Foundations of Physics 2B/3C 2019-2020

Thermodynamics – Lecture 11 Recap

- Looked at examples of first and second order phase changes
- Were introduced to the Clausius-Clapeyron equation for describing phase boundaries

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

- To look at low temperature physics and how to access low temperatures.
- To see how to cool gases via expansion (Joule, Joule-Kelvin).

Thermodynamics – Lecture 12 Aims

- To look at adiabatic cooling, both via expansion and demagnetization.
- To be introduced to the Third Law of Thermodynamics.
- To look at example of Thermodynamics in action, including elastic rods and real gases
- To review Thermodynamics.

Cooling – Joule expansion (free), very small ΔT
– Jole Kelvin (constant enthalpy), cooling if below inversion temperature
– Adiabatic cooling, constant energy, amount of cooling decreases with T

Cool to 4.2K
– Dilution refrigeration
– Adiabatic demagnetisation
– Laser cooling gives coldest temperatures.

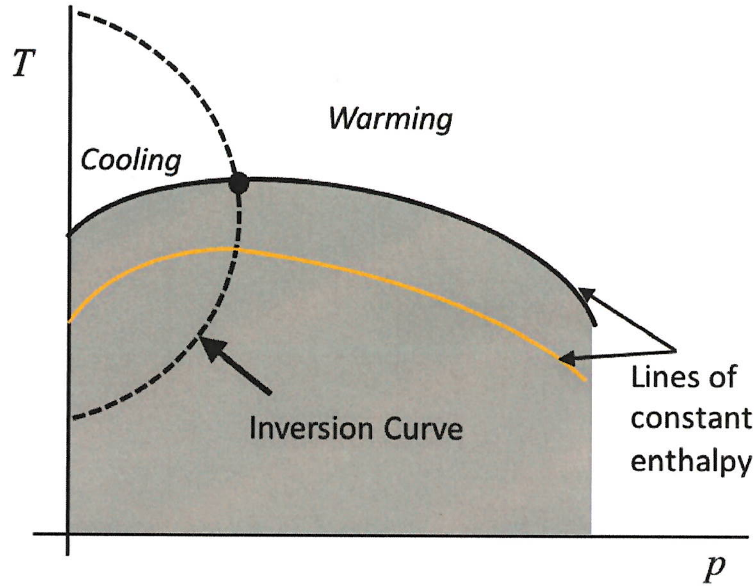


Figure 32: The inversion curve in the Joule-Kelvin (Constant Enthalpy) expansion.

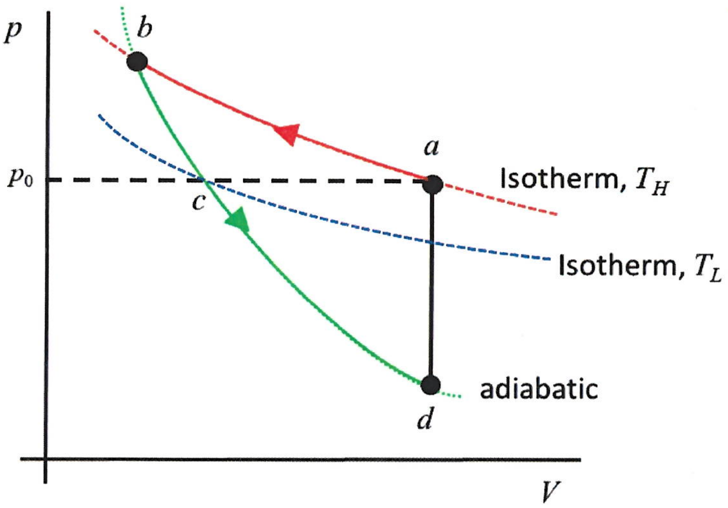


Figure 33: pV diagram for an adiabatic cooling process via expansion.

