

# PHYS2020 Worksheets

Semester One, 2020

- Questions from these worksheets will be used during tutorials
- Solve the problems in groups, writing your answers in the spaces
- Explicitly write down any assumptions or approximations you make
- You may divide the tasks amongst members of your group, but make sure to explain to the others how you got to your answers

# 1 Thermal equilibrium; Ideal Gases

## 1.1 Thermal contact

(5 mins) Give examples to illustrate why you cannot accurately judge the temperature of an object by how hot or cold it feels to the touch.

## 1.2 Two rooms

(10 mins) Rooms A and B are the same size, and are connected by an open door. Room A, however, is warmer (perhaps because its windows face the sun). Are the rooms in equilibrium with each other? Explain.

Which room contains the greater mass of air? Justify your result.

### 1.3 Hot Air Balloons

Consider a hot-air balloon whose mass (including balloon material and payload) is 500kg. Estimate the temperature that the air in the balloon needs to be for it to take off.

What is the mass of the air inside the balloon?

## 2 Heat and Work

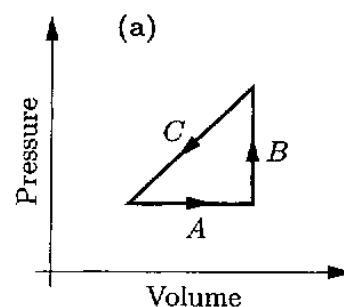
### 2.1 Heat vs temperature

(5 mins) Give an example of a process in which no heat is added to a system, but its temperature increases. Then give an example of the opposite: a process in which heat is added to a system but its temperature does not change.

### 2.2 A cycle

(15 mins) An ideal gas is made to undergo the cyclic process shown right.

- (a) For each of the steps A, B, and C, determine whether each of the following is positive, negative or zero: (i) the work done on the gas, (ii) the change in internal energy of the gas, and (iii) the heat added to the gas. (hint: draw a table)
- (b) Determine the sign of each of these three quantities for the whole cycle. What does it accomplish?



### 2.3 Degrees of freedom

(15 mins) List/sketch the degrees of freedom relevant at room temperature, for each of the following molecules

- (a) helium He
- (b) nitrogen N<sub>2</sub>
- (c) carbon dioxide CO<sub>2</sub>
- (d) water H<sub>2</sub>O

### 3 Energy, enthalpy and heat capacities

#### 3.1 Energy vs Enthalpy

(10 mins) Explain the difference between the change in internal energy and the change in enthalpy accompanying a chemical or physical process.

#### 3.2 Isothermal vs adiabatic

(10 mins) Consider two identical sealed pistons containing air. They are each compressed from an initial volume  $V_i$  to a final volume  $V_f$ , but one is compressed quickly (before heat can escape), and one is compressed very slowly. Which one requires the most amount of work? Include sketches of  $PV$  curves in your explanation.

### 3.3 A nice cup of tea

(20 mins) Your 200 g cup of tea is boiling-hot. About how much ice should you add to bring it down to a comfortable sipping temperature of 65° C? (Assume that the ice is initially at -15°C. The enthalpy of fusion is 6.01 kJ/mol, the enthalpy of vaporization is 40.68 kJ/mol, the specific heat of ice is 2.084 J/g.K, the specific heat of water is 4.184 J/g.K, and the specific heat of steam (at 100°C) is 1.996 J/g.K)

## 4 State functions; Entropy

### 4.1 Entropy and temperature

(20 mins) When the sun is high in the sky, it delivers approximately 1000 watts of power to each square meter of the earth's surface. The temperature of the surface of the sun is about 6000 K, while that of the earth is about 300 K.

- (a) Estimate the entropy created in one year by the flow of solar heat onto a square metre of the earth.
- (b) Suppose you plant grass on this square metre of earth. Some people might argue that the growth of the grass (or of any other living thing) violates the second law of thermodynamics, because disorderly nutrients are converted into an orderly life form. How would you respond?

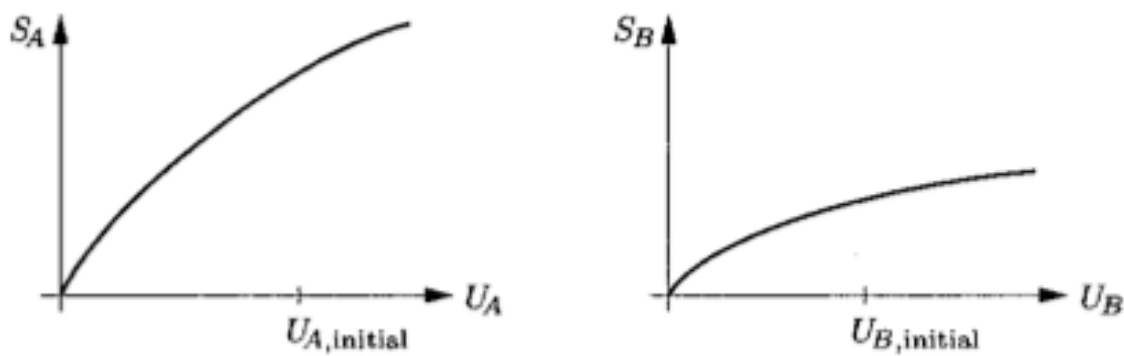
### 4.2 State and path functions

(5 mins) Explain the significance of a physical observable being a state function and compile a list of as many state functions as you can identify.



### 4.3 Entropy and energy

(15 mins) The figure below shows graphs of entropy versus energy for two objects,  $A$  and  $B$ . Both graphs are on the same scale. The energies of these two objects initially have the values indicated; the objects are then brought into thermal contact with each other. Explain what happens subsequently and why, *without* using the word “temperature”.



