Lecture 1: The Thermodynamic Functions

List of Symbols

Symbol	Meaning
C_e	Electronic specific heat coefficient
C_P	Specific heat capacity at constant pressure
C_P^μ	Magnetic component of the specific heat capacity
C_V	Specific heat capacity at constant volume
C_V^L	Debye specific heat function
G	Gibbs free energy
H	Enthalpy
P	Pressure
q	Quantity of heat
S	Entropy
T	Absolute temperature
T_D	Debye temperature
U	Internal energy
V	Volume
w	Work done by a closed system
ω_D	Debye frequency

Internal Energy & Enthalpy

Classical thermodynamics has a formal structure which serves to organise knowledge and to establish relationships between well–defined quantities. It is in this context that extensive observations are taken to imply that energy is conserved. Therefore, the change in the internal energy $\Delta \mathbf{U}$ of a closed system is given by

$$\Delta \mathbf{U} = q - w \tag{1}$$

where q is the heat transferred into the system and w is the work done by the system. The historical sign convention is that heat added and work done by the system are positive, whereas heat given off and work done on the system are negative. Equation 1 may be written in differential form as

$$d\mathbf{U} = dq - dw. \tag{2}$$

For the special case where the system does work against a constant atmospheric pressure, this becomes

$$d\mathbf{U} = dq - PdV \tag{3}$$

where P is the pressure and V the volume.

The specific heat capacity of a material is an indication of its ability to absorb or emit heat during a unit change in temperature. It is defined formally as dq/dT; since $dq = d\mathbf{U} + PdV$, the specific heat capacity measured at constant volume is given by:

$$C_V = \left(\frac{\partial \mathbf{U}}{\partial T} \right)_V. \tag{4}$$

It is convenient to define a new function **H**, the enthalpy of the system:

$$\mathbf{H} = \mathbf{U} + PV. \tag{5}$$

A change in enthalpy takes account of the heat absorbed at constant pressure, and the work done by the $P\Delta V$ term. The specific heat capacity measured at constant pressure is therefore given by:

$$C_P = \left(\frac{\partial \mathbf{H}}{\partial T} \right)_P. \tag{6}$$

A knowledge of the specific heat capacity of a phase, as a function of temperature and pressure, permits the calculation of changes in the enthalpy of that phase as the temperature is altered:

$$\Delta \mathbf{H} = \int_{T_1}^{T_2} C_P \, dT \tag{7}$$

Entropy & Free Energy

Enthalpy is not the only thermodynamic parameter to change with temperature and hence is not a sufficient indicator of whether a reaction can occur spontaneously.

Consider what happens when a volume of ideal gas is opened up to evacuated space (Fig. 1). The gas expands into the evacuated space without any change in enthalpy, since for an ideal gas the enthalpy is independent of interatomic spacing. The state in which the gas is uniformly dispersed is far more likely than the ordered state in which it is partitioned. This is expressed in terms of a thermodynamic function called entropy **S**, the ordered state having a lower entropy. In the absence of an enthalpy change, a reaction may occur spontaneously if it

leads to an increase in entropy (*i.e.* $\Delta S > 0$). The entropy change in a reversible process is defined as:

$$dS = \frac{dq}{T} \qquad \text{so that} \qquad \Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT \qquad (8)$$
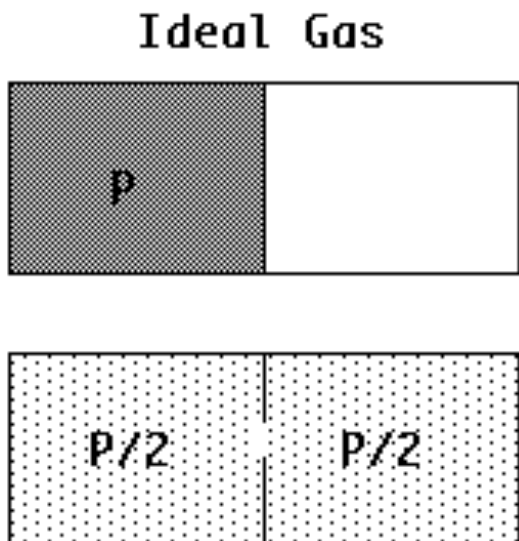
Ideal Gas

Fig. 1: Two isothermal chambers at identical temperature, one containing an ideal gas at a certain pressure P, and the other evacuated. It is expected that if the chambers are connected, then gas will flow into the evacuated chamber in order to equalise pressure. The reverse case, where all the atoms on the right hand side by chance move into the left chamber, is unlikely to occur.

