

# Thermodynamics

02/10/98

## Reading

"Thermal Physics", Finn.

## Thermodynamics

Thermodynamics is about considering a system, the system being what we consider. Everything else in the universe is the surroundings. Doing work ( $dW$ ) on the system or adding or removing heat ( $dH$ ) from the system. The properties of a thermodynamic system are pressure, volume and temperature (for gaseous systems). These properties are known as the **thermodynamic coordinates** thermodynamic state is defined by the thermodynamic coordinates.

### **Q & W are not thermodynamic coordinates.**

$dQ$  and  $dW$  are written with a line across the d's. These are known as inexact differentials. There is no relationship connecting  $W$  and  $Q$  to the thermodynamic coordinates (TC's).  $dQ$  and  $dW$  means a small amount of heat and work.

The volume,  $V$ , is known as the **extensive coordinate** depends on the size of the system. Pressure,  $P$ , and temperature,  $T$ , are the **intensive coordinates** they are independent of the system's size. The TC's are known as **functions of state** They are only defined for the system in **thermodynamic equilibrium** thermodynamics describes only systems in thermodynamic equilibrium.

By the first law of thermodynamics,

$$dQ = dU + dW$$

$dU$  is principally the kinetic energy of the molecules.  $dW$  is the work done (WD).  $dW$  is positive if the system does work on the surroundings.

**fig 1**

We can show,

**eq 1**

is independent of the reversible path between state 1 and state 2.

For a reversible path, both the system and surroundings can be

returned to their initial state. We can define a quantity called **Entropy** such that the entropy difference such that,

**eq 2**

Entropy is therefore a function of state.

For an irreversible path we can show,

**eq 3**

In differential form, ( $dQ$  is still inexact)

$$\begin{aligned} dS & \geq dQ/T \\ & > \text{for irreversible path} \\ & = \text{for reversible path} \end{aligned}$$

This is a mathematical statement of the second law of thermodynamics.

**09/10/98**

The second law of thermodynamics *gives the direction* that changes can take place.

Consider a system which is enclosed by its surroundings which have a very large boundary so that  $dQ=0$  between the system and surroundings. Therefore, from the second law,

$$dS = dS_{\text{system}} + dS_{\text{surroundings}} \geq 0$$

This is the principal of increase of entropy in the universe. It gives the direction of change.

Example 1

Two bodies are brought from isolation into thermal contact. One body has a temperature of  $100^\circ\text{C}$  and the other  $0^\circ\text{C}$ . They finally come into thermal equilibrium, both at  $50^\circ\text{C}$ . This is an irreversible process because system + surroundings cannot be brought back to the initial conditions. If it were, it would violate Clausius's statement of the second law.

To find the entropy change,

$$\Delta S = \text{Integ (final, initial)} \{dQ/T\}$$

But  $dQ = \text{mass specific heat } \cdot dT$

$$\begin{aligned} \Delta S_{\text{tot}} &= \text{Integ (323, 373)} \{C \cdot dT/T\} \\ &= C \cdot [\text{Ln}(T)] \{323, 373\} \\ &= C \cdot \text{Ln}(323/373) \end{aligned}$$

$$=C \quad -0.1439 \text{ J.K}^{-1}$$

$$\begin{aligned} \Delta S_{\text{cold}} &= \int_{323,273} \{C \cdot dT/T\} \\ &= C \cdot \ln(323/273) \\ &= C \quad +0.1682 \text{ J.K}^{-1} \end{aligned}$$

Therefore,

$$\Delta S_{\text{universe}} = 0.0243 \text{ C J.K}^{-1}$$

So it's a positive increase in S, hence it is an irreversible process

### Example 2 (Free expansion of ideal gas)

There are two boxes connected by a pipe. The first is full of a gas of pressure  $P_1$  and volume  $V_1$ . The second box is a vacuum. When the tap is opened, the gas flows into the empty box. This is an irreversible process.

