

Thermodynamics – Lecture 9 Recap

- Saw how problems in thermodynamics can be solved mathematically
- Looked at some applications of entropy, including how effective any process is.
- Were introduced to the concept of Available Energy, and how minimising the Helmholtz or Gibbs functions tells us the most work that can be got out of a process.

Thermodynamics – Lecture 10 Aims

- To see some examples of Available Energy.
- To look at useful work and irreversibility, and see how they are related to the overall Universe Entropy change.
- To consider Phase changes and how they are linked to Latent Heat.
- To see how the Gibbs function defines Phase Changes, how its value is the same across a phase change, but how its derivatives may be discontinuous.

To ΔS_u is 'energy' system provides to surroundings
(and becomes unavailable for work)

Spontaneous process [heat from hot to cold] have
an entropy increase. (heat added at 'cold temperature')
These lead to a decrease in available energy

$$dA = dU + p_0 dV - T_0 dS$$

Example 16.2

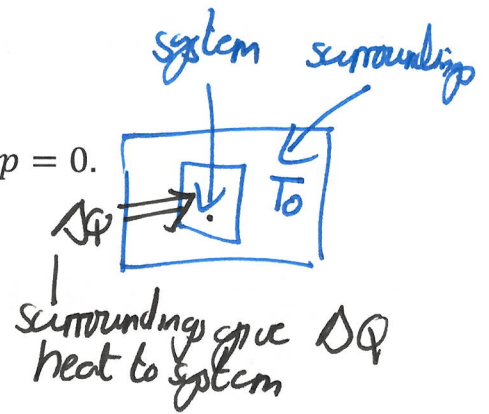
Limit to changes in temperature and volume, $p = p_0$ and $dp = 0$.

$$dU = \delta Q + \delta W \quad dU = \delta Q - p_0 dV$$

At constant volume, $dV = 0$, have $dU \equiv \delta Q$.

Surroundings (at temperature T_0) entropy change

$$\Delta S_{\text{surround}} = -\frac{\Delta Q}{T_0} = -\frac{\Delta U}{T_0}$$



Universe Entropy change

$$\Delta S_U = \Delta S_{\text{system}} + \Delta S_{\text{surround}} = \Delta S_{\text{system}} - \frac{\Delta U}{T_0}$$

$$F = U - TS$$

$$T_0 \Delta S_U = T_0 \Delta S_{\text{system}} - \Delta U \Rightarrow -T_0 \Delta S_U = \Delta U - T_0 \Delta S_{\text{system}}$$

At constant temperature, $F = U - T_0 S$ so $\Delta F = \Delta U - T_0 \Delta S_{\text{system}}$.

Helmholtz is disguised form of Universe entropy change at constant temperature

If ΔS_U increases spontaneously, ΔF decreases by same amount.

Minimise F for most work out

If system internal energy decreases, $\Delta U = U_F - U_I < 0$, work is done on the surroundings ($dU = \delta Q + \delta W$).

$$\delta W < 0 \quad W_F > W_I$$

System entropy could either:

- 1) Decrease (system loses energy to surroundings); the loss of system entropy

ΔS_{system} reduces the work that can be done. Add energy to surroundings

$\Delta U - T_0 \Delta S_{\text{system}}$ becomes less negative, ΔF is smaller

- 2) Increase (system gains energy from surroundings); the entropy of the system

increases, so more work can be done as more internal energy can then be

released as work $\Delta U - T_0 \Delta S_{\text{system}}$ becomes more negative.

$T_0 \Delta S_U$ is the tax surroundings demand from the system, to compensate for the system entropy reduction

Example 16.3

Burning 1 litre of petrol releases 33.00 MJ of heat

Enthalpy $\Delta H = 32.87$ MJ (work against atmosphere, pushing out of way.)

Constant pressure 0.13 MJ of heat is required to drive atmosphere back

Entropy change (more gas molecules after burning) $\Delta S = 8.00 \text{ kJ K}^{-1}$

Helmholtz change $\Delta F = \Delta U - T_0 \Delta S = -35.40$ MJ

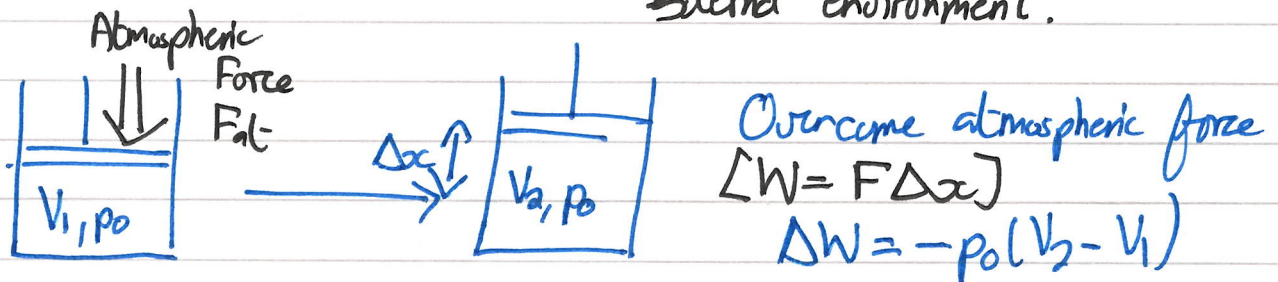
300 K (environment temp)

