

Thermodynamics Revision Guide

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This document is merely a laundry list of what you need to know. It is not a set of revision notes but, combined with the official syllabus and tutorial work, it may be useful for checking things off as you compose your own revision notes, which you should of course do.

1 Zeroth and First Laws

B&B Ch. 11 - 14, Questions 4.1, 4.3 - 4.6, 5.x

- Know the zeroth law (page 31 B&B)
- Know the statement of the first law and mathematical forms

$$\begin{aligned}dU &= dW + dQ \\dU &= dQ - pdV \\dU &= TdS - pdV\end{aligned}$$

- Be able to ‘translate’ this into a first law for other systems than gases, especially the elastic band (see Q6.5), liquid film (Ch. 17 summary) and magnets (Ch. 17 summary).
- Heat capacities:

$$\left. \begin{aligned}C_V &= \left(\frac{dQ}{dT}\right)_V \\C_p &= \left(\frac{dQ}{dT}\right)_p\end{aligned} \right\} \text{(definition)} \rightarrow \begin{aligned}C_V &= \left(\frac{\partial U}{\partial T}\right)_V \text{ (from first law)} \\C_p &= \left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p\end{aligned}$$

- $dU = C_V dT$ for ideal gas only (see example 11.3)
- Isothermal compressibility (fractional ΔV at constant T)

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$

and isobaric expansivity (fractional ΔV at constant p)

$$\beta_p = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

- Work in terms of κ , β (not on question sheet)

$$dW = -pdV = -p \left(\left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT \right)$$

(we can do this because V is a function of state, so can be expressed as a total differential)

$$W = \int_{p_1}^{p_2} \kappa_T V p dp - \int_{T_1}^{T_2} \beta_p V p dT$$

– Isothermal, $dT = 0$

$$W = \int_{p_1}^{p_2} p V \kappa_T dp$$

N.B. for a *solid*, $V, K \approx \text{const.}$

$$\therefore W \approx \frac{1}{2} \kappa_T V (p_2^2 - p_1^2)$$

– Isobaric, $dp = 0$

$$W = - \int_{T_1}^{T_2} p V \beta_p dT$$

N.B. for a *solid*, $V, \beta \approx \text{const.}$

$$\therefore W \approx -pV\beta_p (T_2 - T_1)$$

- $\left(\frac{\partial U}{\partial V}\right)_T$ in measurable quantities = $\frac{C_p - C_V}{\beta_p V} - p$ (Q4.1)

- Relationship between C_p and C_V for ideal gas:

$$C_p - C_V = nR$$

- Adiabatic of an ideal gas:

$$TV^{\gamma-1} = \text{const.} \quad pV^\gamma = \text{const.}$$

- Isotherm of an ideal gas

$$\Delta Q = RT \ln \frac{V_2}{V_1}$$

2 Entropy (and use of Maxwell Relations)

B&B Ch. 14, Questions 4.5 onwards, especially 4.5, 4.6, 5.1

- $dS = \frac{dQ_{rev}}{T}$

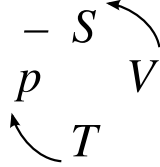
S is a function of state, so if your system is not undergoing a reversible change, choose one with the same end-points which does. This will have the same ΔS .

- $dQ = TdS$ (for reversible changes only) $\Rightarrow dU = TdS - pdV$

- $dS \geq \frac{dQ}{T}$ for an irreversible change, $\therefore dW > -pdV$ (irreversible)

- $\left. \begin{array}{l} H = U + pV \\ G = H - TS \\ F = U - TS \end{array} \right\}$ + the fact that $\frac{\partial^2 x}{\partial y \partial z} = \frac{\partial^2 x}{\partial z \partial y} \rightarrow$ four Maxwell relations

- You must be able to derive them, but the following mnemonic is useful in questions which do not explicitly ask you to prove a Maxwell relation, and when time is short — it allows you to quickly quote one, e.g., $\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S$ etc.



- Prove that for an ideal gas U is a function of T only: Write $U(V, T)$, prove $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p = T \left(\frac{\partial p}{\partial T}\right)_V - p = 0$$

- Change in S where $S = S(T, V)$ 0 useful when volume changes (e.g. Joule expansion)

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

From a Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

By definition

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V \quad (1)$$

$$\therefore dS = \frac{C_V dT}{T} + \left(\frac{\partial p}{\partial T}\right)_V dV$$

Special case: Ideal gas

$$pV = RT \Rightarrow S = C_V \ln T + R \ln V + \text{const.}$$

- Change in S where $S = S(T, p)$

$$dS = \frac{C_p dT}{T} + \left(\frac{\partial V}{\partial T}\right)_p dp$$

(same method as above)

- This allows calculation of $C_p - C_V$ for a non-ideal gas:

$$T \left(\frac{\partial S}{\partial T}\right)_V = C_p - T$$

And from equation ??

$$C_V = C_p - T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V = C_p - T \left(\frac{\partial V}{\partial T}\right)_p \left[\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \right]$$

$$\Rightarrow C_p - C_V = \frac{TV\beta^2}{\kappa_T} \Rightarrow C_p > C_V \text{ for everything!}$$