By the first law of thermodynamics,

$$Q = \Delta u + W$$

In this case the heat absorbed ( $Q$ ) is zero. The work done by the gas is zero because the gas is expanding into a vacuum. Therefore  $\Delta u = 0$  and  $\Delta T = 0$  (for an ideal gas). For these changes there is no temperature change, however, we do have an initial and final pressure and volume coordinates. We want to find the entropy change for this process. We find it by,

$$\Delta S = \int_{\text{ev}} \{dQ/T\}$$

To find  $\Delta S$  we integrate along a reversible **isotherm**

### **fig 1**

For reversible isothermal expansion, we use the first law,

$$\begin{aligned} dQ &= du + dW \\ dQ &= 0 + PdV \end{aligned}$$

For a reversible isothermal  $du = 0$  because the temperature is constant. Therefore,

$$dQ = PdV$$

Therefore,

$$S_f - S_i = \text{Integ} \{PdV/T\}$$

But,  $PV=RT$  (for one mole). Therefore,

$$\begin{aligned} S_f - S_i &= R \int_{V_i}^{V_f} \{dV/V\} \\ &= R \ln(V_f/V_i) \\ &> 0 \end{aligned}$$

Because  $V_f > V_i$ .

### Entropy and Disorder

A solid consists of fairly regularly spaced atoms. As heat is absorbed the solid goes into the liquid phase and the atoms in the substance become less regularly spaced and begin to move around some. As the more heat is absorbed we transit into the vapour stage and the order of the substance is totally lost.

Entropy change

$$\begin{aligned} \Delta S &= \text{Integ} \{dQ/T\} \\ &= 1/T \int dQ \\ &= m.L/T \end{aligned}$$

Where  $L$ =latent heat,  $T$ =temperature of phase change, and  $m$  is the mass. Since  $L$  represents positive heat into the system,  $\Delta S > 0$ .

### Summary

1. Entropy is a function of state.
2. Entropy is related to disorder.
3.  $dS \geq dQ/T$  >Irreversible, =reversible.
4.  $dS \geq 0$  for the universe.

**16/10/98**

### New Thermodynamic Functions

Recall the first law,

$$T.dS = du + P.dV$$

This connects all the state functions,  $P, V, T, S$  &  $U$

We now define a new quantity, **Enthalpy**, or **H**. Enthalpy is defined as,

$$\begin{aligned} H &= u + PV \\ dH &= du + PdV + VdP \\ &= \underline{T.dS + V.dP} \end{aligned}$$

We now define the **Helmholtz function** **F**. Where,

$$\begin{aligned} F &= u - TS \\ dF &= du - T.dS - S.dT \\ &= \underline{-P.dV - S.dT} \end{aligned}$$

Another function is the **Gibb's function** **G**. Which is defined as,

$$\begin{aligned} G &= H - TS \\ &= u + PV - TS \\ dG &= du + PdV + VdP - TdS - SdT \\ &= \underline{VdP - SdT} \end{aligned}$$

u, H, F, G are all specific energies, J/Kg, J/mole. They are all functions of state. They are important for specifying thermodynamic equilibrium, e.g. if P & T of a system doesn't change then dG=0. For example a change of phase (like ice melting at room temperature and pressure).

### Maxwell's Relations

For our system,

$$\begin{aligned} du &= TdS - PdV \\ \text{(this is a differential equation)} \\ &= T(S, V).dS - P(S, V).dV \end{aligned}$$

To find u, integrate this equation.

*To test if something of the form  $dz = P.dx + Q.dy$  can be integrated, the test to see if this can be done, i.f.f.  $(dP/dx) = (dq/dy)$ .*

To find u, integrate this equation, we know that this must be possible (in principal) because u is a function of state.

$$\left(\frac{\partial T}{\partial V}\right) = -\left(\frac{\partial P}{\partial S}\right) \quad \text{Maxwell 1}$$

For H,

$$\left(\frac{\partial T}{\partial P}\right) = \left(\frac{\partial V}{\partial S}\right) \quad \text{Maxwell 2}$$

For F,

$$\left(\frac{\partial P}{\partial T}\right)_{V} = \left(\frac{\partial S}{\partial V}\right)_{T} \quad \text{Maxwell 3}$$

For G,

$$\left(\frac{\partial V}{\partial T}\right)_{P} = -\left(\frac{\partial S}{\partial P}\right)_{T}$$

The cross-product of TS or PV (negative, PT together in numerator or denominator).