Max work you could obtain with no irreversibility

Useful Work + Availability

W_{use} - Useful Work. Work done in a process that can be used for motion [Work not surroundings]

$$W_{use} = \underset{\substack{\uparrow \\ \text{Total work produced}}}{W_{actual}} - \underset{\substack{\uparrow \\ \text{Work done by system on the external environment.}}}{W_{surround}}$$



$$W_{use} = W_{actual} - p_0(V_2 - V_1)$$

W_{rev} - Reversible work, work done by a device that operates using only 'totally internal reversible' processes i.e. a Carnot cycle.

All heat is transferred via Carnot engines + bridges - Quasistatic and there are no temperature differences

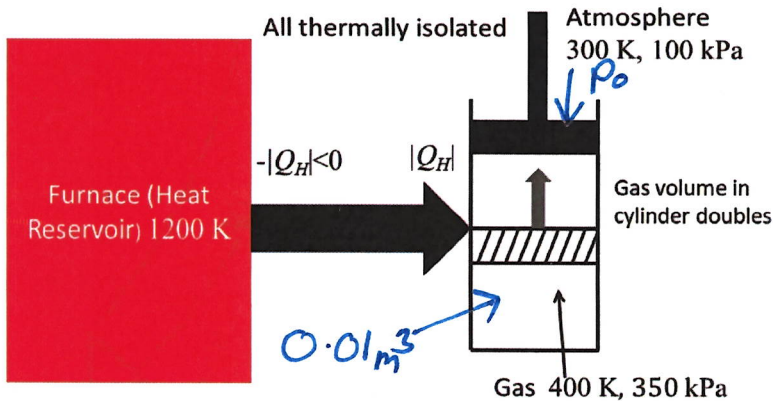
$$I = |W_{rev} - W_{use}| = \underset{\substack{\uparrow \\ \text{Environment temperature}}}{T_0} \underset{\substack{\uparrow \\ \text{Universe entropy change}}}{\Delta S_u}$$

Universe entropy change is a tax on the conversion of heat to work. Always some heat added to 'cold' environment.

Real processes have a lower work potential.

Thermodynamics – Handout 10

Example 16.5



Cylinder gas is isothermal $pV = nRT_G$

$$\Delta W_{Piston} = \int_{V_1}^{V_2} -pdV$$

$$= -nRT_G \int_{0.01}^{0.02} \frac{dV}{V}$$

$$nRT_G = p_1 V_1 \text{ [initial pressure, volume]}$$

$$= -p_1 V_1 \ln 2 = -2.43 \text{ kJ.}$$

$$W_{surr} = p_0(V_2 - V_1) = -1 \text{ kJ.}$$

$$\text{Useful Work} = W_{piston} - W_{surr} = -1.43 \text{ kJ.}$$

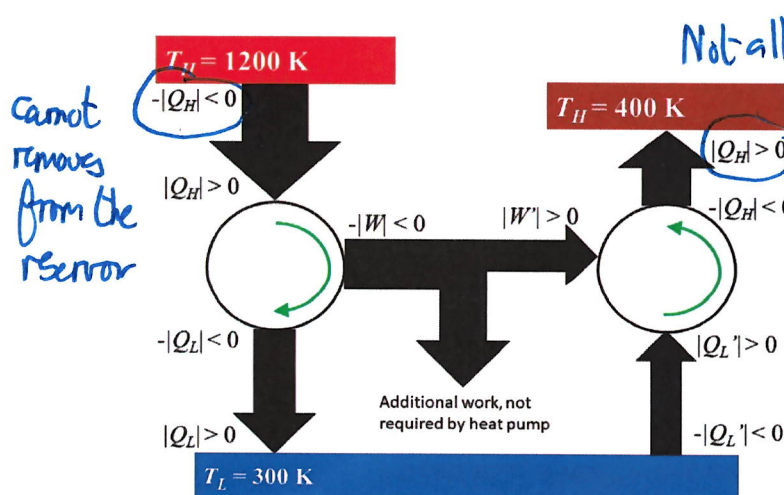
Gas in piston (ideal + isothermal) $dU = 0$

$$dU = \delta Q + \delta W \Rightarrow Q_H = -W_{Piston} = 2.43 \text{ kJ}$$

$$\Delta S_{furnace} = -\frac{Q_H}{T_{furnace}} = -\frac{2.43}{1200} = -2.03 \text{ J K}^{-1}; \Delta S_{Piston} = +\frac{Q_H}{400} = 6.07 \text{ J K}^{-1}.$$

$$\Delta S_{Universe} = 4.05 \text{ J K}^{-1} \Rightarrow I = \Delta S_{Universe} \times T_0 = 4.05 \times 300 = 1.21 \text{ kJ.}$$

