CHAPTER 10

Tables

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Understanding the properties of matter

by Michael de Podesta.

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Table 10.1 Summary of the contributions to the Gibbs free energy in each of the possible states of matter.

	U	−TS	+PV
Solid	In a solid atoms are close together and interact strongly. This terms is therefore large and negative.	The entropy of a solid is very low. This is because solids are highly ordered, which is *a priori* a very unlikely state for matter to be in. However, the entropy is multiplied by temperature. If the temperature is low, *TS* will be small, but if the temperature is large this term will be very significant.	At a given pressure the volume of a solid is close to the minimum volume that a substance can occupy. This makes this term small.
Gas	The interaction between atoms is many orders of magnitude weaker in gases than in solids. In the Ideal Gas theory it is neglected entirely.	The entropy of a gas is very high. This is because gases are completely disordered collections of atoms.	At a given pressure the volume of a gas is as large as it is able to be.
Liquid	The interaction between atoms is of the same order as in the solid state, but the lack of organisation means that the internal energy is generally not quite as low as in a solid.	The entropy of a liquid is a little larger than a solid.	At a given pressure the volume of a liquid is similar to that of a solid.

Table 10.2 Summary of the contributions to the Gibbs free energy $G = U - TS + PV$ in the solid and gas phases. The results of the sum are plotted as a function of temperature in Figure 10.1.

	U (mol^{-1})	TS (mol^{-1})	PV (mol^{-1})
Solid	The cohesive binding energy is given by Table 11.5 as −90.1 kJ mol^{-1}. To estimate U we evaluate: $$-90.1 \times 10^3 + \int C_V(T)dT$$ where $C_V(T)$ is estimated from a Debye model of a solid with a Debye temperature of 100 K.	Estimated from: $$T\left[\int \frac{C_V(T)}{T}dT\right]$$ with $C_V(T)$ estimated from a Debye model of a solid with a Debye temperature of 100 K. The entropy at $T = 0$ K is taken as zero.	We neglect thermal expansion and estimate PV from the density and atomic mass (Table 7.2). At atmospheric pressure we find: $$PV = 1.013 \times 10^5 \times \frac{39 \times 10^{-3}}{830}$$ This term is very small.
Gas	Assuming perfect gas behaviour, we have no binding energy and so we estimate U as: $$0 + \int C_V(T)dT$$ where $C_V(T)$ is estimated from an assumption of perfect gas behaviour as $C_V = 1.5R$ independent of temperature.	Estimated from: $$T\left[\int \frac{C_V(T)}{T}dT\right]$$ with $C_V(T)$ estimated from an assumption of perfect gas behaviour as $C_V = 1.5R$ independent of temperature. The entropy at T = 0 K is chosen so as make the entropy of potassium vapour at 298 K agree with the data from *Emsley*.	We use the perfect gas equation for 1 mole of substance to evaluate : $$PV = RT$$

Table 10.3 Summary of the contributions to the Gibbs free energy $G = U - TS + PV$ in the liquid phase. The results are plotted as a function of temperature along with the results from Table 10.1 in Figure 10.2.

	U (mol^{-1})	TS (mol^{-1})	PV (mol^{-1})
Liquid	The cohesive binding energy of the solid is given by *Kittel* as -90.1 kJ mol^{-1}. Assuming a value of around 90% of this figure we estimate U as: $$-81 \times 10^3 + \int C_V(T) dT$$ where $C_V(T)$ is estimated to be 10% greater than the equivalent solid and to have a lower Debye temperature.	Estimated from: $$T\left[\int \frac{C_P(T)}{T} dT\right]$$ where $C_V(T)$ is estimated to be 10% greater than the equivalent solid and to have a lower Debye temperature. The entropy at $T = 0$ is set equal to zero as for a solid. This will underestimate the entropy of the liquid state.	We consider this term to be the same as the solid.

Table 10.4 The orders of some phase transitions.

First-order	Continuous
Melting/freezing	Superconducting (in zero magnetic field)
Boiling/condensing	Ferromagnetic
Liquid crystals	
Superconducting (in a magnetic field)	