### Measurable Quantities

1) Specific heat, constant volume,

$$C_v = \left(\frac{dQ}{dT}\right)_v = T \left(\frac{\partial S}{\partial T}\right)_v$$

2) Specific heat, constant pressure,

$$C_p = \left(\frac{dQ}{dT}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p$$

3) Isothermal compressibility,

$$K_T = -\left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial P}\right)_T$$

4) Coefficient of volume expansion,

$$\alpha = \left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial T}\right)_P$$

### Changes of state

For a single phase system,

$$V = V(P, T)$$

By the chain rule,

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

If V is constant,  $dV=0$ ,

$$\begin{aligned} 0 &= \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \\ 0 &= \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P \end{aligned}$$

Therefore,

$$\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P = -1$$

**30/10/98**

The PT relationships:

For a PVT system, by the cyclic relationship,

$$\left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial V}\right)_P = -1$$

but,

$$\alpha = \left(\frac{1}{V}\right) \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

... volume expansivity

$$K_T = -\left(\frac{1}{V}\right) \cdot \left(\frac{\partial V}{\partial P}\right)_T$$

... isothermal compressibility

Therefore,

$$-K_T \cdot V \cdot \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{1}{\alpha V}\right) = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha / K_T$$

... The PT relationship

Heat Absorption relationships

$$dW \rightarrow PVT \text{S (or } dQ) \text{ -(rev)-} \rightarrow P'V'T'S'$$

(The P to P' stages are connected by the TdS relationships)

By the second law,

$$dQ = TdS$$

1) dQ is related to dV and dT.

Since,

$$dS = f(V, T)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V \cdot dT + \left(\frac{\partial S}{\partial V}\right)_T \cdot dV$$

$$dQ = TdS = T \left(\frac{\partial S}{\partial T}\right)_V \cdot dT + T \left(\frac{\partial S}{\partial V}\right)_T \cdot dV$$

But we can also measure  $C_v$ ,  $C_p$ ,  $\alpha$ ,  $K_T$  and relate them to the differential terms above. Hence we obtain,

$$\left(\frac{dQ}{dT}\right)_V = C_v$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha / K_T$$

Therefore we write  $dQ$  as,

$$dQ = TdS = C_V dT + (T\alpha / K_T) dV$$

This is known as the **first TdS relationship**

2)  $dQ$  as a function of T and P. Since  $dS = f(P, T)$ ,

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + T \left(\frac{\partial S}{\partial P}\right)_T dP$$

Again, we can relate the differential terms to measurable constants.

$$\left(\frac{dQ}{dT}\right)_P = C_P$$

and

$$\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V$$

We can then write,

$$dQ = TdS = C_P dT - \alpha V T dP$$

This is known as the **second heat absorption (or TdS) relationship**

#### Example 1

A cylinder-piston arrangement is taken from  $P_1$  to  $P_2$ , where  $P_2 > P_1$ . Heat is absorbed during a reversible, isothermal change of pressure. Use 2nd TdS,

$$dQ = TdS = C_P dT - \alpha V T dP$$

$C_P dT$  is zero in this case. Also, assume that the gas is an ideal gas. Therefore,

$$PV = RT \text{ (1 mole)}$$

Hence we write,

$$\alpha = (1/V) \cdot \left(\frac{\partial V}{\partial T}\right)_P = (1/V) \cdot (R/P) = 1/T$$

Therefore,

$$dQ = -(V/P) dP$$

Therefore,

$$Q = - \int_{P_1}^{P_2} \left(\frac{RT}{P}\right) dP \\ = -RT \ln(P_2/P_1)$$

$$(< 0)$$

### Example 2

Consider a metal block. Find the temperature rise during an adiabatic compression.

Use the 2nd **TdS** equation,

$$dQ = TdS = C_p dT - \alpha V T dP$$

For an adiabatic change,

$$dQ = 0$$

Therefore,

$$\begin{aligned} dT &= (\alpha V T / C_p) dP = (\alpha T / C_p \rho) dP \\ &= ((5 \cdot 10^{-5} \cdot 300) / (5 \cdot 10^3 \cdot 10^4)) \cdot 10^5 \\ &= 3 \cdot 10^{-4} \text{ K} \end{aligned}$$

Now, work out the heat exchange when the body returns to room temperature with the pressure still applied to it (ISOBARIC).

Therefore,  $dP=0$ .

$$\begin{aligned} dQ &= C_p dT \\ &= 5 \cdot 10^3 \cdot 3 \cdot 10^{-4} \\ &= 15 \cdot 10^{-2} \text{ J} \end{aligned}$$

### **06/11/98**

#### Adiabatic Change of an Ideal Gas

Consider a reversible adiabatic expansion ( $P_0, V_0$  to  $P, V$ ). Both of the TdS equations are equal to zero for adiabatic processes. So we therefore write,

$$\begin{aligned} dT &= -(1/C_v) \cdot (T \alpha / K_T) \cdot dV \\ &= (1/C_p) / \alpha V T \cdot dP \end{aligned}$$

Therefore,

$$\begin{aligned} dV &= -(C_v/C_p) \cdot K_T V \cdot dP \\ &= -(1/\gamma) \cdot K_T V \cdot dP \end{aligned}$$

