

# Statistical and Thermal Physics



## Second year physics course

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(with thanks to Prof. S. J. Blundell)

## Problem Set 8

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### Some useful constants

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Boltzmann's constant	$k_B$	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Stefan's constant	$\sigma$	$5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$
Proton rest mass	$m_p$	$1.6726 \times 10^{-27} \text{ kg}$
Bohr magneton	$\mu_B$	$9.274 \times 10^{-24} \text{ J T}^{-1}$
Avogadro's number	$N_A$	$6.022 \times 10^{23} \text{ mol}^{-1}$
Standard molar volume		$22.414 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$
Molar gas constant	$R$	$8.315 \text{ J mol}^{-1} \text{ K}^{-1}$
1 pascal (Pa)		$1 \text{ N m}^{-2}$
1 standard atmosphere		$1.0132 \times 10^5 \text{ Pa (N m}^{-2}\text{)}$
1 bar (= 1000 mbar)		$10^5 \text{ N m}^{-2}$

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## PROBLEM SET 8: Real gases, expansions and phase equilibria

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Problem set 8 can be covered in 1 tutorial. The relevant material will be covered in lectures by the end of week 5

### Real gases

8.1 A gas obeys the equation  $p(V - b) = RT$  and has  $C_V$  independent of temperature. Show that (a) the internal energy is a function of temperature only, (b) the ratio  $\gamma = C_p/C_V$  is independent of temperature and pressure, (c) the equation of an adiabatic change has the form  $p(V - b)^\gamma = \text{constant}$ .

8.2 Dieterici's equation of state for 1 mole is

$$p(V - b) = RTe^{-a/RTV}. \quad (1)$$

(a) Show that the critical point is specified by

$$T_c = a/4Rb; \quad V_c = 2b; \quad p_c = a/4e^2b^2.$$

(b) Show that equation (1) obeys a *law of corresponding states*, i.e. show that it can be written in reduced units as

$$\tilde{p}(2\tilde{V} - 1) = \tilde{T} \exp \left[ 2 \left( 1 - \frac{1}{\tilde{T}\tilde{V}} \right) \right],$$

where  $\tilde{p} = p/p_c$ ,  $\tilde{T} = T/T_c$ ,  $\tilde{V} = V/V_c$ .

### Real gas expansions

8.3 Explain why enthalpy is conserved in a Joule–Kelvin process. Show that the Joule–Kelvin coefficient may be written

$$\mu_{\text{JK}} = \left( \frac{\partial T}{\partial P} \right)_H = \frac{1}{C_P} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right].$$

The equation of state for helium gas may be expressed as a virial expansion

$$pV = RT \left( 1 + \frac{B}{V} + \dots \right)$$

in which  $B$  is a function of temperature only. The table below gives some values of  $B$  for 1 mole of helium. Determine the Boyle temperature and the inversion temperature.

Temperature (K)	10	20	30	40	50	60	70
$B \text{ (cm}^3 \text{ mol}^{-1}\text{)}$	-23.3	-4.0	2.4	5.6	7.6	8.9	9.8

8.4 For a van der Waals gas, show that

$$\lim_{p \rightarrow 0} \mu_{JK} = \frac{1}{C_p} \left( \frac{2a}{RT} - b \right) \quad \text{and} \quad T_i^{\max} = \frac{2a}{Rb},$$

where  $T_i^{\max}$  is the maximum inversion temperature.

8.5\* Prove that the equation of the inversion curve of a Dieterici gas is, in reduced units,

$$\tilde{p} = (8 - \tilde{T}) \exp \left( \frac{5}{2} - \frac{4}{\tilde{T}} \right),$$

and sketch it in the  $\tilde{p}$ - $\tilde{T}$  plane. Hence, show that the maximum inversion temperature is  $T_i^{\max} = 2a/(Rb)$ .

### Phase equilibria

8.6 When lead is melted at atmospheric pressure the melting point is 327.0°C, the density decreases from  $11.01 \times 10^3$  to  $10.65 \times 10^3$  kg m<sup>-3</sup> and the latent heat is 24.5 kJ kg<sup>-1</sup>. Estimate the melting point of lead at a pressure of 100 atm.

8.7 Some tea connoisseurs claim that a good cup of tea cannot be brewed with water at a temperature less than 97°C. Assuming this to be the case, is it possible for an astronomer, working on the summit of Mauna Kea in Hawaii (elevation 4194 m) where the air pressure is 615 mbar, to make a good cup of tea without the aid of a pressure vessel?

[Latent heat of vaporisation of water = 40.7 kJ mol<sup>-1</sup>.]

8.8 (a) Show that the temperature dependence of the latent heat of vapourisation  $L$  of an incompressible liquid is given by the following expression:

$$\frac{dL}{dT} = \frac{L}{T} + \Delta C_p - \frac{L}{V_{\text{vap}}} \left( \frac{\partial V_{\text{vap}}}{\partial T} \right)_p,$$

where  $\Delta C_p = C_{p,\text{vap}} - C_{p,\text{liq}}$ .

(b) Treating the vapour as an ideal gas, and assuming  $\Delta C_p$  is independent of temperature, show that  $L = \Delta C_p T + L_0$ .

(c) Show further that when the saturated vapour is expanded adiabatically, some liquid condenses out if

$$C_{p,\text{liq}} + T \frac{d}{dT} \left( \frac{L}{T} \right) < 0.$$

[Hint: For condensation, what is the condition on  $\left( \frac{\partial p}{\partial T} \right)_S$  in relation to the gradient of the liquid–vapour phase boundary in the  $p$ - $T$  plane?]