3 Second Law, Engines

B&B Ch. 13, Questions 5.2, 5.3

- Second Law: No process can *just* convert heat into work. There must be waste heat. (This is Kelvin's statement. Clausius' statement, which can be shown equivalent, is not on the syllabus.)
- Carnot Cycle (reversible)
 1. Isothermal expansion at T_1 , absorbs Q_1
 2. Adiabatic expansion $T_1 \rightarrow T_2$
 3. Isothermal compression at T_2 , rejecting Q_2
 4. Adiabatic compression $T_2 \rightarrow T_1$

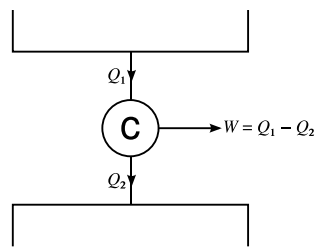


Figure 1: Schematic diagram of a Carnot engine

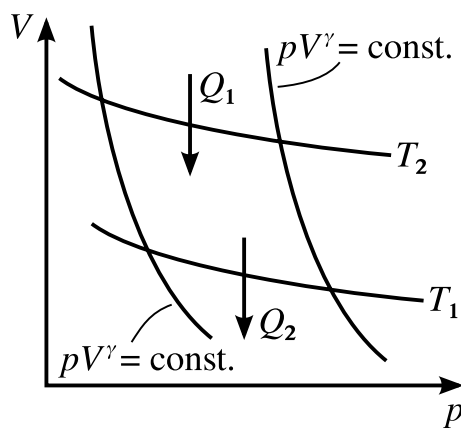


Figure 2: Graph of V against p for a Carnot engine

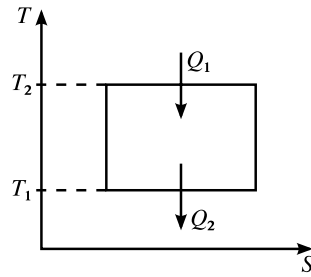


Figure 3: Graph of T against S for a Carnot engine

- Efficiency (definition for an engine):

$$\eta = \frac{W}{Q_{in}} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

- Carnot's theorem: There is no engine more efficient than a Carnot engine
- Proof that $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$ - See Ex. 13.1. Need to prove that $TV^{\gamma-1}$ is constant along an adiabat, and $\Delta Q = RT \ln \frac{V_2}{V_1}$ on an isotherm for this.
- Other engines: Q5.2, 5.3. Otto cycle, heat pump, refrigerator.

4 Expansions, Equations of State

B&B Ch. 27, Questions 5.8, 6.1 - 6.3, 7.2

- Derivations of

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{c_V} \left(T \left(\frac{\partial p}{\partial T}\right)_V - p \right) \quad \text{Joule (Q5.8)}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{1}{c_V} T \left(\frac{\partial p}{\partial T}\right)_V \quad \text{Adiabatic}$$

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{c_p} \left(T \left(\frac{\partial V}{\partial T}\right)_p - V \right) \quad \text{Joule-Kelvin}$$

- Joule expansion

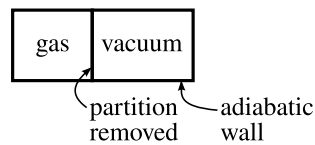


Figure 4: Joule expansion

$$dQ = 0 \quad dW = 0 \text{ (vacuum)}$$

$$\therefore dU = 0$$

Process is irreversible, but can still use $dU = TdS - pdV$ since initial and final states are what matters for U .

- Joule-Kelvin

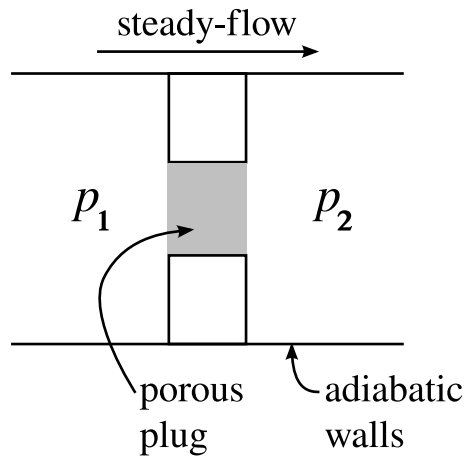


Figure 5: Joule-Kelvin expansion

- Proof that H is constant
- Proof that $\left(\frac{\partial T}{\partial p}\right)_H = 0$ for an ideal gas
- Concept of inversion curve ($\left(\frac{\partial T}{\partial p}\right)_H = 0$) and maximum inversion temperature (max T at which $\left(\frac{\partial T}{\partial p}\right)_H = 0$)
- For a gas obeying Dieterici's equation of state

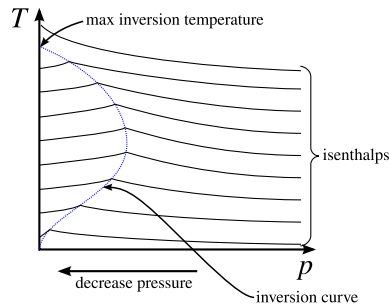


Figure 6: T - p diagram for a Joule-Kelvin cooling process, showing the inversion curve

- Maximum inversion temperature is where the inversion curve meets the T -axis - Joule-Kelvin process does not cool if you start above this temperature, regardless of T
- The inversion curve is the line
$$\left(\frac{\partial T}{\partial p}\right)_H = 0$$
- Your gas might not obey this equation of state, so stop and think before you sketch the above!

