

# PHYS1013

## Energy and Matter

$U_i (n_i, P_i, V_i, \dots)$   $\rightarrow$   $U_f (n_f, P_f, V_f, \dots)$

$W = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln\left(\frac{V_f}{V_i}\right)$

$H = U + pV$   $T(K) = T(^{\circ}C) + 273.15$

$dH = dU + d(pV)$   $dH = dU + pdV + Vdp$

$C_p = (\Delta H / \Delta T)_p$   $\Delta U = Q - W$


$C_p = \left(\frac{\partial H}{\partial T}\right)_p$   $W = P\Delta U$   $\Delta S = nRT \ln\left(\frac{V_f}{V_i}\right)$

$dU = dq + dw$   $dH = dq - pdV + Vdp$   $W = \int_{V_1}^{V_2} P dV$


$H = U + PV$   $dH = C_p dT$   $\Delta H = q_p = C_p \Delta T$   $C_v = (\Delta U / \Delta T)_v$

$dw = -pdv$   $\Delta S = \frac{\Delta_{\text{rev}} H}{T}$   $ds \geq \frac{dq}{T}$

$C_v = \left(\frac{\partial U}{\partial T}\right)_v$



$\Delta U = m(u_2 - u_1) \Delta KE$   
 $= \frac{1}{2} m (v_2^2 - v_1^2) \Delta PE$   
 $= mg(z_2 - z_1)$



$W_b = \frac{P_2 V_2 - P_1 V_1}{1 - \gamma}$   $\eta_{th} = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$

$dH = dq + Vdp$   $\Delta H = \Delta U + V\Delta p$


$Q = \Delta U + P\Delta V$

$dH = (dq)_p$   $\Delta H = q_p$   $T_R = \frac{T}{T_{cr}}$   $dU = C_v dT$

$dU = (dq)_v$   $\Delta U = q_v$   $\Delta U = q_v = C_v \Delta T$

$P_{cr} = \frac{P}{P_{cr}}$   $W_b = P_1 V_1 \ln \frac{V_2}{V_1}$   $= P_1 V_1 \ln \frac{P_1}{P_2} = RT_1 \ln \frac{P_1}{P_2}$

$\Delta U = U_f - U_i = q(\text{heat}) + w(\text{work})$



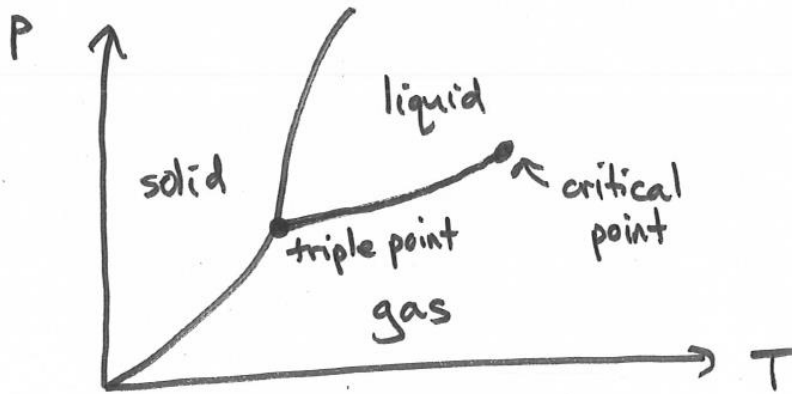
$\gamma_k = \frac{V_{cr}}{RT_{cr}}$

**Thermodynamics**



# PHASES OF MATTER & PHASE CHANGES

A typical phase diagram:



assume we are sat on a phase boundary.

$$G = m_1 g_1 + m_2 g_2$$

$$dg = 0$$

$$dm_1 = -dm_2$$

$$g_1 = g_2$$

# CLAUSIUS - CLAPYRON EQUATION

& we move in T, P but wish to stay on the boundary  $\Rightarrow dq_1 = dq_2$

$$-s_1 dT + v_1 dP = -s_2 dT + v_2 dP$$

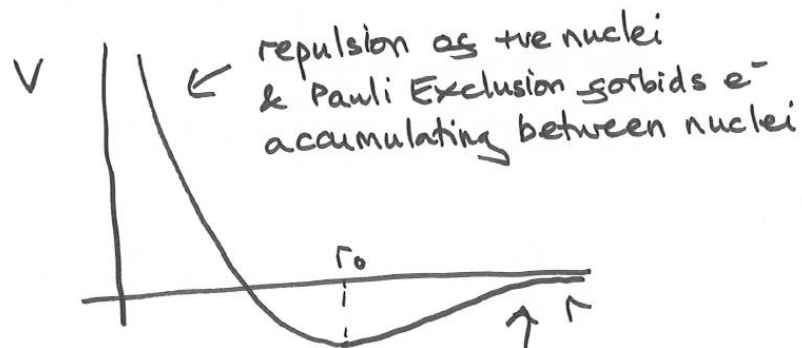
$$\Rightarrow \frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$$

