

Statistical Physics Exam

23rd April 2014

Name	Student Number

Problem 1	Problem 2	Problem 3	Problem 4	Total	Percentage	Mark

Useful constants

gas constant R	$8.31 J / (K \cdot mol)$
Boltzmann constant k_B	$1.38 \cdot 10^{-23} J / K$
Avogadro number N_A	$6.02 \cdot 10^{23} mol^{-1}$
speed of light c	$300 \cdot 10^6 m / s$
Planck's constant h	$6.63 \cdot 10^{-34} J \cdot s$

Problem 1 (25P)

- 1) (2P) Which thermodynamic potential becomes minimal in equilibrium in each of the following situations:
 - at constant number of particles, constant temperature, and constant volume. Helmholtz free energy \mathcal{F}
 - at constant number of particles, constant temperature, and constant pressure. Gibbs free energy \mathcal{G}
- 2) (3P) Consider two gas chambers A and B which are in contact. In equilibrium, which thermodynamic quantities are the same in A and B if
 - a) the systems can exchange heat. Temperature
 - b) the systems can exchange particles. Chemical potential
 - c) the wall between the two systems can move. Pressure
- 3) (4P) Write down the four steps of a Carnot cycle. How do the entropy and temperature change in each step?
 - a) ...Isothermic...expansion $\Delta T = 0$; $\Delta S > 0$
 - b) ...Adiabatic... expansion $\Delta T < 0$; $\Delta S = 0$
 - c) ...Isothermic...compression $\Delta T = 0$; $\Delta S < 0$
 - d) ...Adiabatic... compression $\Delta T > 0$; $\Delta S = 0$

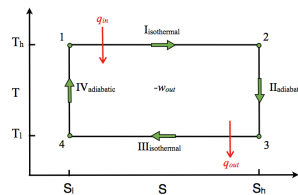


Figure 1: Carnot cycle

- 4) (3P) How do vapour pressure, boiling temperature, and melting temperature of a mixture change compared to the pure liquid?
Vapour pressure decreases, boiling temperature increases, melting temperature decreases.
- 5) (2P) Which corrections does the van-der-Waals gas introduce compared to the ideal gas?
Particles can interact: a represents the attraction between the particles, b the excluded volume:
 $(p + \frac{a}{v^2})(v - b) = kT$
- 6) (2P) How do energy and heat capacity of an ideal monoatomic gas depend on temperature?
Energy $E = \frac{3}{2}Nk_B T$; Heat Capacity $C_v = \frac{3}{2}Nk_B$; $C_p = \frac{5}{2}Nk_B$ (N : number of atoms; k_B : Boltzmann constant)
- 7) (4P) A system has three energy levels, the first of which with $E_1 = \varepsilon_1$, is non-degenerate, the second with $E_2 = 2\varepsilon_1$ is twofold-degenerate, and the third one with $E_3 = 3\varepsilon_1$ is threefold degenerate. Write down the microcanonical partition function of a classical three-particle system for $E_{tot} = 4\varepsilon_1$. $\Omega = \sum_{E_{tot}} = 4\varepsilon_1$

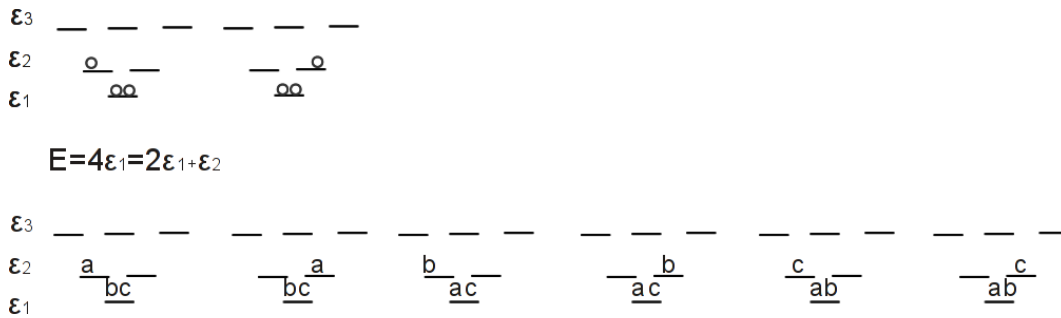


Figure 2: Possible states with $E_{tot} = 4\epsilon_1$. Top: Particles non-distinguishable $\Omega = 2$ Bottom: Particles distinguishable $\Omega = 6$

8) (1P) How does the entropy change in an irreversible process?