## 5 Entropy changes and the thermodynamic identity

### 5.1 The entropic cost of melting

(20 mins) An ice cube (mass 30g) at  $0^{\circ}\text{C}$  is left sitting on the kitchen table, where it gradually melts. The temperature of the kitchen is  $25^{\circ}\text{C}$ .

- (a) Calculate the change in the entropy of the ice cube as it melts into water at  $0^{\circ}\text{C}$ . (Don't worry about the fact that the volume changes somewhat.)
- (b) Calculate the change in the entropy of the water (from the melted ice) as its temperature rises from  $0^{\circ}\text{C}$  to  $25^{\circ}\text{C}$ .
- (c) Calculate the change in the entropy of the kitchen as it gives up heat to the melting ice/water.
- (d) Calculate the net change in the entropy of the universe during this process. Is the net change positive, negative or zero? Is this consistent with the second law?

### 5.2 Another irreversible process

(20 mins) A cylinder contains one litre of air at room temperature and atmospheric pressure. At one end of the cylinder is a massless piston, whose surface area is  $0.01\text{ m}^2$ . Suppose that you push the piston in *very* suddenly, exerting a force of 2000 N. The piston moves only one millimetre, before it is stopped by an immovable barrier of some sort.

- (a) How much work have you done on this system (cylinder + gas + piston)?
- (b) How much heat have you added to the system?
- (c) Assuming that all the energy added goes into the gas (not the piston or cylinder walls), by how much does the internal energy of the gas increase?
- (d) Use the thermodynamic identity to calculate the change in the entropy of the gas (once it has reached its new equilibrium).
- (e) Is the result in (d) consistent with the second law? Explain.

## 6 Thermodynamic cycles

### 6.1 Impossible processes

(15 mins) Clausius says: “No process is possible whose sole result is the transfer of heat from a colder to a hotter body”. Kelvin says: “No process is possible whose sole result is the complete conversion of heat into work”.

- (a) Draw diagrams showing the flow of heat and work between hot and cold reservoirs for each of these impossible processes.
- (b) Explain how these two statements each follow from the second law, which says that the entropy of the universe cannot decrease.
- (c) Couple the impossible process in each case to a Carnot cycle to show that the statements of Clausius and Kelvin are equivalent.

### 6.2 Heat pumps

(20 mins) A heat pump is a device that heats a space at temperature  $T_h$  by pumping in heat from the cold exterior at temperature  $T_c$ . In other words, it's the same as a refrigerator, but its purpose is to warm the hot interior rather than to cool the cold exterior (even though it does both). Let the

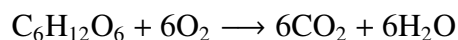
heat removed from the exterior be  $Q_c$ , the heat added to the interior be  $Q_h$  and the electrical work consumed by the heat pump be  $W$ .

- (a) Explain why the “coefficient of performance” (COP) for a heat pump should be defined as  $Q_h/W$ .
- (b) What relation among  $Q_h$ ,  $Q_c$  and  $W$  is implied by energy conservation alone? Will energy conservation permit the COP to be greater than 1?
- (c) Use the second law to derive an upper limit on the COP, in terms of the temperatures  $T_h$  and  $T_c$  alone.
- (d) Explain why a heat pump is better than an electric heater, which simply converts electrical work directly into heat.

## 7 Gibbs Free Energy and Thermodynamic Identities

### 7.1 A work out

(25 mins) A muscle can be thought of as a fuel cell, producing work from the metabolism of glucose:



- (a) Use data from the formulae sheet (or the back of Schroeder) to determine the values of  $\Delta H$  and  $\Delta G$  for this reaction, for one mole of glucose. Assume that the reaction takes place at room temperature and atmospheric pressure.
- (b) What is the maximum amount of work that a muscle can perform, for each mole of glucose consumed, assuming ideal operation?

- (c) Still assuming ideal operation, how much heat is absorbed or expelled by the chemicals during the metabolism of a mole of glucose? (Be sure to say which direction the heat flows.)
- (d) Use the concept of entropy to explain why the heat flows in the direction it does.

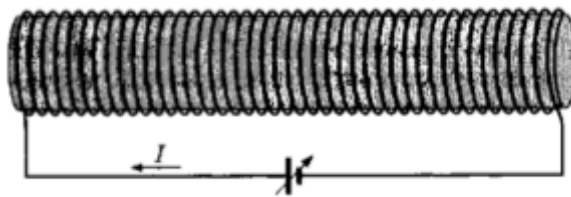
(e) how would your answer to parts (b) and (c) change if the operation of the muscle is not ideal?

## 7.2 Free energy of magnets

(25 mins) In this exercise, we want to develop the appropriate thermodynamic identities for a magnetic specimen (eg a paramagnetic solid) on which work is done by a magnetic field. We will treat our system as a collection of spins, with net magnetic moment  $\vec{M}$ , and ignore any work (eg pV work) on the solid structure that contains the spins. It is convenient to introduce an auxiliary field  $\vec{\mathcal{H}}$  that is related to the actual magnetic field  $\vec{B}$  by the relation

$$\vec{B} = \mu_0 \left( \vec{\mathcal{H}} + \frac{\vec{M}}{V} \right),$$

where  $\mu_0 = 4\pi \times 10^{-7} \text{ N/A}^2$  is the permeability of free space and  $V$  is the specimen volume.



We will take our magnetic specimen to be contained in a long solenoid, as shown above, of length  $L$  containing  $N$  turns. We will assume a cylindrical symmetry and focus on paramagnetic materials, such that all the fields will point either left or right, allowing us to drop the vector notation. Without the specimen present, the field inside the solenoid would be  $B_{\text{empty}} = \mu_0 NI/L$  (remember Ampere's law?). With the specimen present, the dipoles will create their own magnetic field, depending on the net magnetisation  $M$ , which adds to the field created by the external current, to give the total magnetic field  $B = B_{\text{empty}} + B_{\text{dipoles}}$ . The auxiliary field  $\vec{\mathcal{H}}$  is defined in such a way that it depends only on the external current (i.e. the dipole field is essentially 'subtracted off'). Thus  $\mathcal{H} = NI/L$  regardless of whether the specimen is present or not.