$$\frac{dP}{dT} = \frac{L}{T(v_2 - v_1)}$$

$$dq_i = \bar{s}_i dT + v_i dP$$

$$dS = L/T$$

## MODELLING INTER-ATOMIC FORCES



$$F = - \frac{dV}{dr}$$

# VAN DER WAALS GASES

we remove the volume of the  $N$  atoms  
( $b$ )

attractions between molecules tend to reduced pressure

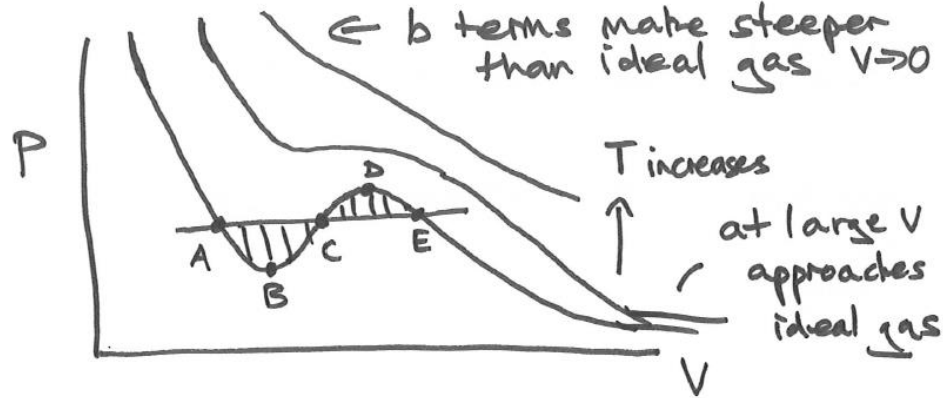
number of collisions  $\propto$  density  $N/V$

attractive force  $\propto$  density too

$$\Rightarrow \Delta P \propto N^2/V^2$$

$$\left(P + \frac{N^2 a}{V^2}\right) (V - Nb) = NkT$$

Isotherms:



A & E are two different  $V$  i.e. different density states  
 $\rightarrow$  liquid & gas

there is a critical point where  
 $\left(\frac{\partial P}{\partial V}\right)_T = 0$  "point of inflection"

What about c?

the ~~pressure~~ volume rises the ~~volume~~ pressure goes up.

it's unstable



B3. The equation of state for a van der Waals gas is given by

$$\left(P + N^2 \frac{a}{V^2}\right) (V - Nb) = NkT$$

Where  $k$  is Boltzmann's constant,  $N$  is the number of molecules,  $P$  pressure,  $V$  volume and  $T$  temperature.

(a) What is the physical model that underlies each of the two parameters  $a$  and  $b$  and why do they enter with the other parameters as shown? [ 3 ]

(b) Show, by directly differentiating the equation of state, in the form above, with respect to  $V$ , that the turning points of isotherms in the  $PV$  plane lie on the curve

$$P = \frac{N^2 a}{V^2} - \frac{2N^3 ab}{V^3} \quad [ 3 ]$$

(c) Show that the maximum of the curve in (b) is given when  $V = 3Nb$  and hence for this point  $P = a/27b^2$  and  $T = 8a/27kb$ . [ 6 ]

(d) Sketch the isotherms of the van der Waals gas on a  $PV$  diagram. [ 3 ]

(e) Explain carefully why the model predicts the existence of two different density states at some  $P, T$  values. How can these phases be interpreted? [ 3 ]

(f) Explain the physical significance of the point identified in (c). [ 2 ]



**B4.** The Clausius-Clapeyron equation for the slope of a phase boundary in the P–T plane of a simple substance is given by

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}.$$

(a) For a gas-liquid transition at low pressure, show that the Clausius-Clapeyron equation can be written as

$$\frac{dP}{dT} = \frac{LP}{RT^2},$$

where  $L$  is the molar latent heat. What approximation was needed? [ 6 ]

(b) Use the Clausius-Clapeyron equation obtained for a gas-liquid transition to show that the vapour pressure of a material has the approximate functional form

$$P_v(T) = P_0 \exp(-L/RT).$$

[ 6 ]

State the key assumption for this result.

(c) The latent heat of vaporisation of water is approximately  $L = 40.8 \text{ kJ mol}^{-1}$ . Given the fact  $P_0 \approx P_{\text{atm}} \exp(12.86)$ , find the pressure of water vapour on the coexistence curve at  $T = 25^\circ\text{C}$  in terms of  $P_{\text{atm}}$ . [ 2 ]

(d) On a summer day the temperature at midday is  $T = 25^\circ\text{C}$  and the relative humidity is found to be 50 %, that is, the partial pressure of water vapour is measured to be half of the value found above. As the evening comes, the temperature falls and reaches the point  $T_D$  (called the *dew point*) where condensation starts. Assuming that the amount of water vapour in air has not changed since midday, what is  $T_D$ ? [ 6 ]





1 more MP to go

Exam 2:30-4:30pm 25<sup>th</sup> May

Section A (do all - 1/3<sup>rd</sup> of marks)

+ Section B (2 from 3 – 2/3rds of marks)

No formula sheet – there is a constants sheet

(see <https://www.southampton.ac.uk/~evans/PHYS1013>)

Good luck!