Entropy increases.

9) (4P) Sketch the Maxwell-Boltzmann distribution of velocities $p(|v|)$ for an ideal gas. What is larger: the average velocity or the most probable velocity?

The Maxwell-Boltzmann distribution for the speed is depicted as below,

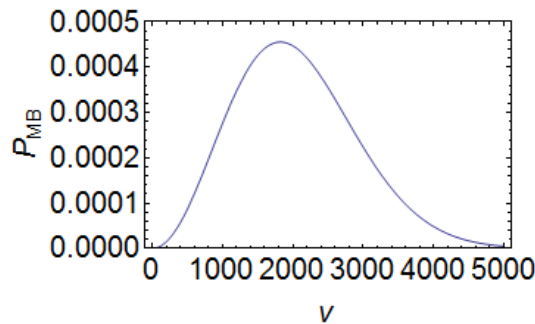


Figure 3: The Maxwell-Boltzmann distribution for the speed

The average speed is larger than the most probable speed.

Problem 2 (25P)

Consider a system of N spins subject to a magnetic field B . The spins are non-interacting with the spin number $s = 1$, distinguishable, and have the non-degenerated energy eigenvalues $\epsilon_m = -\mu B m$ per one spin, where μ is the magnetic moment per one spin, and $m = -1, 0, 1$.

a) (5 points): Calculate the partition function Z_N .

The single-spin partition function Z_1 :

$$\begin{aligned} Z_1 &= \sum_{m=-1}^1 e^{\beta\mu B m} \\ &= 1 + \underbrace{e^{\beta\mu B} + e^{-\beta\mu B}}_{2 \cosh(\beta\mu B)} \\ &= 1 + 2 \cosh(\beta\mu B). \end{aligned} \tag{1}$$

The N -spin partition function Z_N simply leads to

$$\begin{aligned} Z_N &= Z_1^N \\ &= \boxed{[1 + 2 \cosh(\beta\mu B)]^N}. \end{aligned} \tag{2}$$

$$\text{or} = \boxed{[1 + e^{\beta\mu B} + e^{-\beta\mu B}]^N}. \tag{3}$$

b) (5 points): Calculate the average energy E (2 points). For this, you may calculate E using Z_N , or you may calculate E from the average of the total energy eigenvalues. The average energy is a monotonically increasing function of $k_B T$: Find two asymptotic values of E in the limit of $T \rightarrow 0$ and $T \rightarrow \infty$ (2 points), and sketch $E(k_B T)$ (1 point).

The average energy E :

$$\begin{aligned} E &= - \left[\frac{\partial \ln(Z_N)}{\partial \beta} \right]_{N,V} \\ &= \boxed{- \frac{2N\mu B \sinh(\beta\mu B)}{1 + 2 \cosh(\beta\mu B)}}. \end{aligned} \tag{4}$$

$$\text{or} = \boxed{N\mu B \frac{e^{-\beta\mu B} - e^{\beta\mu B}}{1 + e^{\beta\mu B} + e^{-\beta\mu B}}}. \tag{5}$$

or, using the average of the total energy eigenvalues,

$$\begin{aligned} E &= N \langle -\mu B m \rangle \\ &= N \frac{\sum_{m=-1}^1 -\mu B m e^{\beta\mu B m}}{\sum_{m=-1}^1 e^{\beta\mu B m}} \\ &= \boxed{- \frac{2N\mu B \sinh(\beta\mu B)}{1 + 2 \cosh(\beta\mu B)}} \\ \text{or} &= \boxed{N\mu B \frac{e^{-\beta\mu B} - e^{\beta\mu B}}{1 + e^{\beta\mu B} + e^{-\beta\mu B}}}. \end{aligned}$$