- (a) Suppose that the current in the wire is changing, resulting in changes to  $\mathcal{H}$  and  $B$ . Use Faraday's law to show that the power that needs to be supplied to the circuit is

$$P = \mathcal{E}I = V\mathcal{H}\frac{dB}{dt},$$

where  $V$  is the volume of the sample.



- (b) The total work done by the external circuit to make an infinitesimal change in the magnetic field  $dB$  is thus

$$W_{\text{total}} = V\mathcal{H}dB$$

Rewrite this result in terms of  $\mathcal{H}$  and  $M$ , then subtract off the work that would be required even if the specimen were not present. Show therefore that the work done on the system of spins is

$$W = \mu_0\mathcal{H}dM$$

- (c) What is the thermodynamic identity for this system?
- (d) How would you define analogues of the enthalpy and Gibbs free energy for this magnetic system? Derive thermodynamic identities for each of these quantities.
- (e) Can you give a physical interpretation for this magnetic version of Gibbs free energy?

## 8 First-order phase transitions

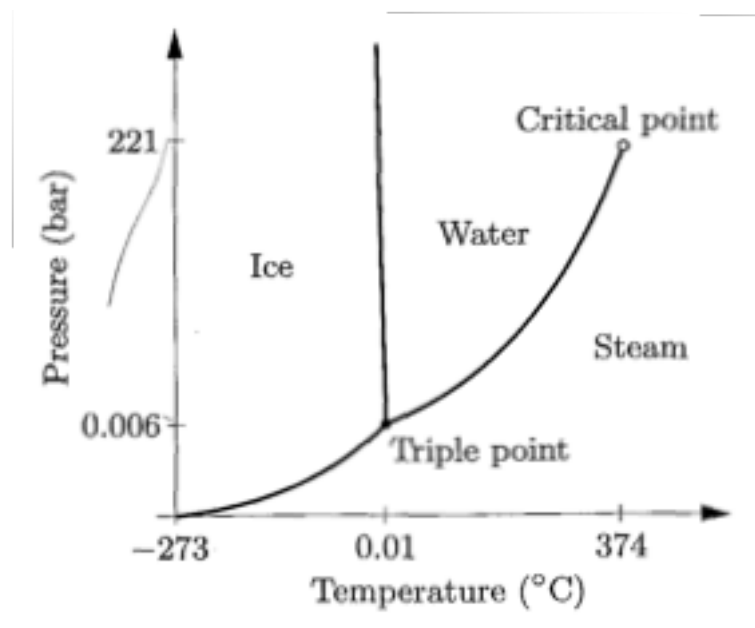
### 8.1 Gibbs free energy and temperature

(5 mins) Sketch a qualitatively accurate graph of  $G$  vs.  $T$  for a pure substance as it changes from solid to liquid to gas at fixed pressure. Think carefully about the slope of the graph, and mark the points at which phase changes occur.



## 8.2 Phase diagram of water

(20 mins) The density of ice is  $917 \text{ kg/m}^3$ . The density of liquid water you should already know. The latent heat of fusion of water is  $333 \text{ kJ/kg}$ .



(a) What is unusual about the solid-liquid phase boundary of water?

- (b) How much pressure do you need to apply to an ice-cube to cause it to melt at  $-1^{\circ}\text{C}$ ?
- (c) Estimate the pressure under the blade of an ice skate. Calculate the melting temperature of ice at this pressure.
- (d) Some author's claim that skaters can glide with very little friction because the increase pressure under the blade melts the ice to create a thin layer of water. (See for example, H.B. Callen, Thermodynamics, 2nd edition, p. 229. This was previously used as the textbook for this course.) Do you agree with this explanation? Justify your answer.

### 8.3 Phase diagram of some rocks

(20 mins) Calcium carbonate  $\text{CaCO}_3$  has two common crystalline forms: calcite and aragonite. Use the thermodynamic data in the table at the back of Schroeder to answer the following questions:

- (a) Which is stable at the earth's surface, calcite or aragonite?
- (b) Calculate the pressure (still at room temperature) at which the other phase becomes stable.
- (c) Calculate the slope of the phase-boundary  $dP/dT$ .
- (d) Use the results of (b) and (c) to sketch the phase diagram of calcium carbonate. (You can do the sketch by hand below, or else use your favourite plotting software.)

## 9 Liquid-vapour transitions

### 9.1 Liquid-vapour Equilibrium

(10 mins)

