Foundations of Physics 2B/3C 2019-2020

Thermodynamics – Lecture 10 Recap

- Saw examples of Available Energy.
- Were introduced to the concept of irreversibility, and how this relates to the overall Universe Entropy change:

$$I = |W_{rev} - W_{use}| = T_0 \Delta S_U$$

- Were introduced to phases.
- Saw how the Gibbs function describes phases, and how it is conserved in a phase change but its derivative might be discontinuous.

Thermodynamics – Lecture 10 Aims

- To look at examples of first and second order phase changes.
- To be introduced to the Clausius-Clapeyron equation for describing phase boundaries.
- To look at low temperature physics and how to access low temperatures.
- To see how to cool gases via expansion (Joule, Joule-Kelvin).
- To look at adiabatic cooling, both via expansion and demagnetization.

Gibbs function - continuous across phase boundary, but its derivatives may be discontinuous

$$\frac{dG}{dT} = V\frac{dp}{dT} - S\frac{dT}{dT} \qquad \div \text{ by } dT \text{ at constant } p$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad [\text{Lim } dT \to 0]$$

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

$$C_\alpha = T\left(\frac{\partial S}{\partial T}\right)_\alpha$$

$$C_\alpha = \left(\frac{\partial Q}{\partial T}\right)_\alpha \qquad \delta Q = TdS$$

First order changes - solid melting to liquid, liquid to a gas, sublimation
- An applied ~~field~~ magnetic field superconducting to normal conducting phase transition

Second order - Ferromagnet to paramagnetic
- Super conducting to normal conducting when there is no applied field
- Liquid helium to a superfluid

pVT surfaces can be plotted - it looks complicated, so project to a pT or a pV surface
Tend to represent on pT as pressure + temperature to vary in a lab.

Critical Temperature, T_c: Isothermal compression, produces no sharp liquid — vapour transition
System is fluid like, low density fluid to high density.

Triple point, T_3: Single point in phase space were all 3 phases coexist.

Plasma - Fourth phase (ionised atoms). Require extreme conditions + very different to solids, liquids + gases.

Isotherm path $a \to f$

Until **a** - substance is a gas.

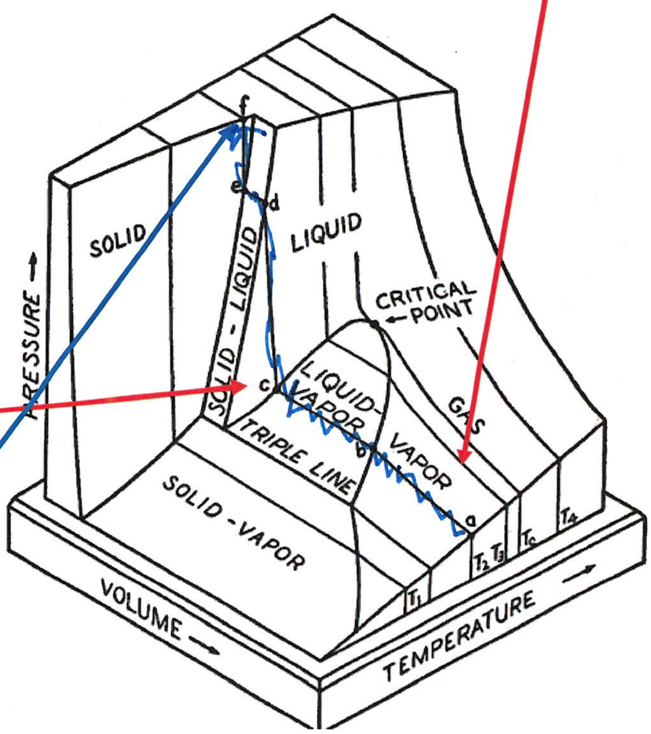
ab – substance becomes a vapour (temperature lower critical