For $T \rightarrow 0$:

$$\boxed{E \rightarrow -N\mu B.} \quad (6)$$

For $T \rightarrow \infty$:

$$\boxed{E \rightarrow 0.} \quad (7)$$

1 point: The average energy is plotted as below:

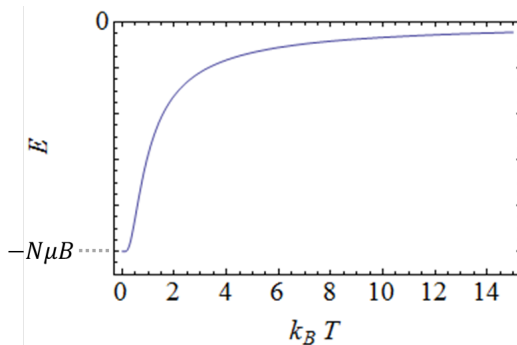


Figure 4: The average energy E as a function of $k_B T$

c) **(6 points):** Sketch the heat capacity $C_B(k_B T)$. For this, you may calculate C_B using E , or you may calculate C_B using the energy fluctuations, or you may use the sketch of $E(k_B T)$.

The heat capacity C_B :

$$\begin{aligned} C_B &= \left[\frac{\partial E}{\partial T} \right]_B \\ &= \frac{2B^2 \mu^2 N \cosh\left(\frac{B\mu}{k_B T}\right)}{k_B T^2 \left(2 \cosh\left(\frac{B\mu}{k_B T}\right) + 1\right)} - \frac{4B^2 \mu^2 N \sinh^2\left(\frac{B\mu}{k_B T}\right)}{k_B T^2 \left(2 \cosh\left(\frac{B\mu}{k_B T}\right) + 1\right)^2} \\ &= \boxed{\frac{2N\mu^2 B^2 \left(2 + \cosh\left(\frac{\mu B}{k_B T}\right)\right)}{k_B T^2 \left(1 + 2 \cosh\left(\frac{\mu B}{k_B T}\right)\right)^2}}. \end{aligned} \quad (8)$$

or, using the energy fluctuations,

$$\begin{aligned} C_B &= \frac{\langle \Delta E^2 \rangle}{k_B T^2} = N^2 \frac{\langle (-\mu B m)^2 \rangle - \langle -\mu B m \rangle^2}{k_B T^2} \\ &= \frac{2B^2 \mu^2 N \cosh\left(\frac{B\mu}{k_B T}\right)}{k_B T^2 \left(2 \cosh\left(\frac{B\mu}{k_B T}\right) + 1\right)} - \frac{4B^2 \mu^2 N \sinh^2\left(\frac{B\mu}{k_B T}\right)}{k_B T^2 \left(2 \cosh\left(\frac{B\mu}{k_B T}\right) + 1\right)^2} \\ &= \boxed{\frac{2N\mu^2 B^2 \left(2 + \cosh\left(\frac{\mu B}{k_B T}\right)\right)}{k_B T^2 \left(1 + 2 \cosh\left(\frac{\mu B}{k_B T}\right)\right)^2}}. \end{aligned} \quad (9)$$

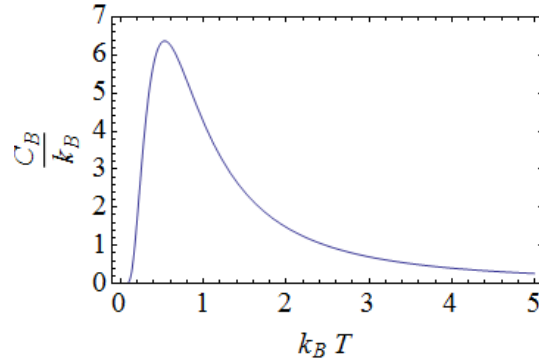


Figure 5: The heat capacity per the Boltzmann constant C_B/k_B as a function of $k_B T$

- d) **(4 points)**: Write down the Helmholtz free energy \mathcal{F} in terms of Z_N and $k_B T$ (1 point). Calculate \mathcal{F} (3 points).