Where  $\gamma = C_p/C_v$  which is called the ratio of specific heats. For an ideal gas,

$$PV = nRT$$

$$PdV_T + VdP_T = 0$$

(at constant T)

But,

$$\begin{aligned} K_1 &= -(1/V) \cdot (dV/dP) \\ &= -(1/V) \cdot (V/P) \\ &= -1/P \end{aligned}$$

Hence,

$$\begin{aligned} dV &= -(1/y)(V/P)dP \\ y \cdot \int (dV/V) &= - \int (dP/P) \\ y \cdot \ln(V/V_0) &= -\ln(P/P_0) \\ \ln(V/V_0)^y &= \ln(P_0/P) \\ (V/V_0)^y &= P_0/P \end{aligned}$$

$$PV^y = \text{Constant}$$

Also to find the temperature change,

$$PV/T = \text{Constant}$$

Isothermal and adiabatic compression of a gas

Consider a cylinder -piston at initial state  $P_1, V, T_1$ . It is then compressed to the state,  $P_2, V/2, T_2$ .

For an isothermal compression,

$$T_1 = T_2$$

Therefore,

$$\begin{aligned} P_1 V &= P_2 (V/2) \\ P_2 &= 2P_1 \end{aligned}$$

For adiabatic compression

$$\begin{aligned} PV^y &= \text{const} \\ P_1 V^y &= P_2 (V/2)^y \\ (y=5/3 \text{ for monatomic gas}) \\ P_2 &= (2^y) \cdot P_1 = 3.17 P_1 \end{aligned}$$

To find  $T_2$ ,

$$\begin{aligned} P_1 V/T_1 &= 3.17 P_1 (V/2)/T_2 \\ T_2 &= 1.58 T_1 \end{aligned}$$

### Specific Heats of gases

Consider one mole of a gas ( $N_A$ ,  $6 \cdot 10^{23}$  atoms/molecules). The energy per degree of freedom is  $\frac{1}{2}kT$ . So the total internal energy of the gas is,

$$\begin{aligned} u &= 3 \cdot \frac{1}{2} k T N_A \\ &= 3 \cdot \frac{1}{2} R T \end{aligned}$$

Therefore,

$$C_v = (du/dT)_v = 3 \cdot \frac{1}{2} R$$

For an ideal gas,

$$C_p = C_v + R$$

Therefore,

$$\begin{aligned} \gamma &= C_p / C_v \\ &= (5R/2) / (3R/2) \\ &= 5/3 \end{aligned}$$

*for a monatomic gas!*

However, diatomic gases have more than three degrees of freedom as for monatomic gases. Diatomic gases actually have **seven** degrees of freedom. This gives gamma as 9/7.

$$\begin{aligned} \gamma &= 9/7 \\ &\text{for a diatomic gas!} \end{aligned}$$

### Difference of specific heats

From the first TdS equation,

$$dQ = C_v dT + T \left( \frac{\partial P}{\partial T} \right)_v dV$$

For heating at constant pressure we get a change in the temperature. Therefore,

$$\left( \frac{dQ}{dT} \right)_p = C_p = C_v + T \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial V}{\partial T} \right)_p$$

On the RHS, the first differential is the PT relationship and the second differential term is  $\alpha \cdot V$ . So we now get,

$$\begin{aligned} C_p &= C_v + T \left( \frac{\alpha}{K_T} \right) \alpha V \\ &= C_v + \left( T \alpha^2 V / K_T \right) \end{aligned}$$

For solids,  $C_p$  is approximately equal to  $C_v$ . In liquids however,  $C_p$  is

greater than  $C_v$ .

For an ideal gas,

$$\begin{aligned} \alpha &= 1/T \\ &\& \\ K_T &= 1/P \end{aligned}$$

So,

$$\begin{aligned} C_p &= C_v + (TVP/T\dot{y}) \\ &= C_v + nR \end{aligned}$$

For one mole,

$$C_p = C_v + R$$

**13/11/98**

### Expansion of Gases - Cooling and Liquifraction.

There are three ways in which gases can be expanded.

1) Free expansion - expansion without work. For instance, if we release a gas into an evacuated chamber which has a volume many times that of the contained gas. If the gas is ideal there is no cooling, otherwise the cooling effect is very small, less than one kelvin.