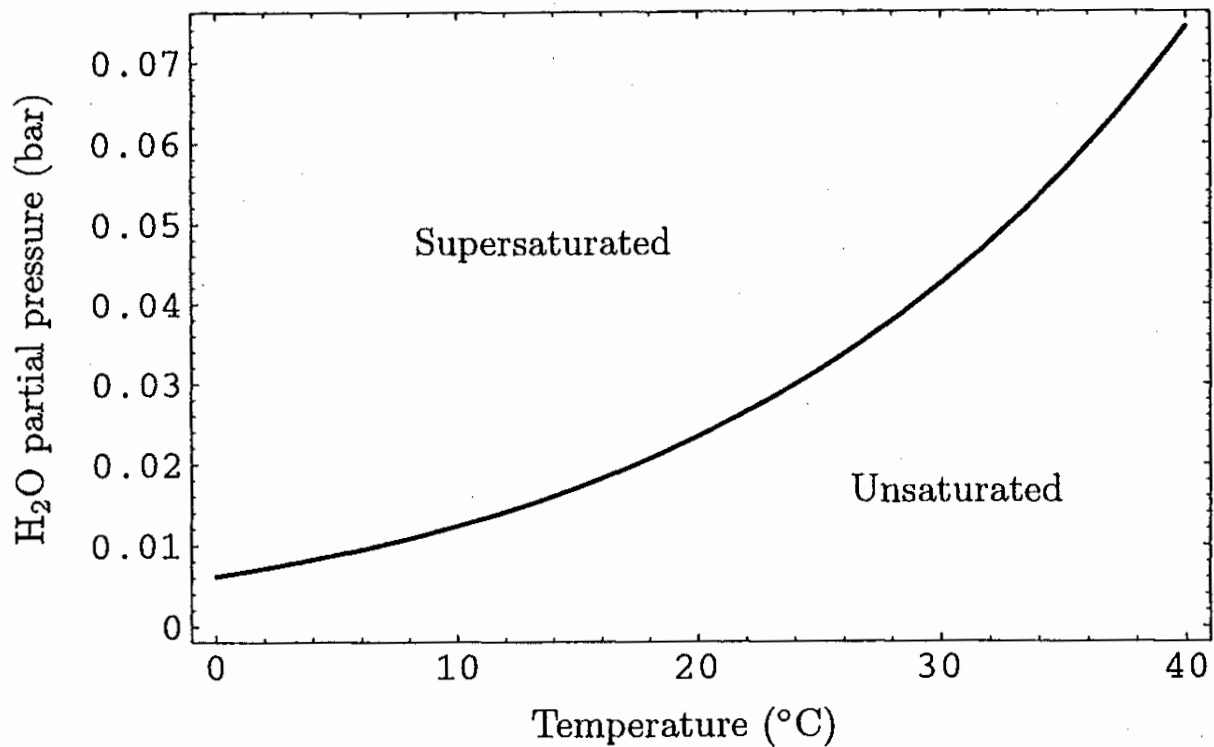
Consider a quantity of  $\text{H}_2\text{O}$  at room temperature in two situations: (i) held in a closed container by a piston that maintains the pressure at 1 bar and (ii) placed in a container that is open to the atmosphere.

- (a) Write down the conditions in each case for the quantity of water to be in equilibrium with its surroundings. (Use diagrams if it helps explain what you mean)
- (b) What is the thermodynamically stable phase - liquid or vapour - in each case, if the relative humidity is less than 100%? *Hint: The chemical potential of an ideal gas as a function of pressure is  $\mu(P) = \mu(P^o) + kT \ln(P/P^o)$ , where  $P^o$  is some convenient reference pressure.*

## 9.2 Vapour-pressure line

(20 mins)

Recall that the relative humidity is the ratio of partial pressure of water vapour to the equilibrium vapour pressure. When the relative humidity is 100%, so that water vapour is in diffusive equilibrium with liquid water, we say that the air is saturated. The *dew point* is the temperature at which the relative humidity would be 100% for a given partial pressure of water vapour. Below is a graph of the vapour pressure of water as a function of temperature (which can be found by solving the Clausius-Clapeyron equation). Use this graph to answer the following questions.



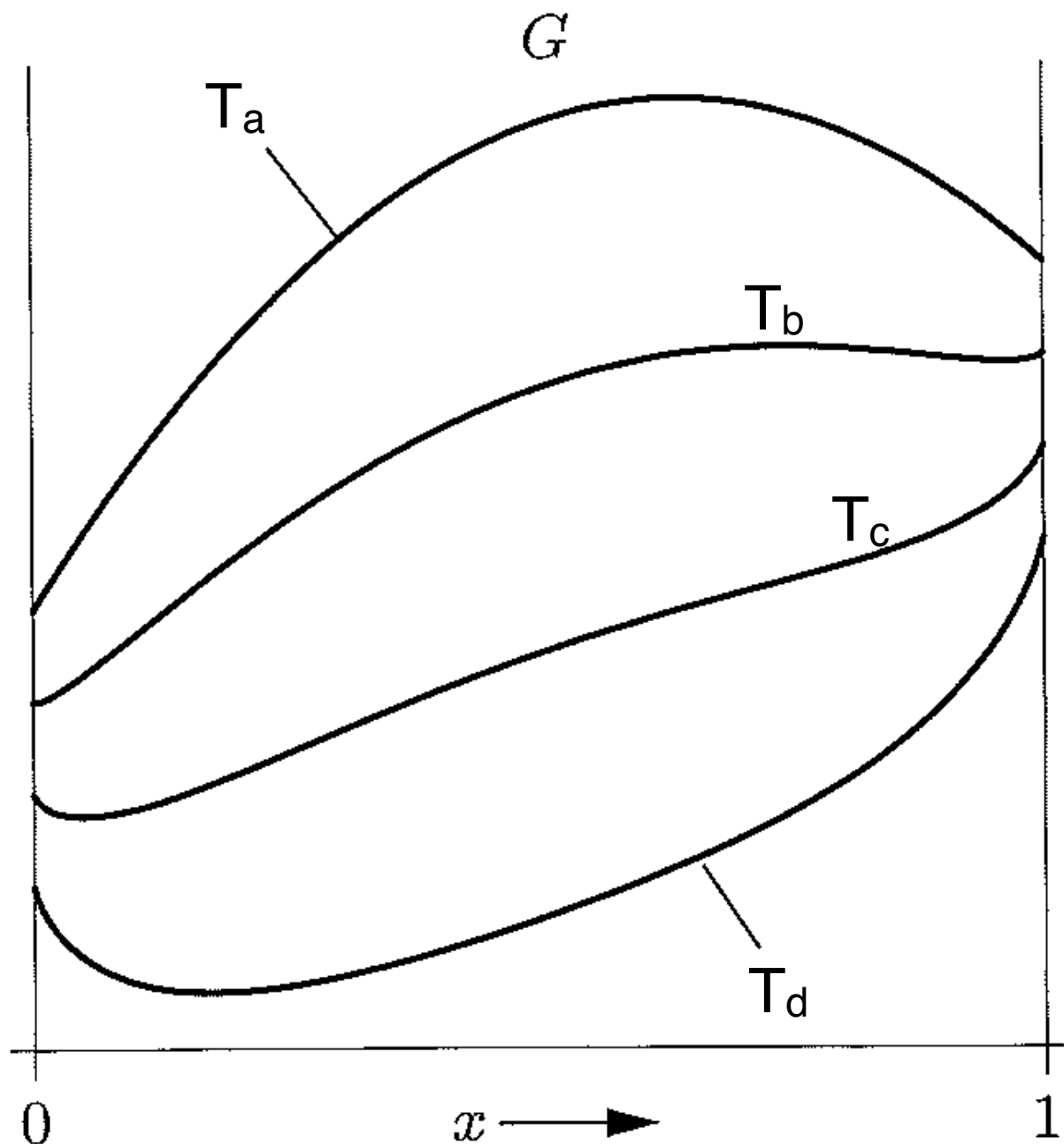
- (a) The temperature on a certain summers day is 30°C. What is the partial pressure of water if the relative humidity is 90%? What is the corresponding dew point? What is the dew point if the relative humidity is 40%?