The Helmholtz free energy \mathcal{F} :

$$\begin{aligned} \mathcal{F} &= -\frac{\ln(Z_N)}{\beta} \\ &= \boxed{-Nk_B T \ln[1 + 2 \cosh(\beta\mu B)]}. \end{aligned} \quad (10)$$

- e) **(5 points)**: Sketch the magnetization $\mathcal{M}(k_B T)$. For this, you may calculate the average of the total magnetic moment $\langle -N\epsilon_m/B \rangle$, or you may calculate \mathcal{M} using the average energy E , or you may calculate \mathcal{M} using the Helmholtz free energy \mathcal{F} .

The magnetization \mathcal{M} :

$$\begin{aligned} \mathcal{M} &= -\left(\frac{\partial \mathcal{F}}{\partial B}\right)_{N,T} \\ &= \boxed{\frac{2N\mu \sinh\left(\frac{\mu B}{k_B T}\right)}{1 + 2 \cosh\left(\frac{\mu B}{k_B T}\right)}}. \end{aligned} \quad (11)$$

or, using the average energy E ,

$$\begin{aligned} \mathcal{M} &= -E/B \\ &= \boxed{\frac{2N\mu \sinh\left(\frac{\mu B}{k_B T}\right)}{1 + 2 \cosh\left(\frac{\mu B}{k_B T}\right)}}. \end{aligned}$$

or, using the average of the total magnetic moment,

$$\begin{aligned} \mathcal{M} &= \langle -N\epsilon_m/B \rangle \\ &= \frac{\sum_{m=-1}^1 N\mu m e^{\beta\mu B m}}{\sum_{m=-1}^1 e^{\beta\mu B m}} \\ &= \boxed{\frac{2N\mu \sinh\left(\frac{\mu B}{k_B T}\right)}{1 + 2 \cosh\left(\frac{\mu B}{k_B T}\right)}}. \end{aligned}$$

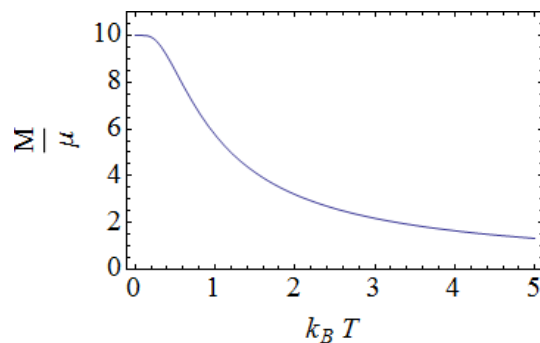


Figure 6: The magnetization per the magnetic moment \mathcal{M}/μ as a function of $k_B T$

Problem 3 (25P)

Consider N spinless non-interacting free bosons of mass m in a volume V at temperature T .

- a) **(2 points)** Write down the average occupation \bar{n}_ϵ of single particle state with energy ϵ as a function of the chemical potential μ and the temperature T .

Bose-Einstein distribution

$$\bar{n}_\epsilon = \frac{1}{e^{(\epsilon-\mu)/(k_B T)} - 1} \quad (12)$$

- b) **(5 points)** Find the density of states $D(\epsilon)d\epsilon$.