It is evident that neither the enthalpy nor the entropy change can be used in isolation as reliable indicators of whether a reaction should occur

spontaneously. It is their combined effect that is important, described as the Gibbs free energy **G**:

$$\mathbf{G} = \mathbf{H} - T\mathbf{S}. \tag{9}$$

The Helmholtz free energy **F** is the corresponding term at constant volume, when **H** is replaced by **U** in equation 9. A process can occur spontaneously if it leads to a reduction in the free energy. Quantities such as **H, G** and **S** are path independent and therefore are called *functions of state.*

More About the Heat Capacity

The heat capacity can be determined experimentally using calorimetry. The data can then be related directly to the functions of state **H, G and S**. The heat capacity varies with temperature and other factors and hence is important in determining the stabilities of phase. It is useful to factorise the specific heat capacities of each phase into components with different origins; this is illustrated for the case of a metal.

The major contribution comes from lattice vibrations; electrons make a minor contribution because the Pauli exclusion principle prevents all but a few from participating in the energy absorption process. Further contributions may come from magnetic changes or from ordering effects in general. As an example, the net specific heat capacity at constant pressure has the components:

$$C_P\{T\} = C_V^L\left\{\frac{T_D}{T}\right\}C_1 + C_eT + C_P^\mu\{T\} \tag{10}$$

where $C_V^L\{\frac{T_D}{T}\}$ is the Debye specific heat function and T_D is the Debye temperature. The function C_1 corrects $C_V^L\{\frac{T_D}{T}\}$ to a specific heat at

constant pressure. C_e is the electronic specific heat coefficient and C_P^μ the component of the specific heat capacity due to magnetic effects.

The Debye specific heat has its origins in the vibrations of atoms, which become increasingly violent as the temperature rises. These vibrations are elastic waves whose wavelengths can take discrete values consistent with the size of the sample. It follows that their energies are quantised, each quantum being called a phonon. The atoms need not all vibrate with the same frequency, so that there is a vibration spectrum to be considered in deriving the total internal energy $\mathbf{U}$ due to lattice vibrations. The maximum frequency of vibration in this spectrum is called the Debye frequency ω_D, which is proportional to the Debye temperature T_D through the relation

$$T_D = \frac{h\omega_D}{2\pi k} \tag{11}$$

where h and k are the Planck and Boltzmann constants respectively. The internal energy due to the atom vibrations is:

$$\mathbf{U} = \frac{9NkT^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{(e^x - 1)} \, dx \tag{12}$$

where $x = h\omega_D/(2\pi kT)$ and N is the total number of lattice points in the specimen. Since $C_V^L = d\mathbf{U}/dT$, it follows that the lattice specific heat capacity at constant volume can be specified in terms of the Debye temperature and the Debye function (equation 12). The theory does not provide a complete description of the lattice specific heat since T_D is found to vary slightly with temperature. In spite of this, the Debye function frequently can be used quite accurately for $C_V^L\{T\}$ if an average T_D is calculated for the range $T_D/6 - T_D$.