Isothermal compression $a \to b$
Adiabatic expansion $b \to c$
Adiabatic steeper than isotherm, so return at lower temperature

Isotherms closer together as $T \to 0$
[Always reduces temp]

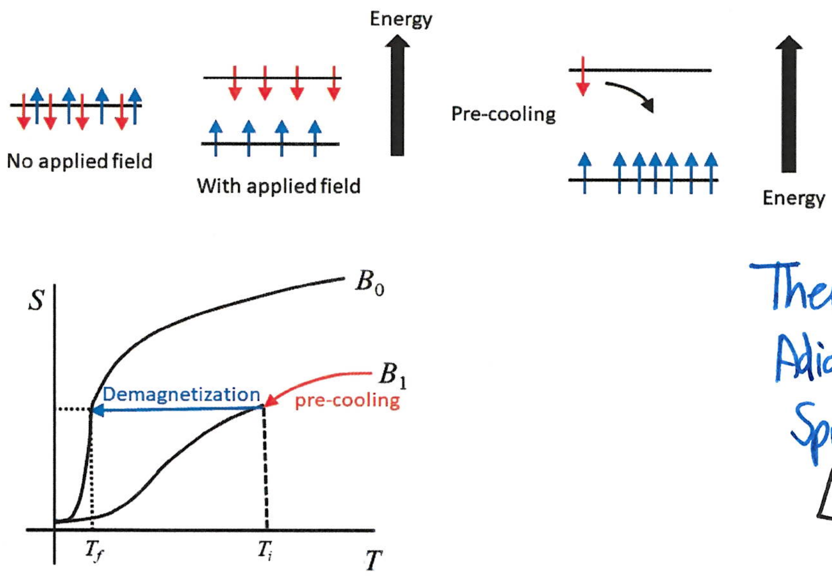


Figure 34: Adiabatic demagnetisaton: both the process and the TS diagram.

Magnetic material in field at ~1K.
Field means most spins are up (energetically favourable)

Thermally isolated magnetic material
Adiabatically remove field.
Spin alignment becomes random
[Spin entropy increases]

$\Delta S_{tot} = 0$, so magnetic material entropy has decreased

Less ordered ~~material~~ spins, so molecules holding spins more ordered
More order = Lower temperature

19. Third Law of Thermo

Second law gives entropy changes between states

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \qquad \Delta S = \int_{T_1}^{T_2} \frac{C_p\,dT}{T} = S(T_0) + \int_{T_0}^{T_2} \frac{C_p\,dT}{T}$$

What is $S(T_0)$? — Statistically $S = k_B \ln \Omega$
— Classically define entropy at some temperature
$T = 0\,K \qquad S = 0$

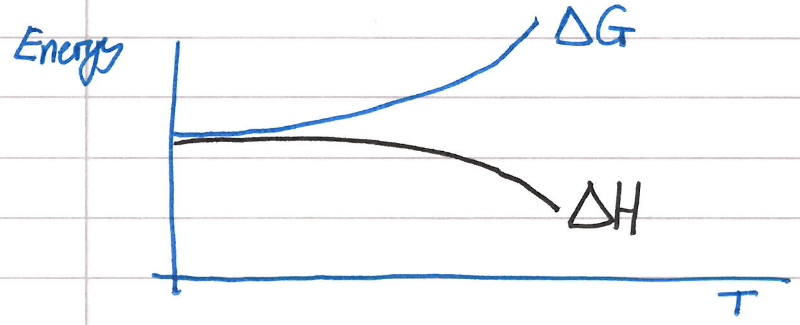
Nernst noted $\Delta H < 0$ exothermic
$\Delta H > 0$ endothermic

$$H = U + pV \qquad dH = TdS + Vdp$$
$$= TdS \equiv \delta Q \quad \text{if } dp = 0$$

Gibbs function $G = U + pV - TS$ is minimised ($\Delta G = G_f - G_i < 0$) to give the max non-mechanical work

Constant temp $G = H - TS$
$$\Delta G = \Delta H - T_0 \Delta S$$

To minimise ΔG maximise $\Delta S > 0$



At low T would expect $\Delta G \to \Delta H$

Experimentally happens asymptotically
$\Delta S \to 0$!