2) Expansion with adiabatic work. In a cycle the gas is compressed adiabatically, so temperature and pressure increases and volume decreases. Then the gas is held at constant volume and heat flows from the system. As this happens the pressure drops. We are now at what we consider as our initial state  $i$ . The gas is then allowed to expand adiabatically to the final state. As this happens, the pressure and temperature decrease.

During the adiabatic expansion,

$$\begin{aligned} P_i V_i^\gamma &= P_f V_f^\gamma \\ (P_i V_i / T_i)^\gamma &= (P_f V_f / T_f)^\gamma \\ (P_i^{1-\gamma} \cdot T_i^\gamma)^\gamma &= (P_f^{1-\gamma} \cdot T_f^\gamma)^\gamma \\ P_i^{(1-\gamma)/\gamma} \cdot T_f &= P_f^{(1-\gamma)/\gamma} \cdot T_i \\ T_f &= T_i \cdot (P_i / P_f)^{((1-\gamma)/\gamma)} \\ &= T_i \cdot (P_f / P_i)^{-((1-\gamma)/\gamma)} \end{aligned}$$

If  $P_f/P_i=0.1$ ,  $\gamma=5/3$  and  $T_i=293$  gives  $T_f$  to be 117 (or cools by 40%).  
Cooling by adiabatic work is good at high temperatures but it becomes ineffective at low temperatures.

3) Joule Thomson expansion.

Consider gas in a tube, which diffuses through a porous plug

(something like cotton wool). Say gas coming into the tube has internal energy  $u_1$  volume  $V_1$  and temperature  $T_1$ . Once it passes through the plug it will be in an new state with values  $u_2, V_2, T_2$ . Consider 1 mole of gas, by the first law,

$$\mathbf{Q=(u_2-u_1)+W}$$

$$\mathbf{(W=work\ done\ by\ gas)}$$

If the system is isolated  $Q=0$ . Then the work done by the gas can be written as,

$$\mathbf{W=u_1-u_2}$$

So now consider one mole of the gas moving into the tube, towards the plug. At the incoming side of the plug the pressure is  $P_1$ , as some gas just starts to seep through, the pressure on the other side is  $P_2$ . So the work done on the gas is  $P_1V_1$ . As the gas passes into the other side of the plug and we have the state  $P_2, V_2$ . So the work done by the gas is  $P_2V_2$ . Hence the net work done by the gas is,

$$\mathbf{P_2V_2-P_1V_1=u_1-u_2}$$

Therefore,

$$\mathbf{u_2+P_2V_2=u_1+P_1V_1}$$

$$\mathbf{H_2=H_1}$$

Therefore, this is an isenthalpic expansion. We wish to find the change in temperature with pressure for constant enthalpy. i.e.,

$$\mathbf{(\partial T/\partial P)_H=\alpha}$$

Where  $\alpha$  is known as the Joule Thomson coefficient. To find  $\alpha$  we use the cyclic relationship using the three variables, H,T and P.

$$\mathbf{(\partial H/\partial T)_P \cdot (\partial T/\partial P)_H \cdot (\partial P/\partial H)_T = -1}$$

But enthalpy is,

$$\mathbf{H=u+PV}$$

$$\mathbf{dH=dU+PdV+VdP}$$

$$\mathbf{dH=TdS+VdP}$$

Therefore,

$$\mathbf{(\partial H/\partial T)_P = T(\partial S/\partial T)_P = (dQ/dT)_P = C_P}$$

Also,

$$\mathbf{(\partial H/\partial P)_T = T(\partial S/\partial P)_T + V}$$

$$=-T(\partial V/\partial T)_{P+V}$$

Therefore,

$$\alpha=(\partial T/\partial P)_H=(1/C_p).(T(\partial V/\partial T)_P-V)$$

Therefore, for cooling  $\alpha>0$  ( $dP$  is negative and  $dT$  is negative for cooling.).

Consider an ideal gas,

$$PV=nRT$$

Therefore,

$$P(\partial V/\partial T)_P=nR$$

Therefore,

$$(\partial V/\partial T)_P=nR/P=V/T$$

Hence,

$$\alpha=0$$

**18/11/98**

For real gases however,

**fig 1**

If we start at  $P_1, T_1$  and increase the volume and the temperature increases but the pressure drops. this continues upto a maximum, which is called the **inversion point** Past this point the volume decreases. The curve on an indicator diagram is called an **isenthalpic curve** A whole family of such curves can be drawn. If they are drawn on a  $P, T$  plot we can trace out the locus of the maximum temperatures. These are the **inversion temperatures** Above such temperatures one cannot cool the gas,

**Fig 2**

For a real gas,  
 He,  $T_i(\max)=286$   
 H<sub>2</sub>,  $T_i(\max)=195$   
 N<sub>2</sub>,  $T_i(\max)=621$   
 A,  $T_i(\max)=723$   
 CO<sub>2</sub>,  $T_i(\max)=1500$

For most normal pressures we get cooling if  $T < T_i(\text{max})$ .