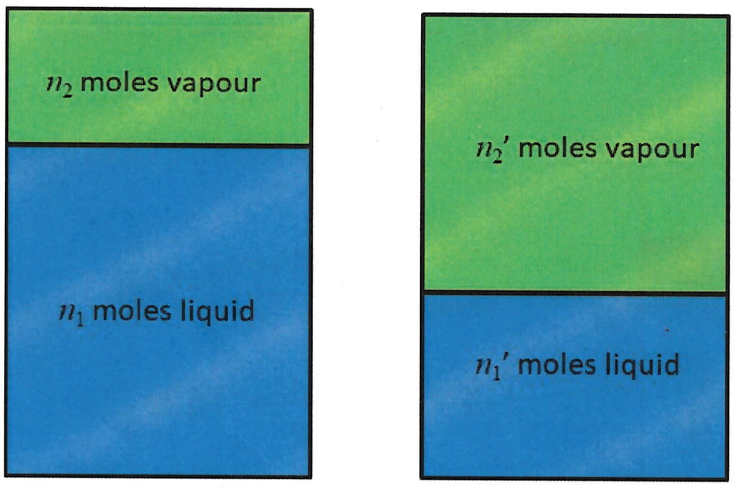
At **b** - substance separates into two phases (liquid and gas) having the same temperature and pressure. The liquid and gas occupy different volumes

At **c** all the material is in liquid phase, until **d**

de –constant pressure freezing.

Above **e**, all the material is solid.





Example 17.1

$$dG = -SdT + Vdp.$$

At a phase change pressure and temperature are constant on either side $dG = 0$ $G_i = G_f$.

Use specific Gibbs functions (per unit mass).

$g = G/n$

Total number mols $N = n_1 + n_2 \equiv n_1' + n_2'$ $[dN = 0]$

Liquid and vapour have Gibbs functions g_1 and g_2 before and g_1', g_2' after the system undergoes a volume change (afterwards have more vapour less liquid).

The total Gibbs functions for each system, before and after the expansion are

$$G = n_1 g_1 + n_2 g_2 \quad ; G' = n_1' g_1' + n_2' g_2'.$$

$n_1 + n_2 = n_1' + n_2'$ (total amount of stuff unchanged) and $G = G'$, $(dG = 0)$

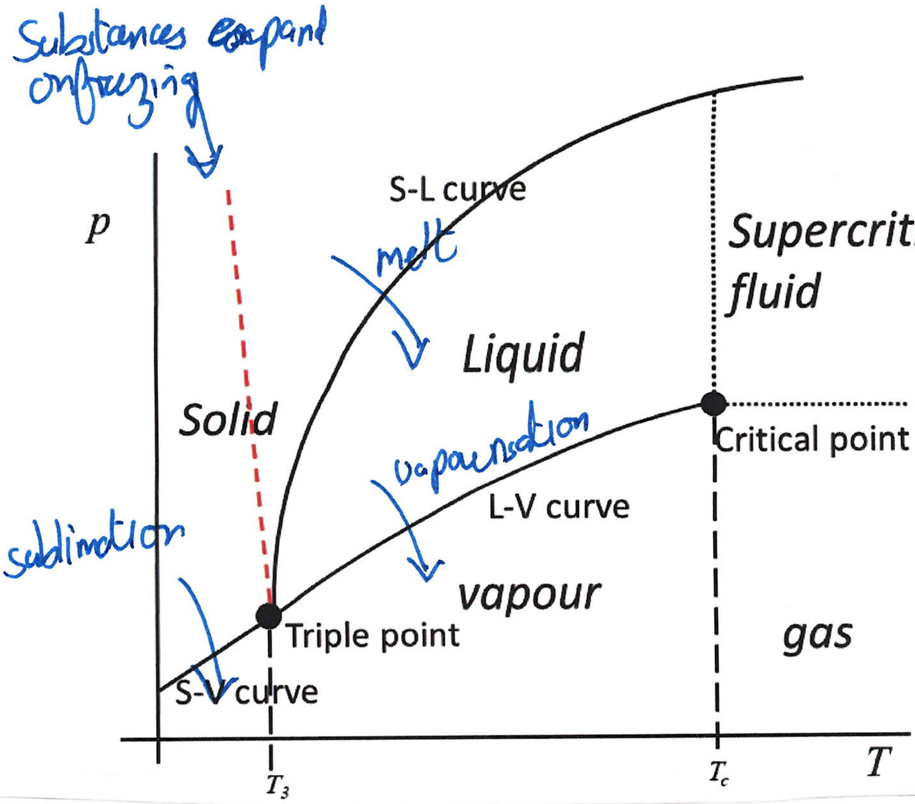
Only satisfied if Gibbs function takes same value in both phases $g_1 = g_2$ and $g_1' = g_2'$.