- (b) Consider the effect of seeing your breath on a cold morning. Suppose the air you exhale is  $35^{\circ}\text{C}$  with 90% relative humidity, and the surroundings air is  $10^{\circ}\text{C}$  with 50% humidity. Mark these points on the phase diagram above and explain why a cloud of droplets will form as your breath mixes with the surrounding air. How low would the relative humidity of the surrounding air have to be in order to avoid this effect?



## 10 Free Energy of Mixtures

### 10.1 Miscible vs Immiscible Combinations



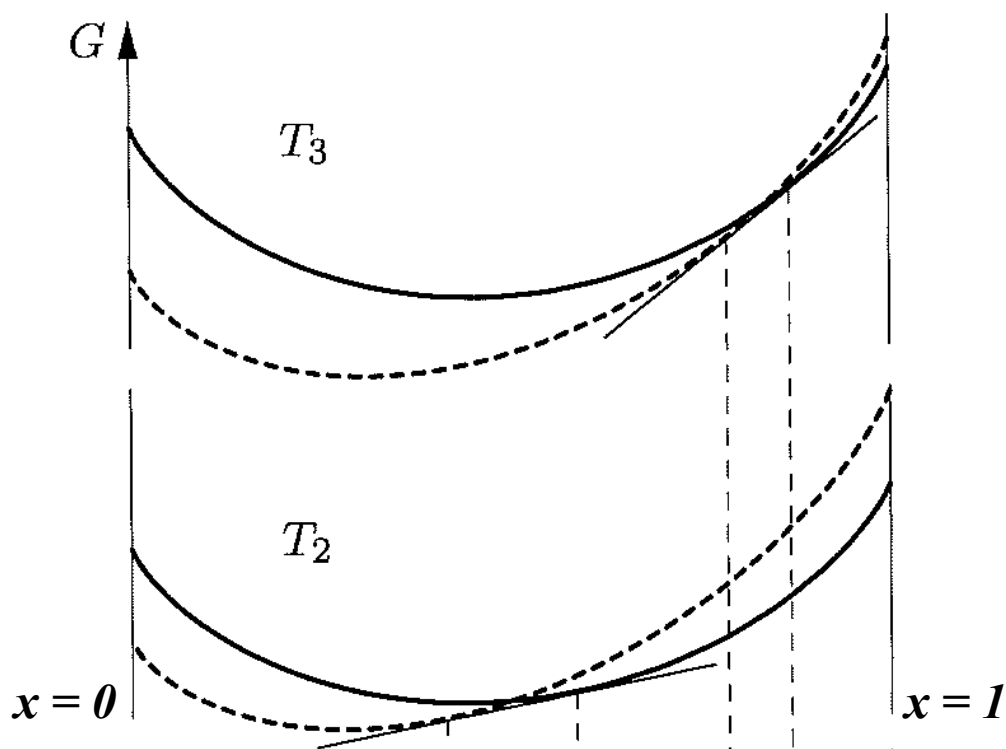
The diagram above shows the Gibbs free energy of a hypothetical mixture as a function of composition for four different temperatures

- List the four temperatures in order of increasing temperature.
- At which temperature is the mixture dominated by molecular interactions?
- At which temperature is the mixture dominated by the entropy mixing?

- (d) Describe what you would see at temperature  $T_c$  at overall composition  $x = 0.5$ . In your answer, estimate the composition of each component.

- (e) Between which two temperatures does the critical point lie, above which two separated phases cannot exist.
- (f) Sketch a phase diagram ( $T$  versus  $x$ ) showing the miscible (homogeneous) and immiscible (separated phase) regions. On your diagram, indicate the four temperatures  $T_a$  to  $T_d$ . ?

