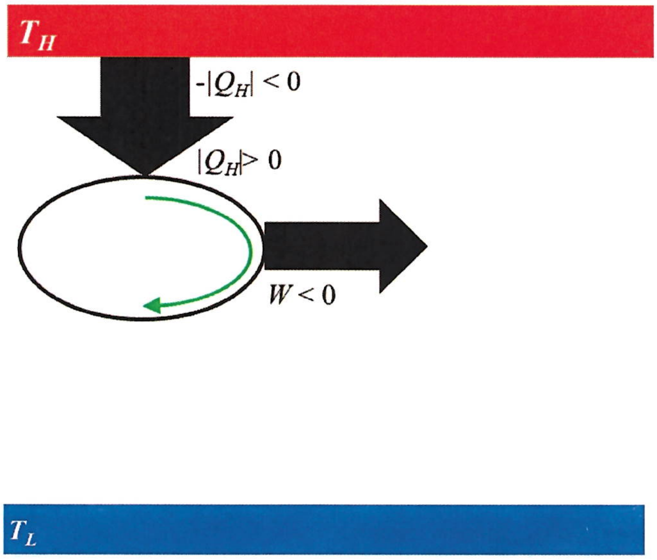


Figure 25: Equivalence of Entropy and Kelvin Statements of the Second Law.

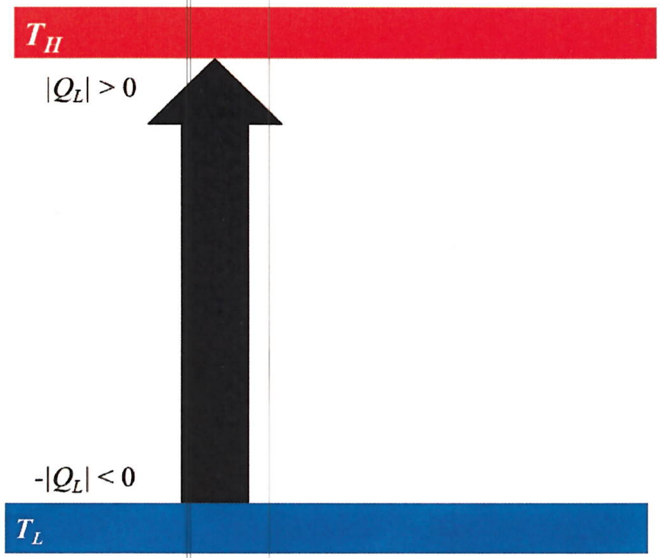


Figure 26: Equivalence of Clausius and Kelvin Statements of the Second Law.

Proof 13.1

Have a Kelvin Violator

1st law $dU = 0 \therefore \delta Q = -\delta W$

$W_{cycle} = -|Q_H|$

[No heat rejected]

Heat $-|Q_H|$ out of hot

$$\Delta S_H = \int \frac{\delta Q_{rev}}{T_H}$$

$$= \frac{1}{T_H}\int \delta Q_{rev}$$

$$= \frac{-|Q_H|}{T_H} < 0$$

$\Delta S_E = 0$ [cycle]