### Fig 3

Also see Fig.4

### Fig 4

Gas is passed from a condenser to a primary heat exchanger.

The gas supplied to the first heat exchanger is cooled by allowing it to perform adiabatic work. The gas is then passed to a second heat exchanger in which it performs a Joule-Thomson expansion which cools it further. As the gas passes from the heat exchanger chamber, it passes over the incoming coil (back out to the condenser) and begins to pre-cool the incoming gas. Eventually liquid begins to form inside the secondary heat exchanger chamber.

For Helium it must cool the gas below the maximum inversion temperature. We can achieve the boiling point of Helium, 4.2 Kelvin. By overpumping, which is reducing the pressure of the surface, we get down to 1.5 Kelvin.

### The Thermodynamics of a magnetised body.

#### **Paramagnetism**

This occurs in materials such as,  $\text{CuSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$ . It occurs from the unpaired spins of the transition metal ions. The net magnetic moment of the inner electrons shells of the metals are zero because all the electrons are paired off anti-parallel. Out in the d shell however, there are unpaired electrons. Due to the Pauli exclusion principle, in iron, there are three electrons in the the d sub shells which exist with parallel spins. In copper there are nine electrons in the d shell, in eight sub shells the electrons are paired off, but there is one unpaired electron to cause a dipole.

For an atoms ( $\mu$  in it's electromagnetic sense),

$$\mu = g \cdot \mu_B \cdot S$$

$g$  is the Landé g factor ( $=2.00$ ).  $\mu_B$  is the bohr magneton, it is defined as,

$$\mu_B = \frac{eh}{2m_p}$$

$S$  is the quantum spin number, for iron it is,  $3/2$  and for copper is  $1/2$ .

The magnetisation,  $M$ , is an important quantity, it is the magnetic

moment per unit volume

$$\mathbf{M} = g \mu_B \mathbf{S} N B(\mathbf{H}, T)$$

$N$  is the number of atoms per unit volume and  $B(\mathbf{H}, T)$  is called the Brillouin function ( $H$  is the magnetic field).

For a body with no applied field, all of the spins are pointing in random directions and in bulk cancel out. *There is no alignment of spins!* For a material where there is a small applied field ( $H$ ) but the temperature is high, the magnetisation greater than zero but is small. The temperature tends to disrupt any alignment. If  $H$  is high and  $T$  is small though, all the atoms cannot help but become aligned and the magnetisation reaches a **saturation** value.

If we plot  $M$  in terms of  $H$  we would see a line increasing linearly, as  $H$  increases and we reach the saturation value of  $M$  the line begins to curve and will level off at  $M_{\text{sat}}$ . As the temperature decrease the function will get steeper. The shape of the function is determined by the Brillouin function,

$$\mathbf{M} \propto \mathbf{H}/T \\ = C \cdot (\mathbf{H}/T)$$

The above can be considered as an equation of state, where  $C$  is the Curie's constant.

**20/11/98**

The work done by a magnetic material

Consider a body of a particular paramagnetic material placed as the core to a conductive core which is carrying a current  $i$ . The work done on a unit volume of paramagnetic material is  $= \mu_0 \cdot H \cdot dM$  ( $M$  is the magnetisation). By the first law,

$$dQ = du + dW \text{ (dW is done by the material)}$$

If we now rewrite the first law,

$$T \cdot dS = du - \mu_0 \cdot H \cdot dM$$

If we now make an analogy to a PVT system,

$$T \cdot dS = du + P \cdot dV$$

we can incorporate the magnetic quantities,

$$P \rightarrow H, V \rightarrow \mu_0 M$$

Maxwell's relationship becomes,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

**(Recall PTTP, PT together positive)**

after substituting in the magnetic quantities,

$$\left(\frac{\partial S}{\partial H}\right)_T = \alpha_0 \left(\frac{\partial M}{\partial T}\right)_H$$

### The Magnetocaloric effect

This is the change in temperature of a magnetic body with magnetic fields for a adiabatic change. The thermodynamic variables are:

S - the entropy, T - the temperature, H - the magnetic field, M - the magnetic field.

However we only need three variables to completely define a thermodynamic system, in this case we shall leave out M.