## 10.2 Liquid-vapour transitions in a mixture

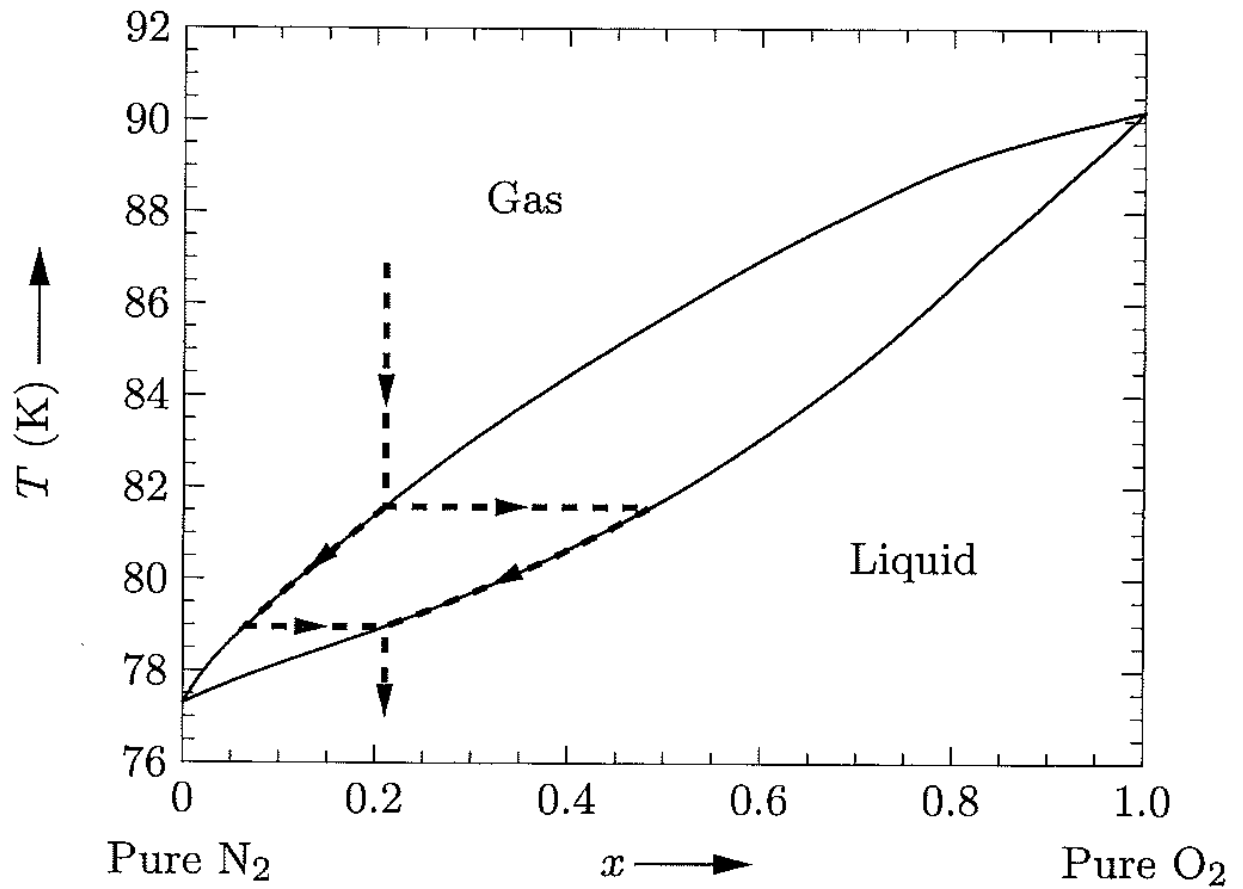


The picture above shows the Gibbs free energy of the gaseous (dashed) and liquid (solid) phases of a hypothetical mixture as a function of composition.

- Which temperature is higher  $T_2$  or  $T_3$ ?
- Suppose you had a 50:50 mixture of the two substances. Describe qualitatively what you would see at the two different temperatures.

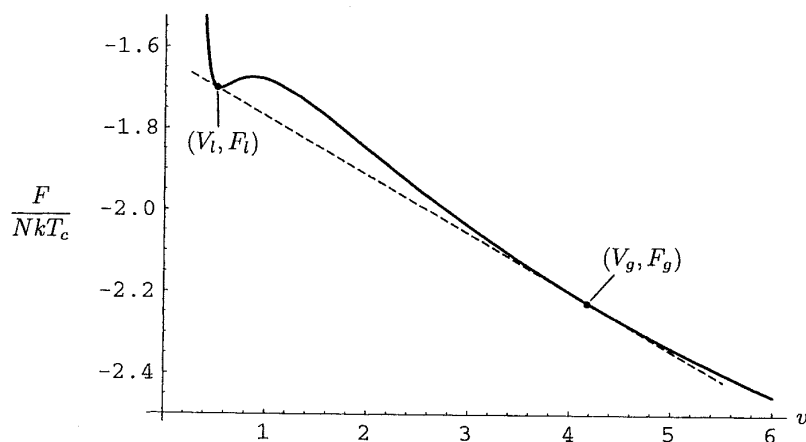
- If any liquid condenses at either of these temperatures (again in a 50:50 mixture), estimate its composition.

- (d) Suppose you cool a mixture of 50% nitrogen and 50% oxygen until it liquifies. Describe, using the diagram below, the cooling sequence in detail, including the temperatures and compositions at which liquefaction begins and ends. (*The dashed line on the diagram indicates what happens to the mixture at the composition found in air.*)



### 10.3 van der Waals gas at fixed volume

The following plot shows the dependence of the Helmholtz free energy of the van der Waals gas as a function of reduced volume at a given temperature below the critical temperature.



- (a) Write down a brief form of the second law for a system at fixed temperature and volume.

- (b) At volumes  $V_l$  and below, the system is a liquid, and at volumes  $V_g$  and above the system is a gas. Describe the state of the system between at volumes in between the two points (hint: what is the significance of the straight line joining the two points?)

## 11 Reaction Equilibrium

### 11.1 A Binary Reaction: $A \leftrightarrow B$

(30 mins) In this question you will consider the equilibrium state of a binary reaction between two substances  $A$  and  $B$ . Let  $G_A^\circ$  and  $G_B^\circ$  be the molar Gibbs free energy of each substance in its pure form at standard temperature and pressure, and let  $x$  be the fraction of molecules that are of type  $A$ .