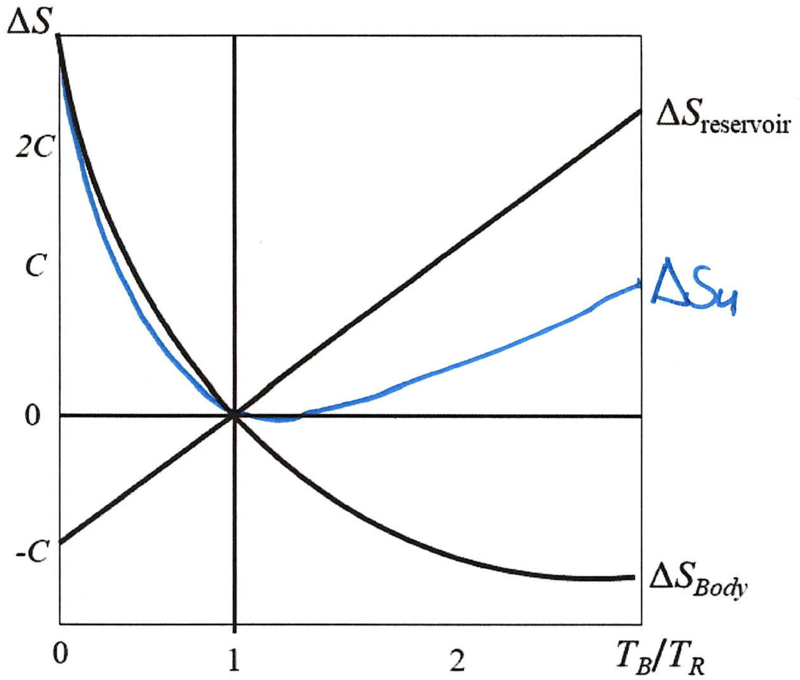
Universe entropy

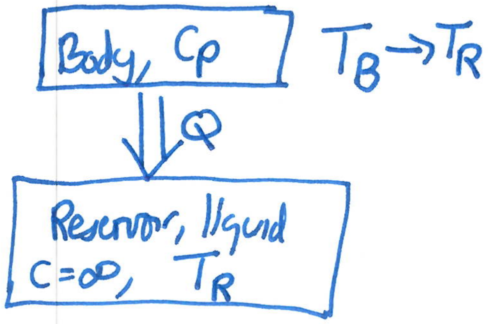
$$\Delta S_U = \Delta S_H + \Delta S_E$$

$$= -\frac{|Q_H|}{T_H} < 0$$

Violates entropy statement

Exercise 7





Body's temperature $T_B \to T_R$ as heat transfer brings to thermal equilibrium with the reservoir.

Figure 27: The entropy changes of a body and a reservoir for all temperatures. The body is initially at T_B, with heat capacity C_p, and it gets immersed in a reservoir at constant temperature T_R.

Example 13.4

$$\int \frac{\delta Q_{rev}}{T} = \int_{T_B}^{T_R} \frac{C_p dT}{T} \longrightarrow \Delta S_{Body} = C_p \ln\left(\frac{T_R}{T_B}\right)$$

$$\Delta Q_{Body} = C_p \Delta T = C_p (T_R - T_B). \qquad \Delta Q_B = \int C_p dT$$

Energy lost (gained) by the body is equal + opposite to heat rejected (taken in) by the liquid

$$\Delta Q_{liquid} = -\Delta Q_{Body}.$$

$$\Delta S = \int \frac{1}{T_R} \delta Q$$

constant

$$\Delta S_{Liquid} = -\frac{\Delta Q_{Body}}{T_R} = -C_p \frac{(T_R - T_B)}{T_R}.$$

Reservoir entropy from body energy change

$$\Delta S_{Total} = C_P \left[\ln\left(\frac{T_R}{T_B}\right) - \frac{T_R - T_B}{T_R}\right] = C_p \left[\frac{T_B}{T_R} - \ln\left(\frac{T_B}{T_R}\right) - 1\right] \geq 0.$$

$$\ln x = -\ln(1/x)$$

$$x - \ln x - 1 \geq 0 \qquad \forall x \text{ and } x \neq 1$$

$\Delta S_u > 0$ no matter what the starting temperatures

$T_R \neq T_B$, $T_R, T_B > 0$ [in Kelvin]

Thermodynamic identity

$$\boxed{dU = \delta Q + \delta W = TdS - pdV}$$

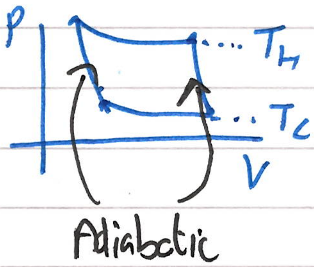
This holds for all processes. Energy conservation.
dU, dS, dV are exact differentials, hold for all paths between equilibrium states.

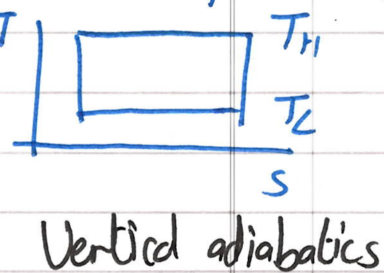
δW replaced by 'other' works Fdx, Bdm, ...

Temperature - Entropy diagram

TS diagram

Can be simpler to analyse than pV diagram (fridges)





pV Area $\oint pdV = W_{cycle}$

$\oint TdS = \Delta Q$

Cycle nett heat
[Sign depends on direction around the cycle]

Isochore / Isobare on TS

$\left(\frac{\partial T}{\partial S}\right)_V$ or $\left(\frac{\partial T}{\partial S}\right)_p$ Describe gradients

Find these derivatives

$S = \int \left(\frac{\partial S}{\partial T}\right)_V dT$ etc.

$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$