Since, S, T & H are functions of state, changes in these for a unit volume of a system of magnetic material,

$$dS = \left(\frac{\partial S_V}{\partial H}\right)_T dH + \left(\frac{\partial S_V}{\partial T}\right)_H dT$$

Recalling the Maxwell equation from above, we can substitute the  $\partial S/\partial H$  term. Hence, by Maxwell, and using the specific heat ( $C = dQ/dT$ ).

$$C_H = dQ_H/dT = T \cdot \left(\frac{\partial S_m}{\partial T}\right)_H$$

$C_H$  is the specific heat per unit mass  
Also,

$$\begin{aligned} c &= \text{Mass/Vol} = \partial S / \partial S_m \\ &= (S/V) / (S/m) \end{aligned}$$

The specific heat then becomes,

$$C_H = (T/c) \cdot \left(\frac{\partial S}{\partial T}\right)_H$$

Therefore,

$$dS_V = \alpha_0 \left(\frac{\partial M}{\partial T}\right)_H dH + (c C_H / T) dT \quad (1)$$

This is equivalent to the second TdS equation.  
For an adiabatic change,  $dQ=0$ ,  $dS=0$

$$dT_S = -(\alpha_0 T / c C_H) \cdot \left(\frac{\partial M}{\partial T}\right)_H dH$$

Assume Curie's law (where C is Curie's constant),

$$M = C \cdot (H/T)$$

Therefore,

$$\left(\frac{\partial M}{\partial T}\right)_H = -CH/T^2$$

Therefore,

$$\begin{aligned} dT_s &= (\alpha_0 T / \zeta C_H) \cdot (CH/T^2) \cdot dH \\ &= (\alpha_0 CH / \zeta C_H T) \cdot dH \end{aligned}$$

As the magnetic field is reduced, the temperature decreases, as  $dT$  gets larger as the actual temperature drops.

The following is how this process is used experimentally. Consider a sample of Cerium magnesium nitrate, this is a very good material as it produces large magnetic fields. The sample is placed in contact with liquid Helium and the sample of material which is wished to be cooled is placed in contact with our magnetic material. A coil is placed around it and the sample is then magnetised isothermally, the liquid Helium provides a good heat reservoir. As the sample cools, the spins of the atoms are cooled. Their motion is less chaotic, their alignment is not as random now.

The sample is then thermally isolated and its magnetisation is increased. It is isolated by means of evacuating the gas in the container of the magnetic material (which is surrounded by the liquid helium reservoir).

The magnetic material is then adiabatically demagnetised, as  $M$  goes to zero, the temperature continues to go down.

If we use liquid Helium (4) its boiling point is 4.2 K, if it is over pumped it will go down to 1.3 K, then using adiabatic demagnetisation takes it further down to 50 mK! Using Helium-3 (which is more expensive) gives a BP of 3.3K over pumping takes it to 0.4 K and adiabatic demagnetisation takes it to 1 mK.

## 27/11/98

### Phase Equilibrium in a one component system.

e.g. consider ice floating in water, this is a *two phase equilibrium* system. Also, a compressed gas where condensation has occurred this is a two phase equilibrium system too.

In such systems we draw *phase diagrams* of T versus P.

**Fig One**

Condition for therodynamic equilibrium on the equilibrium curves  
Consider,

$$\mathbf{G=H-TS=U+PV-TS}$$

**Gibb's function for the total system**

**Therefore,**

$$\mathbf{dG=dU+PdV+VdP-TdS-SdT}$$

$$\mathbf{dG=VdP-SdT}$$

During a change of phase,  $\mathbf{dP=dT=0}$ . Therefore,  $\mathbf{dG=0}$  (for the system).  
Consider a gas being compressed in a cylinder piston. The mass of gas,  $m_1$ , and the mass of liquid,  $m_2$ , change by  $dm_1$  and  $dm_2$  respectively.  $dm_1$  is negative and  $dm_2$  is positive, the two changes are equal and opposite. The total Gibb's function is,

$$\mathbf{G=g_1m_1+g_2m_2}$$

For equilibrium,

$$\mathbf{dG=0=g_1dm_1+g_2dm_2}$$

$$\mathbf{dG=g_1dm_1+g_2dm_2}$$

But ,

$$\mathbf{-dm_1=dm_2}$$

**Therefore,**

$$\mathbf{g_1=g_2}$$

Clausius - Clapeyron Equation

Consider a PT plot, and two points A and B are points on an equilibrium curve, seperating phase 1 and phase 2.