Nernst stated 'Entropy tends to zero, for a system in internal equilibrium near absolute zero.

$$\lim_{T\to 0}\left(\frac{\partial \Delta G}{\partial T}\right)_p = 0 = \lim_{T\to 0}\left(\frac{\partial \Delta H}{\partial T}\right)_p$$ Slopes of $\Delta G, \Delta H$

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

$$G = H - TS = H + T\left(\frac{\partial G}{\partial T}\right)_p$$

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_p$$

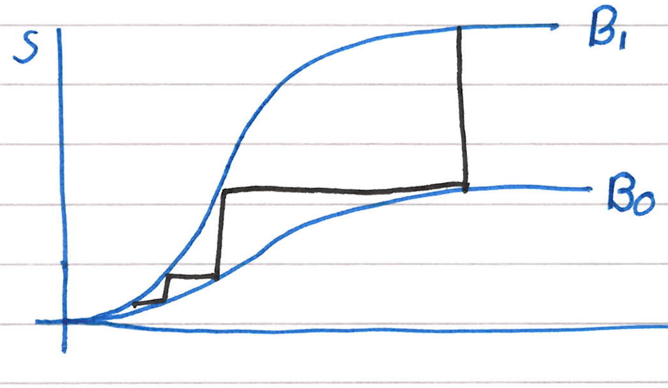
As $\Delta G, \Delta H \to 0$ as $T \to 0$ $\qquad \lim_{T\to 0} T\left(\frac{\partial \Delta G}{\partial T}\right)_p = 0$

$$\lim_{T\to 0} T\left[\left(\frac{\partial G_{II}}{\partial T}\right)_p - \left(\frac{\partial G_I}{\partial T}\right)_p\right] = -\lim_{T\to 0}(S_2 - S_1)$$

$$S_2 \to S_1 \to \Delta S \to 0$$

Planck strengthened to at $T = 0$, $S = 0$

Consequences: Heat capacities $\to 0$ as $T \to 0$
Thermal expansion stops
Gases don't remain ideal.
Can't get to absolute zero (in a finite number of steps)



B_1, B_0 approach as $T \to 0$
$\Delta T \to 0$

20. Thermodynamics in action

Potential pV, Yx — Y intensive force (p), x extensive displacement (V)

Work $\delta W = -p\,dV$

Rod length x under tension f — $\delta W = +f\,dx$, Potential $-fx$

Can consider real gases

$$pV = RT \longrightarrow \left(p + \frac{a}{V^2}\right)(V - b) = RT$$

Molecular interactions

Gas molecules are not point particles

Virial expansion $\frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{T^2} + \ldots$

Can calculate $\left(\frac{\partial p}{\partial V}\right)_T$, $\left(\frac{\partial V}{\partial T}\right)_p$ ....

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Thermodynamics – Handout 12

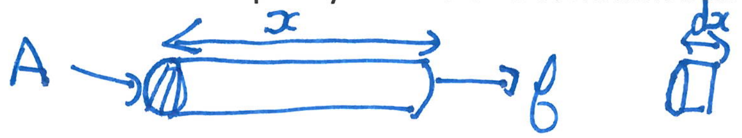
19.2 $$C_\alpha = T\left(\frac{\partial S}{\partial T}\right)_\alpha \quad \Rightarrow \quad \Delta S(p,T) = \int_{T_1}^{T_2} \frac{C_p dT}{T} \quad = C_P(\ln(T_2) - \ln(T_1)).$$

$$\lim_{T_1 \to 0} (\ln(T_1)) \to -\infty$$

Cp goes to zero more quickly to prevent 'blow-up'

Must have a heat capacity of zero or a contradiction of Nernst's theorem!

20.1



A rod of area, A, length x is placed under tension, f, which extends it by dx at constant temperature,.

Young's modulus, $E_T = \frac{Stress}{Strain}$, stress $\sigma = \frac{df}{A}$ strain, $\epsilon = \frac{dx}{x}$.

$$E_T = \left(\frac{df}{A} \div \frac{dx}{x}\right)_T \qquad E_T = \frac{x}{A}\left(\frac{\partial f}{\partial x}\right)_T.$$

Expansivity at constant temperature $\alpha_f = {}^1/_x \left({}^{\partial x}/_{\partial T}\right)_f$.