- (a) Write down the molar Gibbs free energy of the of the total system, assuming ideal mixing
- (b) Sketch the Gibbs free energy of the system as a function of  $x$ . (Assume that  $G_A^\circ > G_B^\circ$ .)

- (c) Assuming that  $A$  and  $B$  can interconvert, use calculus to derive an expression that relates  $G_A^\circ$  and  $G_B^\circ$  to the equilibrium value of  $x$ .

(d) Express the equilibrium constant  $K \equiv \exp(-\Delta G^\circ/RT)$  in terms of  $x$ , where  $\Delta G^\circ = G_B^\circ - G_A^\circ$ .

(e) Explain why the equilibrium state isn't pure  $B$ , even though  $G_A^\circ > G_B^\circ$ .

## 11.2 Partial pressures in a gaseous reaction

(30 mins) Consider the fixation of Nitrogen described by the reaction  $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ . For the following questions assume that you start with a gas containing 3 parts hydrogen gas to 1 part nitrogen gas in a sealed chamber kept at a certain pressure  $P_{\text{tot}}$ .

- (a) Write down the “law of mass action” for this system, relating the equilibrium partial pressures to the equilibrium constant  $K$ .

- (b) Write down two other constraints on the partial pressures. (Hint one of them involves the total pressure  $P_{\text{tot}}$ .)

- (c) At  $T = 298\text{K}$ , the equilibrium constant for this reaction is  $K = 5.9 \times 10^5$ . Suppose the total pressure is kept at 1 atmosphere. Determine the equilibrium partial pressure of  $\text{N}_2$ . (*Hint: You may expect that in equilibrium  $P_{\text{N}_2}, P_{\text{H}_2} \ll P_{\text{NH}_3}$ , so use this to simplify your expressions, then check at the end that your approximations are justified.*) What fraction of the nitrogen atoms are in the ammonia gas?



- (d) At  $T = 773\text{K}$ , the equilibrium constant for this reaction is  $K = 6.9 \times 10^{-5}$ . Suppose the total pressure of the system is again 1 atmosphere. Determine the equilibrium partial pressure of  $\text{NH}_3$ . (*Hint: You may expect that in equilibrium  $P_{\text{N}_2}, P_{\text{H}_2} \gg P_{\text{NH}_3}$ , so use this to simplify your expressions, then check at the end that your approximations are justified.*) What fraction of the nitrogen atoms are in the ammonia gas?

- (e) Suppose now that you attempt the reaction  $T = 773\text{K}$ , but now at some high pressure  $P_{\text{tot}}$ . Determine what this pressure needs to be to have at least half the nitrogen atoms contained within the ammonia gas. (*Hint: You can no longer assume that in equilibrium  $P_{\text{N}_2}, P_{\text{H}_2} \gg P_{\text{NH}_3}$ .*)

## 12 Continuous Phase Transitions

### 12.1 Ferromagnetism and the Curie Point

Iron undergoes a continuous transitions from a ferromagnet to a paramagnet at the Curie temperature  $T_c = 1043\text{K}$ .

- (a) Sketch typical arrangements of the magnetic dipole moments of the iron atoms above and below the transitions temperature  $T_c$ , in the absence of an external field.



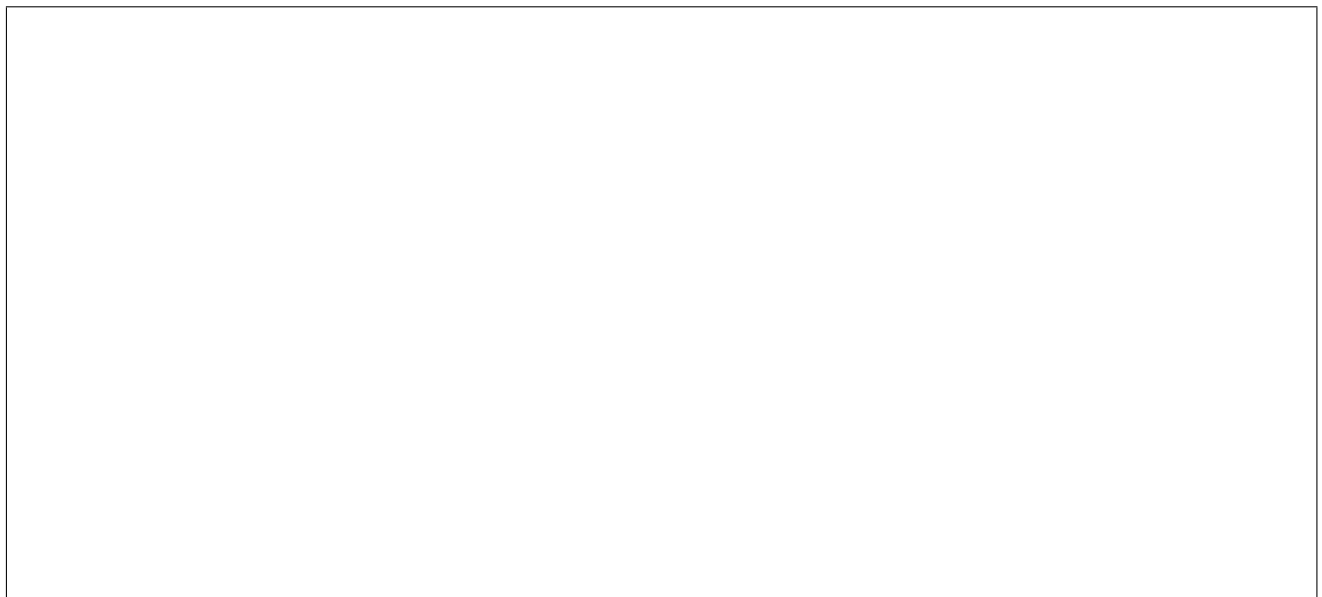
- (b) Let  $\mathbf{m}$  denote the average magnetisation (the total magnetic moment per unit volume) for a system at pressure  $P$  and temperature  $T$ . Explain why  $\mathbf{m}$  is a suitable order parameter for the paramagnet-ferromagnet transition.