The density of state in phase space is

$$D(\epsilon) = \frac{1}{h^3} \int d^d q d^d p \delta(\epsilon - H(\vec{q}, \vec{p})) \quad (13)$$

For a free particle the energy function is $H(\vec{q}, \vec{p}) = \frac{p^2}{2m}$. For a particle in 3D ($d = 3$) one gets:

$$D(\epsilon) = \frac{4\pi V}{h^3} \int_0^\infty p^2 \delta\left(\epsilon - \frac{p^2}{2m}\right) dp \quad (14)$$

Now, one has to use the rule for composing a delta distribution with a function:

$$\delta(g(p)) = \sum_{i, g(p_i)=0} \frac{1}{|g'(p_i)|} \delta(p - p_i) \quad (15)$$

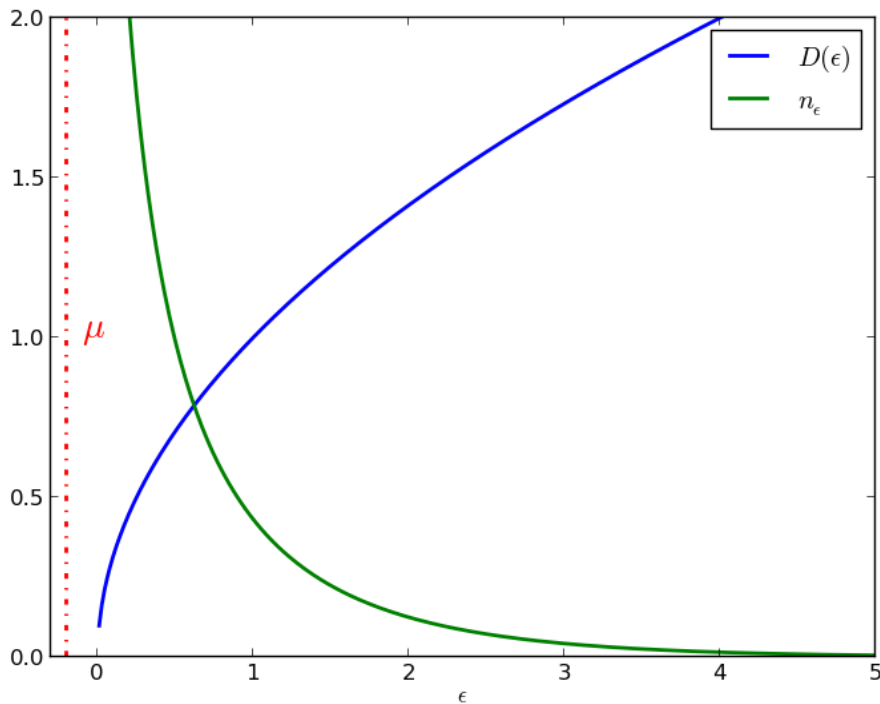
For $g(p) = \epsilon - \frac{p^2}{2m}$, $g'(p) = -\frac{p}{m}$ and $p_0 = \sqrt{2m\epsilon}$, so:

$$\delta\left(\epsilon - \frac{p^2}{2m}\right) = \frac{m}{\sqrt{2m\epsilon}} \delta\left(p - \sqrt{2m\epsilon}\right) \quad (16)$$

The density of state becomes

$$D(\epsilon) = \frac{2\pi V}{h^3} (2m)^{3/2} \sqrt{\epsilon} \quad (17)$$

- c) **(5 points)** Sketch $D(\epsilon)$ and \bar{n}_ϵ as a function of the single particle energy $\mu < \epsilon$ (Remember $\mu < 0$). What happens to \bar{n}_ϵ close to μ ?



Close to $\epsilon = \mu$, \bar{n}_ϵ diverges as the denominator in the distribution function approaches zero.

- d) **(3 points)** Express the density of particles as an integral over energy.