- See Q6.2 and 6.3 for some example equations of state. Take note of the trick for evaluating $\left(\frac{\partial V}{\partial T}\right)_p$, which is needed to calculate the Joule-Kelvin coefficient. For such gases it is usually algebraically easier to evaluate $\left(\frac{\partial p}{\partial T}\right)_V$ and $\left(\frac{\partial p}{\partial V}\right)_T$ and note that

$$\left(\frac{\partial V}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T}$$

- Be comfortable with the critical point and reduced units (Q7.2)
- Be able to describe liquefaction of helium by the Joule-Kelvin process
 - diagram, general description
 - pre-cooling using, for example, Joule expansion to get below the maximum inversion temperature
 - use a counter-current heat exchanger
 - for maximum efficiency, work on the inversion curve

5 Phase Changes

- To prove the Clausius-Clapeyron equation, you must start by showing that a system in contact with a heat and pressure reservoir (which is the usual situation outside a laboratory) minimises its Gibbs energy.

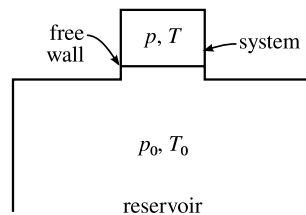


Figure 7: A system connected to a thermal and pressure reservoir

Element of heat dQ moves into (or out of) system

$$dQ \leq T_0 dS$$

$$dU = dQ - p_0 dV$$

$$\therefore dU + p_0 dV - T_0 dS \leq 0$$

$$d(U + p_0 V - T_0 S) \leq 0$$

$$dG \leq 0$$

i.e. system will undergo spontaneous changes reducing G , until equilibrium is reached (when $dQ = TdS$). For an alternative proof, see B&B 16.5.

- Next step is to show that this implies that two phases coexisting in equilibrium at a given T, p will have equal specific Gibbs energies:

$$G = m_1 g_1 + m_2 g_2$$

$$dG = g_1 dm_1 + g_2 dm_2$$

at equilibrium in contact with a p, T reservoir

$$dG = 0$$

From conservation of mass,

$$dM = dm_1 + dm_2 = 0$$

$$\therefore g_1 = g_2$$

- Now we can prove the Clausius-Clapeyron equation!

$$g_1(T, p) = g_2(T, p)$$

$$g_1(T + dT, p + dp) = g_2(T + dT, p + dp)$$

$$g_1(T, p) + \left(\frac{\partial g_1}{\partial T}\right)_p dT + \left(\frac{\partial g_1}{\partial p}\right)_T dp = g_2(T, p) + \left(\frac{\partial g_2}{\partial T}\right)_p dT + \left(\frac{\partial g_2}{\partial p}\right)_T dp$$

$$\left(\frac{\partial g_1}{\partial T}\right)_p - \left(\frac{\partial g_2}{\partial T}\right)_p = \left[\left(\frac{\partial g_2}{\partial p}\right)_T - \left(\frac{\partial g_1}{\partial p}\right)_T\right] \frac{dp}{dT}$$

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

(see B&B 16.4 - from the definition of Gibbs energy and the first law)

$$\therefore (s_2 - s_1) = (V_2 - V_1) \frac{dp}{dT}$$

Let ℓ = heat transfer of phase change = $T(s_2 - s_1)$

$$\therefore \frac{dp}{dT} = \frac{\ell}{T(V_2 - V_1)}$$

- Typical phase boundaries

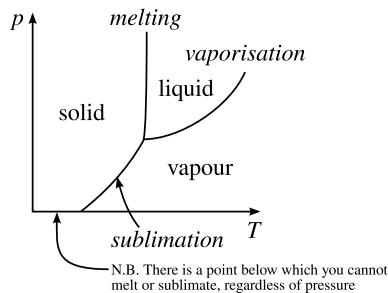


Figure 8: A p - T diagram for a typical substance.

- But for water, the liquid-solid boundary has a negative gradient:

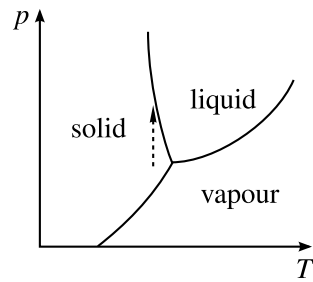


Figure 9: Phase diagram for water

A large enough increase of pressure on such a solid can melt it. This is often erroneously cited as the reason ice skates glide on a film of liquid water. As can be seen above, the gradient of the liquid-solid boundary is very steep, and realistic pressures are not sufficient. The actual mechanism for ice skates is more complicated - see, for example, <http://amasci.com/miscon/ice.txt> and <http://www.ccmr.cornell.edu/education/ask/index.html?qid=1138>.