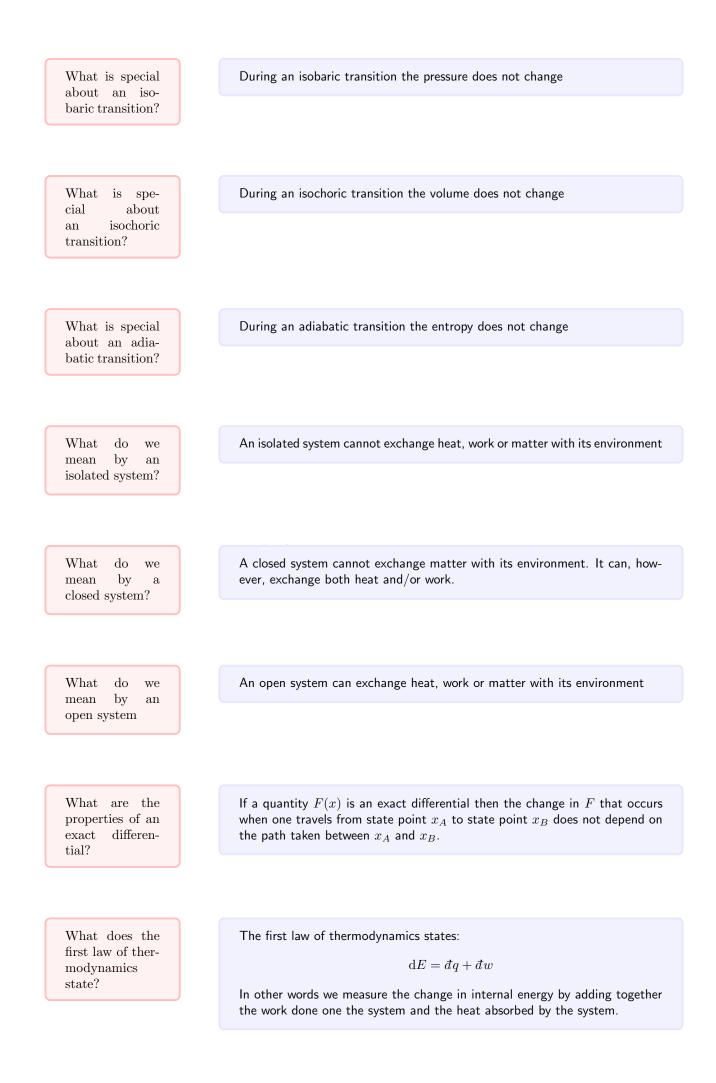# Key Ideas : AMA4004

The baloons below contain many of the important ideas and theorems that are covered in this module. If you have a good understanding of what everything on this sheet means then you have a good understanding of the module content. I would recommend that you stick these sheets in the first few pages of the hardback book that you keep your notes inside and that you consult these notes regularly as you work through the module.

What is a thermodynamic variable?	A thermodynamic variable is a quantity that describes the state of a macroscopic system. Many of these quantities can be easily measured or controlled in experiments.
What property do extensive variables have?	If the value of a thermodynamic variable depends on the size of the system then it is said to be an extensive quantity. The values of extensive quantities depend on the number of atoms (mols) that are present in the system.
What property do intensive variables have?	If the value of a thermodynamic variable does not depend on the size of the system then it is said to be an intensive quantity. The values of intensive quantities do not depend on the number of atoms (mols) that are present in the system. The density of an extensive variable (e.g. Number of atoms in a volume) is an intensive quantity. Quantities that are intrinsically intensive (i.e. not densities of extensive quantities) are also called **fields.**

List as many thermodynamic variables as you can, what symbols are used to represent these quantities, are they intensive or extensive and what pairs of variables are conjugate?

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Extensive	Intensive
Volume (V)	Pressure (-P)
Strain (ν)	Strain (σ)
Number of atoms of type i (N_i)	*Chemical potential of species i (μ_i)*
Entropy (S)	Temperature (T)
Magnetization (M)	Magnetic Field Strength (H)
Polarization (P)	Electric Field Strength (E)

What does it mean when we state that a system is in an equilibrium state?	A system is said to be at equilibrium if it does not change over macroscopic timescales. At equilibrium extensive variables do not change in time and intensive variables take on a single, uniform value across the whole system. Equilibrium states are completely characterised by a small set of thermodynamic variables.
What is special about an isothermal transition?	During an isothermal transition the temperature does not change.