$\alpha_f > 0$, apart from rubber $\alpha_f < 0$

dependent

independent

How does tension in wire ~~change~~ at constant length change with temperature?

$$\left(\frac{\partial f}{\partial T}\right)_x = -\left(\frac{\partial f}{\partial x}\right)_T \left(\frac{\partial x}{\partial T}\right)_f = -\frac{E_T A}{x}\alpha_f x = -E_T A \alpha_f.$$

$$\Delta T > 0 \Rightarrow \Delta f < 0 \text{ if } \alpha_f > 0$$

Consider $F = U - TS$, $dF = dU - TdS - SdT \quad \Rightarrow \quad dF = +f dx - SdT$. $F = F(x,T)$

$$dU = TdS + f dx \qquad dF = \left(\frac{\partial F}{\partial x}\right)_T dx + \left(\frac{\partial F}{\partial T}\right)_x dT$$

Helmholtz exact
$$\left(\frac{\partial^2 F}{\partial T \partial x}\right) = \left(\frac{\partial^2 F}{\partial x \partial T}\right) \quad \left(\frac{\partial f}{\partial T}\right)_x = -\left(\frac{\partial S}{\partial x}\right)_T.$$

Experimentally, tension, f at constant length depends on temperature, $f = kT$.

$$\left(\frac{\partial f}{\partial T}\right)_x = k$$

Entropy change with length at constant temperature

$$\int \left(\frac{\partial S}{\partial x}\right)_T dx = \Delta S = -\int \left(\frac{\partial f}{\partial T}\right)_x dx = -\int_{x_1}^{x_2} k dx = -k(x_2 - x_1).$$

Stretching band, $x_2 > x_1$, decreases entropy! More ordered.

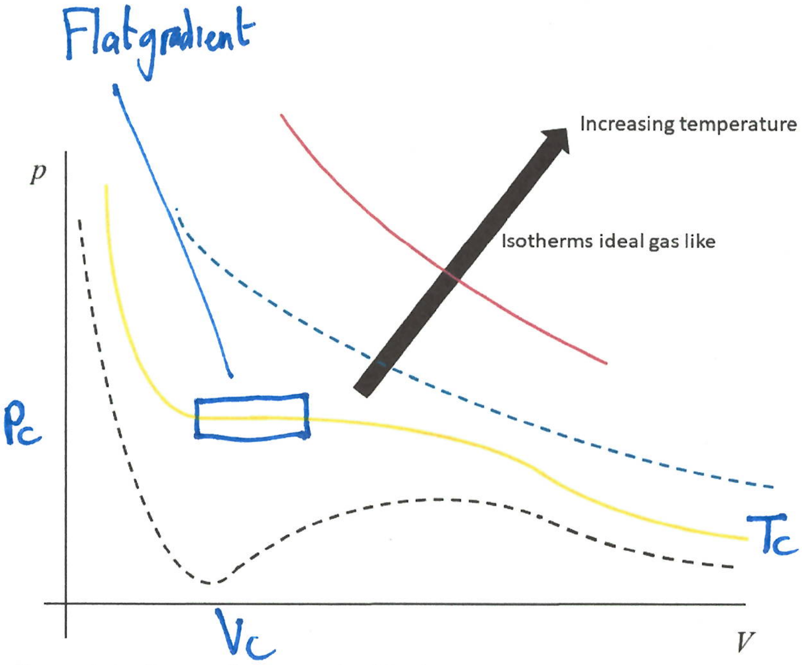


Figure 1: Isotherms for a van der Waals gas

Isotherms go from ideal gas shaped in top right, to 'S' shape at low volume and pressure.

$\left(\frac{\partial p}{\partial V}\right)_T$ isotherm gradient

Effect on isothermal compressibility, $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$?

For an Ideal gas, $\kappa_T > 0$ since $\left(\frac{\partial V}{\partial p}\right)_T < 0$ always.

Van der Waals gas

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

At critical point, (p_c, T_c, V_c) $\longrightarrow$ Point of inflection

$$\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0.$$

Below T_c $\left(\frac{\partial p}{\partial V}\right)_T > 0$ so $\kappa_T < 0$!

Pressurise gas $\Delta p > 0$ must accompanied by $\Delta V > 0$

Gas is unstable!

~~For van der Waals, below T_c, $\left(\frac{\partial p}{\partial V}\right)_T > 0$ so $\kappa_T < 0$!~~

Small change in pressure gets amplified.