$dG = g_1 dn_1 + g_2 dn_2$ $\quad dN = 0 \Rightarrow dn_1 = -dn_2$

$0 = g_1 dn_1 - g_2 dn_2 \Longrightarrow g_1 = g_2$

Foundations of Physics 2B/3C 2019-2020

Thermodynamics – Handout 11

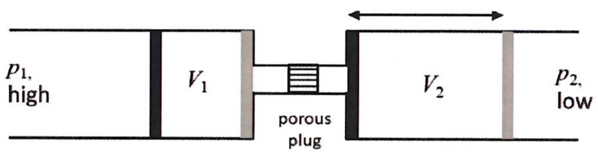


Liquid/gas are a fluid

Below Tc have liquid+gas

Above Tc compressing the fluid doesn't produce condensation

Figure 31: Phase diagram in the pT plane, including showing the positions of the critical and triple points



Constant enthalpy process – change pressure and look at effect on temperature. Want sign of $\left(\frac{\partial T}{\partial p}\right)_H$.

$W = p_1 V_1$, $\qquad\qquad W = -p_2 V_2$.

Internal energy changes from U_1 to U_2.

$$(U_2 - U_1) = p_1 V_1 - p_2 V_2 \quad \Rightarrow \quad U_2 + p_2 V_2 = U_1 + p_1 V_1 \quad \Rightarrow \quad H_2 = H_1.$$

$$\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p \left(\frac{\partial H}{\partial p}\right)_T.$$

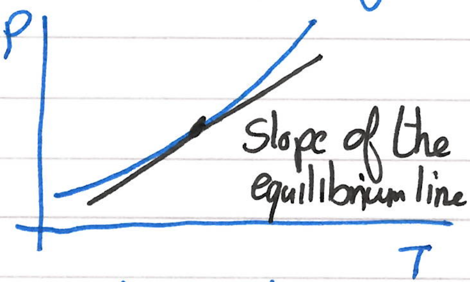
$$H = U + pV \quad \Rightarrow \quad dH = dU + pdV + Vdp = TdS - Vdp.$$

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = V - T\left(\frac{\partial V}{\partial T}\right)_p.$$

$$\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{C_p}\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right].$$

Clausius - Clapeyron equation

What is the slope in the pT plane as move from phase i to phase f.



$$\left(\frac{\partial p}{\partial T}\right)_{i\to f}$$

Start from the first TdS equation

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

Phase change: $S_i \to S_f$; $T = T_0$ so $dT = 0$
$V_i \to V_f$

$$T_0(S_f - S_i) = 0 + T_0\left(\frac{\partial p}{\partial T}\right)_{i\to f}(V_f - V_i)$$

The Latent heat $L = T_0 \Delta S$

$$\frac{L_{i\to f}}{T_0(V_f - V_i)} = \left(\frac{\partial p}{\partial T}\right)_{i\to f}$$

Also find by considering conservation of Gibbs function (on DVD)

Liquid to gas $V_f >> V_i$

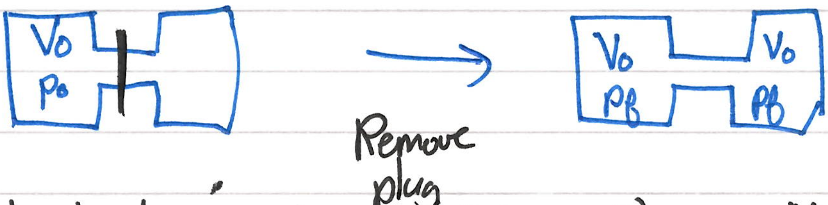
$$\left(\frac{\partial p}{\partial T}\right)_{i\to f} = \frac{L_{i\to f}}{T_0 V_f} \qquad V_f = \frac{RT_0}{p} \text{ [Ideal]}$$

$$= \frac{L_{i\to f}}{RT_0^2/p}$$

$$\int \frac{dp}{p} = \int \frac{L_{i\to f}}{RT^2}\, dT$$

18. Low Temperatures

Cool gas by expanding it, simplest is Joule expansion



$V_0 \to 2V_0$
$p_0 \to p_0/2$

No heat supplied ($\delta Q = 0$); No work ($\delta W = 0$)