Intermediate result:

$$\frac{N}{V} = \frac{2\pi}{h^3} \left(\frac{2m}{\beta}\right)^{3/2} \int_0^\infty \frac{x^{1/2}}{\exp(x - \beta\mu) - 1} dx \quad \text{where } \beta = \frac{1}{k_B T} \quad (18)$$

$$\begin{aligned} N &= \int \bar{n}_\epsilon D(\epsilon) d\epsilon \\ &= \int_0^\infty d\epsilon \frac{1}{e^{\beta(\epsilon-\mu)} - 1} \frac{2\pi V}{h^3} (2m)^{3/2} \sqrt{\epsilon} \end{aligned} \quad (19)$$

Making the substitution $x = \beta\epsilon$ the integral turns into:

$$\frac{N}{V} = \frac{2\pi}{h^3} \left(\frac{2m}{\beta}\right)^{3/2} \int_0^\infty \frac{x^{1/2}}{e^{x-\beta\mu} - 1} dx \quad (20)$$

- e) **(5 points)** Using the fact that the density does not change if the temperature is lowered, determine whether μ increases or decreases as T is lowered.

$$\frac{N}{V} = \underbrace{\frac{2\pi}{h^3} \left(\frac{2m}{\beta}\right)^{3/2}}_A \underbrace{\int_0^\infty \frac{x^{1/2}}{e^{x-\beta\mu} - 1} dx}_B \quad (21)$$

As T is lowered, the density on the left hand side does not change, but the terms A and B , which do depend on the temperature change individually.

$$T \rightarrow 0 \Rightarrow \beta = \frac{1}{k_B T} \rightarrow \infty \Rightarrow A \rightarrow 0 \quad (22)$$

B has to change in such a way, that the product AB remains constant:

$$A \rightarrow 0 \Rightarrow B \rightarrow \infty \Rightarrow e^{-\beta\mu} \rightarrow 1 \quad (23)$$

Since we know, that $\beta \rightarrow \infty$, μ has to go to 0 faster. Since initially $\mu < 0$, this implies that μ increases towards 0 as T is lowered.

f) **(5 points)** At the critical temperature $\mu \approx 0$ and Bose-Einstein condensation sets in. Find the critical temperature T_c as a function of the density. Leave your answer in terms of a dimensionless integral.

g) At $T = T_c$, $\mu = 0$.

$$\frac{N}{V} = \frac{2\pi}{h^3} (2mk_B T_c)^{3/2} \underbrace{\int_0^\infty \frac{x^{1/2}}{e^x - 1} dx}_{\text{dimensionless integral } I \approx 2.315} \quad (24)$$

Solving for the critical temperature gives:

$$T_c = \frac{1}{2mk_B} \left(\frac{h^3 N}{2\pi I V} \right)^{2/3} \quad (25)$$

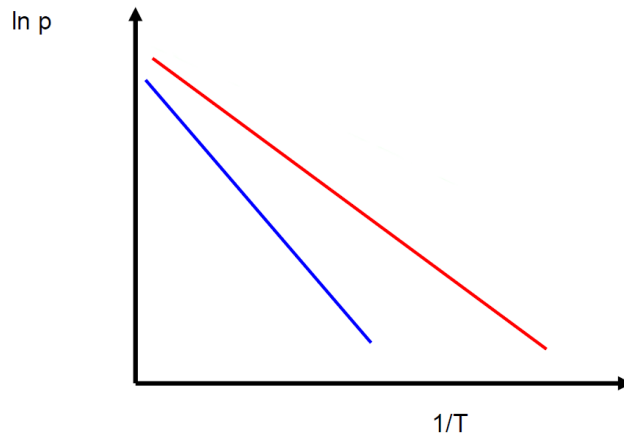


Figure 7: Qualitative results of the two series of experiments.