- (c) Adopting a phenomenological approach (originally due to Landau), we can write the Gibbs free energy of the system of magnetic dipoles in the form

$$G(T, B, m) = a(T - T_c)m^2 + bm^4 - mB, \quad (1)$$

where  $m = |\mathbf{m}|$ ,  $B$  is the external magnetic field and where  $a$  and  $b$  are positive constants<sup>1</sup>. Sketch the free energy as a function of  $m$  for temperatures both greater than and less than  $T_c$ .



<sup>1</sup>Essentially this expression comes from a multidimensional Taylor-series expansion where only the lowest nonzero terms in  $m$ ,  $B$  and  $(T - T_c)$  are kept.

- (d) What is the condition for equilibrium at fixed  $T$  and  $B$ ? Use Gibbs free energy to derive an expression for how the equilibrium value of  $m$  varies with temperature above and below  $T_c$  in the absence of an external field. Draw a sketch of this temperature dependence.

- (e) Iron cooled through the Curie point is said to display spontaneously broken symmetry. Explain what this means in this magnetic system.

## 12.2 Critical exponents (Optional Extra)

**Table 1.1.** Definitions of critical exponents

Exponent	Definition
$\alpha$	$c_B \sim \alpha^{-1} ( ( T - T_c /T_c)^{-\alpha} - 1 ), T \rightarrow T_c, B = 0$
$\beta$	$m \sim (T_c - T)^\beta, T \rightarrow T_c \text{ from below}, B = 0$
$\gamma$	$\chi_T \sim  T - T_c ^{-\gamma}, T \rightarrow T_c, B = 0$
$\delta$	$m \sim B^{1/\delta}, B \rightarrow 0, T = T_c$
$\eta$	$G^{(2)}(r) \sim 1/r^{d-2+\eta}, T = T_c, B = 0$
$\nu$	$\xi \sim  T - T_c ^{-\nu}, B = 0$

The critical exponents (defined in the table above) describe how various quantities behave around the critical point.

- (a) Using the expression for  $m(T)$  derived in 1(d), determine a value for the critical exponent  $\beta$ .

- (b) Using the Gibbs free energy given above, derive an expression for the magnetic susceptibility  $\chi_T = (\partial m / \partial B)_T$  in terms of  $a$ ,  $b$  and  $T - T_c$  in the limit of zero external field. (*Hint: Find an expression relating the equilibrium value of  $m$  to the external field  $B$ , calculate the derivative and then take the limit that  $B \rightarrow 0$ . Alternatively use the fact that  $B = (\partial F / \partial m)_T$ , where  $F \equiv G + mB$ .) Is there a divergence at  $T = T_c$ ? If so, derive a value for the critical exponent  $\gamma$ .*

- (c) Using the Gibbs free energy given above, derive an expression for the heat capacity  $c_B \equiv (\partial U / \partial T)_B = T(\partial S / \partial T)_B$  in terms of  $a$ ,  $b$  and  $T - T_c$ . (Hint: The thermodynamic identity shows that  $S = -(\partial G / \partial T)_B$ .) Is there a divergence at  $T = T_c$ ? If so, derive a value for the critical exponent  $\alpha$ .

- (d) Compare the values to experimentally determined values (see table below). How satisfactory is this phenomenological theory?

**Table 1.2.** Values of critical exponents

	Xe	Binary fluid	$\beta$ -brass	$^4\text{He}$	Fe	Ni
D	1	1	1	2	3	3
$\alpha$	$< 0.2$	$0.113 \pm .005$	$0.05 \pm .06$	$-0.014 \pm .016$	$-0.03 \pm .12$	$0.04 \pm .12$
$\beta$	$0.35 \pm .015$	$0.322 \pm .002$	$0.305 \pm .005$	$0.34 \pm .01$	$0.37 \pm .01$	$0.358 \pm .003$
$\gamma$	$1.3^{+.1}_{-.2}$	$1.239 \pm .002$	$1.25 \pm .02$	$1.33 \pm .03$	$1.33 \pm .015$	$1.33 \pm .02$
$\delta$	$4.2^{+.6}_{-.3}$	$4.85 \pm .03$		$3.95 \pm .15$	$4.3 \pm .1$	$4.29 \pm .05$
$\eta$	$0.1 \pm .1$	$0.017 \pm .015$	$0.08 \pm .07$	$0.021 \pm .05$	$0.07 \pm .04$	$.041 \pm .01$
$\nu$	$\approx 0.57$	$0.625 \pm .006$	$0.65 \pm .02$	$.672 \pm .001$	$0.69 \pm .02$	$0.64 \pm .1$

NOTES: From data published in Ahlers (1980), Anders and Stierstadt (1981), Bally *et al.* (1968), Chang *et al.* (1979), Cohen and Carver (1977), Collins (1969), Heller (1967), Hiroyoshi (1980), Kobeissi (1981), Kumar *et al.* (1983), Rucker *et al.* (1971), Rowlinson and Winton (1982), Soeffge (1980), Suter and Hohenemser (1978), Vygovskiy and Yergin (1972).  $\alpha$  and  $\beta$  for a binary fluid are for methanol-hexane, while  $\gamma$ ,  $\eta$  and  $\nu$  are for a mixture of trimethylpentane and nitroethane. The data for helium relate to the He I-He II transition.  $\delta$  for a binary fluid,  $\alpha$  for  $\beta$ -brass, and both  $\gamma$  and  $\eta$  for helium have been calculated from the other exponents using formulae from §1.5.1.