1st law $dU = \delta Q + \delta W = 0$

How does temperature with volume at constant internal energy

$$\left(\frac{\partial T}{\partial V}\right)_U = \mu_J$$

Ideal gases have $\mu_J = 0$, so can't cool an ideal gas by Joule expansion ☹

Real gases particles interact, can cool via Joule expansion, but the cooling is minimal.

Joule-Kelvin expansion – cooling at constant enthalpy

$$\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H$$

[If change the pressure at constant enthalpy (H), how does temperature change?]

$$\mu_{JK} = -\frac{1}{C_p}\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] = \left(\frac{\partial T}{\partial p}\right)_H$$

Change pressure $p_1 \to p_2$, what is ΔT?

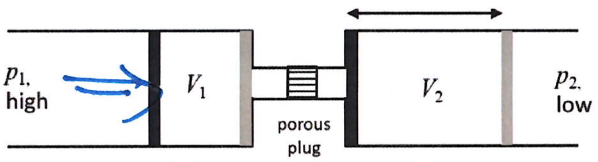
$$\Delta T = \int_{p_1}^{p_2}\left(\frac{\partial T}{\partial p}\right)_H dp = \int -\frac{1}{C_p}\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp$$

Joule-Kelvin can either increase or decrease the temperature depending on the starting pressure.

Adiabatic cooling always cools

Figure 31: Phase diagram in the pT plane, including showing the positions of the critical and triple points

Force gas through plug from high to low pressure



Constant enthalpy process – change pressure and look at effect on temperature. Want sign of $\left(\frac{\partial T}{\partial p}\right)_H$.

$W = p_1V_1$, Force gas by doing positive work $\qquad W = -p_2V_2$. Gas does work on the piston

Internal energy changes from U_1 to U_2. No heat $\delta Q = 0$, $dU = \delta W$

add differential work

$$(U_2 - U_1) = p_1V_1 - p_2V_2 \quad \Rightarrow \quad U_2 + p_2V_2 = U_1 + p_1V_1 \quad \Rightarrow \quad H_2 = H_1.$$

$H = U + pV$

Reciprocity theorem $\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p \left(\frac{\partial H}{\partial p}\right)_T.$

$TdS - pdV$

$$H = U + pV \quad \Rightarrow \quad dH = dU + pdV + Vdp = TdS + Vdp.$$

$\div\, dH$ by dp at constant T

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = V - T\left(\frac{\partial V}{\partial T}\right)_p.$$

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

$C_p = \left(\frac{\partial H}{\partial T}\right)_p$

$$\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{C_p}\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right].$$

[Enthalpy plays same role at constant pressure as the internal energy at constant volume]