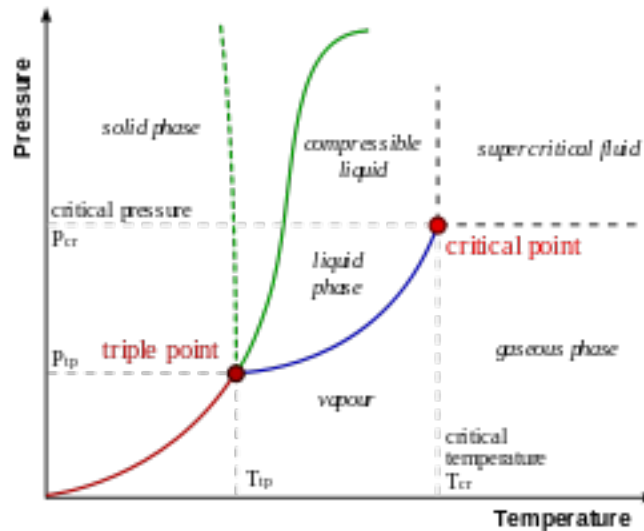


Figure 8: Phase diagramme of a typical compound, e.g. carbon dioxide. Blue: boiling curve, red: sublimation curve, green: melting curve

Problem 4 (25P)

In two series of experiments the vapour pressure p of pure compound is measured at different temperatures T . In the first series, the gas is in equilibrium with its liquid, in the second series, the gas is in equilibrium with its solid phase. The results are qualitatively shown in Fig. 7.

- (6P) Draw a phase-diagramm (p, T) of a typical compound (e.g. Carbon Dioxide) with gas, liquid and solid phase, and label all important points, lines, and areas.
- (2P) Write down the differential equation which describes the coexistence curves.

The gas-liquid and gas-solid equilibrium can be described by the Clausius Claperon equation

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \quad (26)$$

where ΔH is the heat of vapourisation or heat of sublimation, respectively.

- c) **(3P)** Which three approximations are introduced to solve the above equation for the gas-solid coexistence curve?

Neglecting the volume of the solid $V_{gas} \gg V_{solid}$; i.e. $\Delta V = V_{gas} - V_{solid} \approx V_{gas}$,

treating the vapour as an ideal gas $V_{gas} = \frac{nRT}{p}$,

and neglecting the temperature dependence of the heat of ΔH

we can integrate eq.26 (for $n = 1$)

$$\begin{aligned}\frac{1}{p} dp &= \frac{\Delta H}{RT^2} dT \\ \int_{p_0}^p \frac{1}{p} dp &= \int_{T_0}^T \frac{\Delta H}{RT^2} dT \\ \ln \frac{p}{p_0} &= -\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \\ \ln p &= -\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \ln p_0\end{aligned}\tag{27}$$

Same approximations can be made for the liquid-gas transition.

- d) **(4P)** What do slope and intercept of the curves in Fig.7 tell you?

In Fig.7 the linearised form of the integrated eq.26 is plotted:

$$\ln p = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta H}{R} \cdot \frac{1}{T_0} + \ln p_0$$

the slope is $-\frac{\Delta H}{R}$. and the intercept $\frac{\Delta H}{R} \cdot \frac{1}{T_0} + \ln p_0$. Hence, from the slope one can determine the heat of vapourisation. Using

$$\Delta G = -RT \ln \frac{p}{p_0}$$

and

$$\Delta G = \Delta H - T\Delta S$$

we get

$$\begin{aligned}\ln \frac{p}{p_0} &= -\frac{\Delta G}{RT} \\ \ln \frac{p}{p_0} &= -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R}\end{aligned}$$

and hence the intercept is $\frac{\Delta S}{R} + \ln p_0$ from which we get the change in entropy for the transitions.

- e) **(5P)** Which of the two curves corresponds to the experiment of the gas-liquid equilibrium and which one to the gas-solid (explain briefly)?

Blue: solid-gas; Red: liquid-gas. The enthalpy H is a state function, hence $\Delta H_{s \rightarrow g} = \Delta H_{s \rightarrow l} + \Delta H_{l \rightarrow g}$. Since H increases with the transition to the higher-temperature phase these ΔH are all positive and therefore $\Delta H_{s \rightarrow g} > \Delta H_{l \rightarrow g}$. The slope of the curve corresponding to the solid-gas experiment is thus steeper.