At low temperatures $(T \ll T_D)$, $\mathbf{U} \to 3NkT^4\pi^4/(5T_D^3)$ so that $C_V^L \to 12\pi^4 NkT^3/(5T_D^3)$ and the lattice specific heat thus follows a T^3 dependence. For $T \gg T_D$, the lattice heat capacity can similarly be shown to become temperature independent and approach a value $3Nk$, as might be expected for N classical oscillators each with three degrees of freedom (Fig. 2).
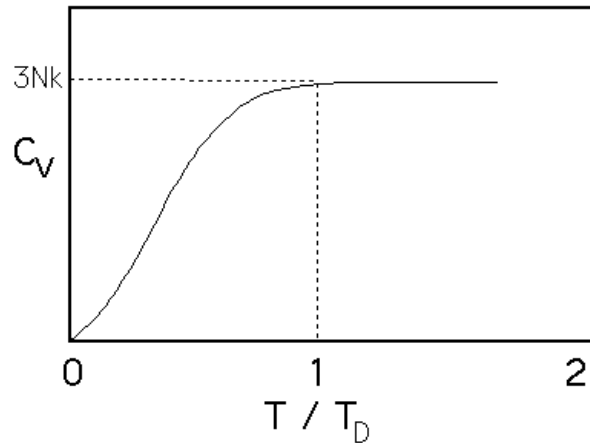

Fig. 2: The Debye function.

Fig. 3 shows the variation in the specific heat capacities of allotropes of pure iron as a function of temperature. Ferrite undergoes a paramagnetic to ferromagnetic change at a Curie temperature of 1042.15 K.

The Equilibrium State

Equilibrium is a state in which "no further change is perceptible, no matter how long one waits". For example, there will be no tendency for diffusion to occur between two phases which are in equilibrium even though they may have different chemical compositions.

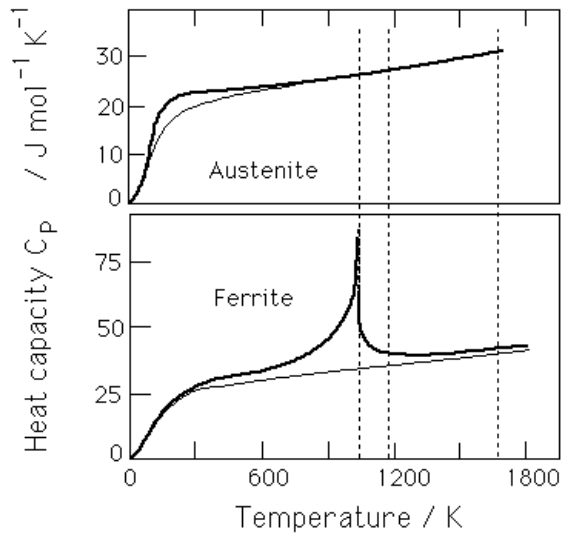An equilibrium phase diagram is vital in the design of materials.

Fig. 3: The specific heat capacities of ferrite and austenite as a function of temperature (after Kaufman, 1967). The thin lines represent the combined contributions of the phonons and electrons whereas the thicker lines also include the magnetic terms. The dashed vertical lines represent the Curie, $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \delta$ transitions.

It contains information about the phases that can exist in a material of specified chemical composition at particular temperatures or pressures. It carries information about the chemical compositions of these phases and the phase fractions. The underlying thermodynamics reveals the *driving forces* which are essential in kinetic theory. We shall begin the discussion of phase equilibria by revising some of the elementary thermodynamic models of equilibrium and phase diagrams, and then see how these can be adapted for the computer modelling of phase diagrams as a function of experimental thermodynamic data.

Allotropic Transformations

Consider equilibrium for an allotropic transition (*i.e.* when the structure changes but not the composition). Two phases α and γ are said to be in equilibrium when they have equal free energies:

$$G^\alpha = G^\gamma \tag{13}$$

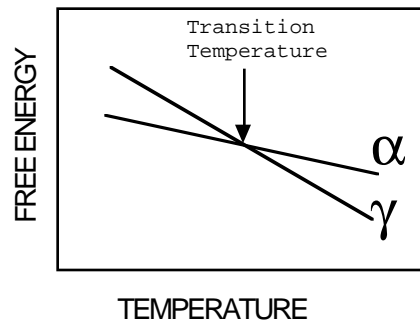When temperature is a variable, the transition temperature is also fixed by the above equation (Fig. 4).

Fig. 4: The transition temperature for an allotropic transformation.