In an expansion, pressure always drops

And initial pressure below the inversion point we get a reduction in temperature

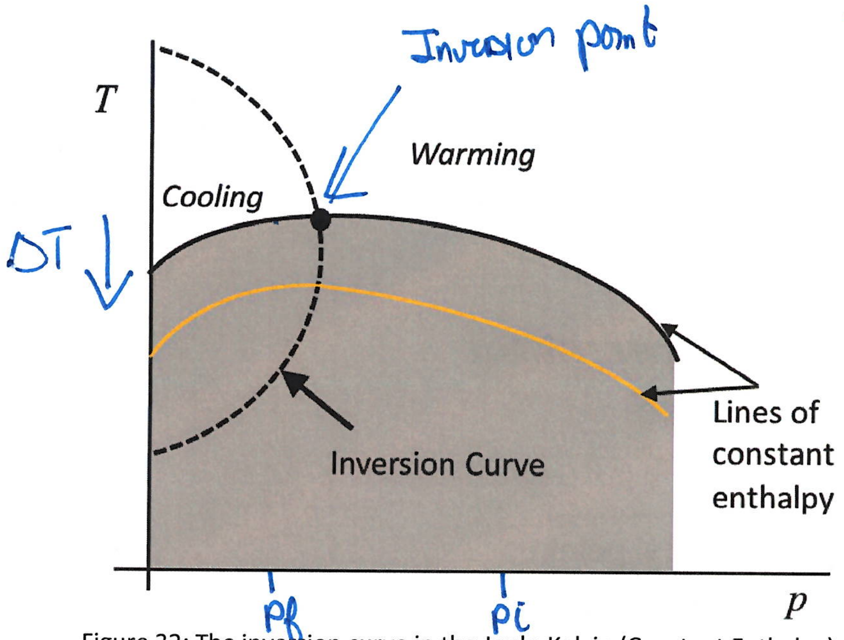


Figure 32: The inversion curve in the Joule-Kelvin (Constant Enthalpy) expansion.

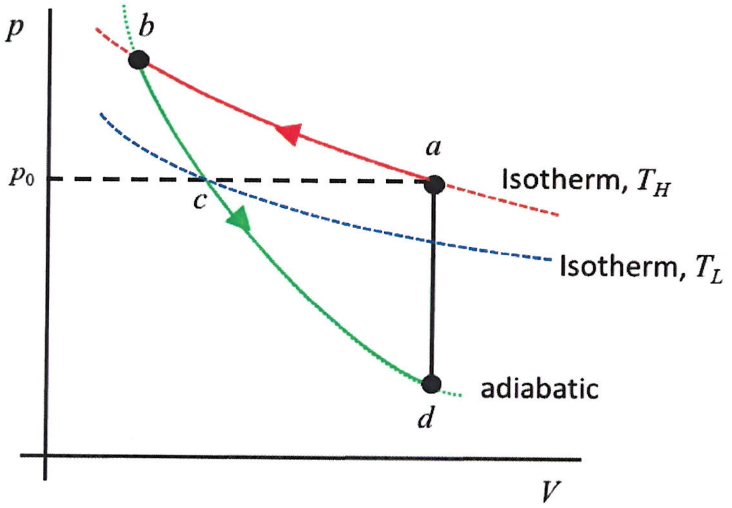


Figure 33: pV diagram for an adiabatic cooling process via expansion.

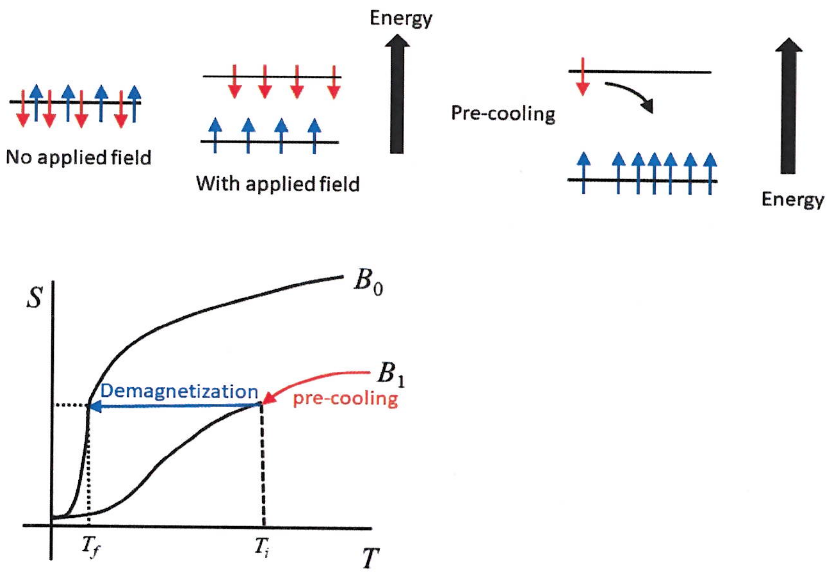


Figure 34: Adiabatic demagnetisaton: both the process and the TS diagram.