[Entropy reservoir + gas are at constant T] Lowest available temperature



Not all engine work is required by the heat pump.

$$\eta_{engine} = \frac{|Work_{engine}|}{Q_H} = 2.43 \text{ kJ}$$

$$1 - \frac{T_{surround}}{T_{furnace}} = 75 \%$$

$$|W_{engine}| = 1.82 \text{ kJ}$$

Work input to heat pump transferring heat $Q_H = 2.43 \text{ kJ}$ into the gas, (still does -1.43 kJ of useful work)

$$COP_H = \frac{|Q_H|}{\text{Work Supplied}} = \frac{T_{gas}}{T_{gas} - T_{surround}} = 4 \Rightarrow |W_{pump}| = 0.61 \text{ kJ.}$$

$$-1.43 \quad -1.82 \quad +0.61$$

$$W_{reversible} = W_{use} + W_{engine} + W_{pump} = -1.43 - 1.82 + 0.61 = -2.64 \text{ kJ}$$

$$I = |W_{rev} - W_{use}| = |-2.64 - (-1.43)| = 1.21 \text{ kJ.}$$

$$-1.43$$

As before

Irreversibility is the additional work the Carnot cycle produces

17. Phases of a Substance

Phases are fascinating. A small change in one property (eg the temperature) can vastly affect another (volume) as we move across a phase boundary [Consider vapourisation]

At phase transition, both phases coexist but must have total particle number conserved.

A phase is a homogeneous region of (p, V, T) space, with the region having a definite boundary.

Phase change requires the addition (removal) of energy to make something happen. Latent heat.

$$L = \Delta Q_{rev} = \int_1^2 T_0 dS = T_0 \int_1^2 dS = T_0 \Delta S$$

Phase changes correspond to entropy changes.
Entropy increases/decreases in the phase change depending on whether order decreased/increased.

Gibbs function is conserved at a phase boundary (takes same value on either side of the phase change)

$$G = U + pV - TS \quad \text{can show} \quad dG = Vdp - SdT$$

Phase change $dp = 0$, $dT = 0$ $\therefore dG \equiv 0$

Gibbs is conserved its derivatives may be discontinuous.

Example 17.1

First order phase change

— First derivative of Gibbs being discontinuous

$$\left(\frac{\partial G_1}{\partial T}\right)_p \neq \left(\frac{\partial G_2}{\partial T}\right)_p$$

G_1, G_2 are the Gibbs functions in phases 1 & 2

$$\frac{dG}{dT} = \frac{V dp}{dT} - \frac{S dT}{dT}$$

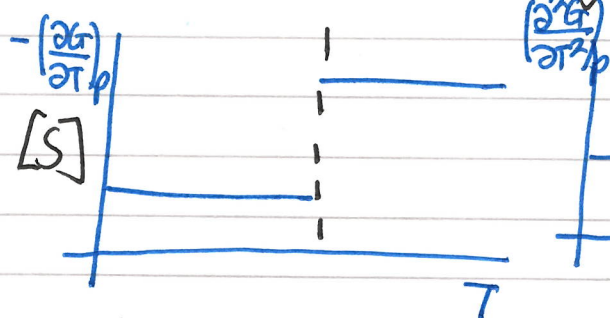
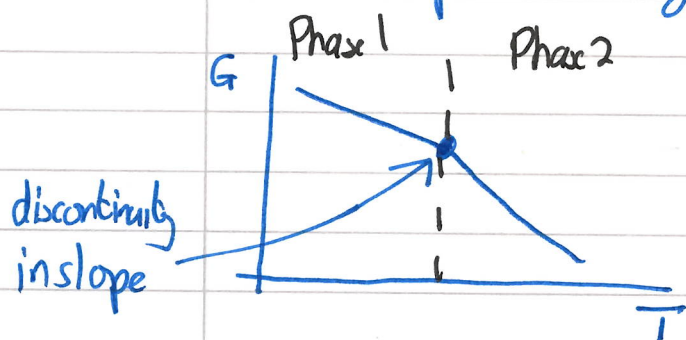
÷ by dT at constant p

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

For this phase change

$$S_1 \neq S_2$$

An entropy change



Higher temperature has higher entropy.

$$S = -\left(\frac{\partial G}{\partial T}\right)_p ; \quad \left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\left(\frac{\partial S}{\partial T}\right)_p = -\frac{C_p}{T}$$