- f) **(5P)** How can you determine at which pressure and temperature all three phases coexist based on the results of the above experiments (explain)?

At the triple point, all three phases coexist. Hence all three coexistence lines intersect at that point. From the plotted experimental data we get

$$\ln \frac{p}{p_0} = -\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

$$p = p_0 \exp \left[-\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$$

for each of the two experiments. Setting the two curves equal gives the intersection:

$$\ln p = -\frac{\Delta H_{lg}}{R} \left(\frac{1}{T} - \frac{1}{T_0^l} \right) + \ln p_0^l$$

$$\ln p = -\frac{\Delta H_{sg}}{R} \left(\frac{1}{T} - \frac{1}{T_0^s} \right) + \ln p_0^s$$

$$-\frac{\Delta H_{lg}}{R} \left(\frac{1}{T} - \frac{1}{T_0^l} \right) + \ln p_0^l = -\frac{\Delta H_{sg}}{R} \left(\frac{1}{T} - \frac{1}{T_0^s} \right) + \ln p_0^s$$

$$\frac{\Delta H_{sg}}{R} \left(\frac{1}{T} - \frac{1}{T_0^s} \right) - \frac{\Delta H_{lg}}{R} \left(\frac{1}{T} - \frac{1}{T_0^l} \right) = \ln p_0^s - \ln p_0^l$$

$$\frac{\Delta H_{sg}}{RT} - \frac{\Delta H_{sg}}{RT_0^s} - \frac{\Delta H_{lg}}{RT} + \frac{\Delta H_{lg}}{RT_0^l} = \ln p_0^s - \ln p_0^l$$

$$\frac{\Delta H_{sg}}{RT} - \frac{\Delta H_{lg}}{RT} = \ln p_0^s - \ln p_0^l + \frac{\Delta H_{sg}}{RT_0^s} + \frac{\Delta H_{lg}}{RT_0^l}$$

$$\frac{\Delta H_{sg} - \Delta H_{lg}}{RT} = \ln p_0^s - \ln p_0^l + \frac{\Delta H_{sg}}{RT_0^s} + \frac{\Delta H_{lg}}{RT_0^l}$$

$$\frac{1}{T} = \frac{\left(\ln p_0^s - \ln p_0^l + \frac{\Delta H_{sg}}{RT_0^s} + \frac{\Delta H_{lg}}{RT_0^l} \right)}{\frac{\Delta H_{sg} - \Delta H_{lg}}{R}}$$

$$T = \frac{\frac{\Delta H_{sg} - \Delta H_{lg}}{R}}{\left(\ln p_0^s - \ln p_0^l + \frac{\Delta H_{sg}}{RT_0^s} + \frac{\Delta H_{lg}}{RT_0^l} \right)}$$

... and plug in T to get p

$$\ln \frac{p}{p_0} = -\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

$$\ln p = -\frac{\Delta H_{lg}}{R} \left(\frac{\left(\ln p_0^s - \ln p_0^l + \frac{\Delta H_{sg}}{RT_0^s} + \frac{\Delta H_{lg}}{RT_0^l} \right)}{\frac{\Delta H_{sg} - \Delta H_{lg}}{R}} - \frac{1}{T_0^l} \right) + \ln p_0^l$$

$$p = p_0^l \exp \left[-\frac{\Delta H_{lg}}{R} \frac{1}{T} + \frac{\Delta H_{lg}}{R} \frac{1}{T_0^l} \right]$$

$$p = p_0^l \exp \left[-\frac{\Delta H_{lg}}{R} \cdot \frac{\left(\ln \frac{p_0^s}{p_0^l} + \frac{\Delta H_{lg}}{RT_0^s} + \frac{\Delta H_{sg}}{RT_0^l} \right)}{\left(\frac{\Delta H_{sg}}{R} - \frac{\Delta H_{lg}}{R} \right)} + \frac{\Delta H_{lg}}{RT_0^l} \right]$$