What is special about an isobaric transition?	During an isobaric transition the pressure does not change
What is special about an isochoric transition?	During an isochoric transition the volume does not change
What is special about an adiabatic transition?	During an adiabatic transition the entropy does not change
What do we mean by an isolated system?	An isolated system cannot exchange heat, work or matter with its environment
What do we mean by a closed system?	A closed system cannot exchange matter with its environment. It can, however, exchange both heat and/or work.
What do we mean by an open system	An open system can exchange heat, work or matter with its environment
What are the properties of an exact differential?	If a quantity $F(x)$ is an exact differential then the change in F that occurs when one travels from state point x_A to state point x_B does not depend on the path taken between x_A and x_B.
What does the first law of thermodynamics state?	The first law of thermodynamics states: $$\mathrm{d}E = đq + đw$$ In other words we measure the change in internal energy by adding together the work done one the system and the heat absorbed by the system.

What does the second law of thermodynamics state?	The second law of thermodynamics states: $$\Delta_{A\to B} S \geq \int_A^B \frac{\mathrm{d}q}{T}$$ The equality sign holds when the transition is reversible, the inequality holds when the transition is irreversible. A consequence of this law is that the entropy of an isolated system can never decrease.
What is the combined statement of the first and second laws of thermodynamics?	When the first and second laws of thermodynamics are combined we arrive at the following expression for change in internal energy $\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V$
How is the enthalphy defined?	The enthaply, H, is equal to $H = E + PV$
How is the Helmholtz free energy defined?	The Helmholtz free energy, F, is defined as $F = E - TS$
How is the Gibbs free energy defined?	The Gibbs free energy, G, is defined as $G = E + PV - TS$
What is the difference between a first order and a continuous phase transition?	In a first order phase transition there is a discontinuity in the first derivative of the thermodynamic potential at the phase boundary. In a continous phase transition the first derivative of the thermodynamic potential is continuous but a discontinuity in one of the higher order derivatives still ensures that the change in the thermodynamic potenital cannot be expressed using a Taylor series if the transition crosses the phase boundary.
Explain the meanings of the terms microstate and phase space.	Any physical system can adopt one of a number of microstates. For a quantum system these are the various quantum levels. For a classical system these are the various combinations of velocities and positions for the atoms in the system. Phase space is the set of all possible microstates that a system can adopt.

State the axioms of information theory and give an expression for the information.	We define a quantity I (the information) contained in a probability distribution by requiring that this quantity has the following properties (Khinchine)

We define a quantity I (the information) contained in a probability distribution by requiring that this quantity has the following properties (Khinchine)

- The information depends only on the probability distribution.
- The uniform distribution contains the minimum information.
- If we enhance the sample space with impossible events the information does not increase.
- Information is additive.

It is possible to show, starting from these axioms, that the information contained in a probability distribution that has N possible outcomes in the sample space, Ω, that have probabilities given by the vector $\mathbf{p}$, is equal to:

$$I(\mathbf{p}) = k \sum_{i=1}^{N} p_i \ln p_i$$

Describe the canonical ensemble

In the canonical ensemble the number of atoms, the volume and the temperature are fixed. The probability of being in a particular microstate is:

$$p_i = \frac{e^{-\beta E_i}}{Z}$$

and the partition function is:

$$Z = \sum_i e^{-\beta E_i}$$

Describe the isothermal isobaric ensemble

In the isothermal isobaric ensemble the number of atoms, N, the pressure, P, and the temperature, T, are fixed. The probability of being in a particular microstate is:

$$p_i = \frac{e^{-\beta E_i} e^{\beta P V_i}}{Z}$$

and the partition function is:

$$Z = \sum_i e^{-\beta E_i} e^{-\beta P V_i}$$

Describe the grand canonical ensemble

In the grand canonical ensemble the chemical potential, μ, the volume, V, and the temperature, T, are fixed. The probability of being in a particular microstate is:

$$p_i = \frac{e^{-\beta E_i} e^{+\beta \mu N_i}}{Z}$$

and the partition function is:

$$Z = \sum_i e^{-\beta E_i} e^{+\beta \mu N_i}$$

Describe the microcanonical ensemble	In the microcanonical ensemble the number of atoms, N, the volume, V, and the internal energy, E, are fixed. The probability of being in a particular microstate is:

$$p_i = \frac{\delta(E_i - E)\delta(V_i - V)\delta(N_i - N)}{\Omega}$$

The partition function, Ω, for this ensemble is simply the total number of states that have energy E, volume V and number of atoms N. In other words:

$$\Omega = \sum_i \delta(E_i - E)\delta(V_i - V)\delta(N_i - N)$$

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