At A,

$$g_1=g_2$$

At B,

$$g_1+dg_1=g_2+dm_2. \text{ Therefore, } dg_1=dg_2$$

Therefore,

$$\mathbf{v_1 \cdot dP - s_1 \cdot dT = v_2 \cdot dP - s_2 \cdot dT}$$

$$\mathbf{(s_2 - s_1) \cdot dT = (v_2 - v_1) \cdot dP}$$

**Therefore,**

$$\mathbf{(dP/dT)_{eq} = (s_2 - s_1) / (v_2 - v_1)}$$

**But,**

$$s_2 - s_1 = (\Delta Q)/T = l/T$$

Where  $l$  is the **latent heat** of the process.

$$(dP/dT)_{eq} = l/(T(v_2 - v_1))$$

Here are some alternative statements of the Clausius-Clapeyron equations.

$$(dP/dT)_{sub} = l_{sol}/(T(v_{vap} - v_{sol}))$$

$$(dP/dT)_{vap} = l_{vap}/(T(v_{vap} - v_{liq}))$$

$$(dP/dT)_{fus} = l_{fus}/(T(v_{liq} - v_{sol}))$$

The first two are usually zero because  $v_{vap} \gg v_{sol}, v_{liq}$ . The third is large and is usually positive because  $v_{liq} > v_{sol}$ . The exception however is water, the third statement is negative for water. This is because  $v_{sol} > v_{liq}$ . The triple point for water, where solid, liquid, and vapour coexist, is 4.58 mmHg pressure and 273.16 K temperature. The fusion curve at atmospheric pressure is 0.01 K

**04/12/98**

### Vapour Pressure - Temperature Relationship

#### **Fig One (Equilibrium Vapour/Liquid curve, as in last lecture)**

Recall the Clausius-Clapeyron equation.

$$(dP/dT)_{eq} = l_{vap}/(T(v_{vap} - v_{liq}))$$

We know from experience in most cases the gaseous volume is much greater than the liquid volume, so we can make the approximation,

$$(dP/dT)_{eq} = l_{vap}/(T v_{vap})$$

Also, for an ideal gas which we assume our substance is,

$$P v_{vap} = RT$$

Where the volume is the volume per mole (as is the latent heat Joules per moles, which is equal to the product of the specific latent heat and molecular mass (Kg/mol)). Therefore the differential term can be further rewritten in terms of more readily measurable quantities,

$$(dP/dT)_{eq} = (L.M. 10^3 . P)/(T^2 R)$$

$$\text{Integ (P, } \uparrow \text{) (dP/P) = (LM. } \uparrow \text{ } \downarrow \text{) / R) . Integ (T, } \uparrow \text{) (dT/T)}$$

$$\ln(P/P_0) = -(LM. \uparrow \downarrow / R) . (1/T - 1/T_0)$$

$$\ln(760/5) = (20 \cdot 4 / 8.13) \cdot ((1/T) - (1/4.2))$$

$$T = 1.33 \text{ K}$$

### First and Second order phase changes.

#### First Order changes

Consider the regular cylinder-piston arrangement where a liquid forms at the bottom of the cylinder. Also for solid ice floating in liquid water. We found that the specific Gibbs's function,  $g$ , was continuous. However for these systems, the specific volume and specific entropy are said to be discontinuous, they have different values in liquid and vapour phases.

#### Second order phase changes

The specific values,  $g$ ,  $v$  &  $s$  are all continuous. The differentials of these are however, discontinuous. These are shown below,

$$\left( \frac{\partial v}{\partial T} \right)_p, \left( \frac{\partial v}{\partial p} \right)_T, \left( \frac{\partial s}{\partial T} \right)_p, \left( \frac{\partial s}{\partial p} \right)_T$$

are all discontinuous.

The following are also discontinuous by consequence,

$$\begin{aligned} C_p &= T \left( \frac{\partial s}{\partial T} \right)_p \\ \alpha &= (1/v) \left( \frac{\partial v}{\partial T} \right)_p \\ k &= (1/v) \left( \frac{\partial v}{\partial p} \right)_T \end{aligned}$$

Now let us consider some real examples of second order changes.

- Magnetic materials

Consider a cubic lattice of  $\text{NiCl}_2$ . The Nickel atoms are cooperatively magnetic, i.e. their spins align themselves. If we now plot the materials magnetic susceptibility,  $X_m$  against temperature. The plot we see two exponential curves effectively, both maximum at the same temperature, the Neil Temperature,  $T_n$ . Above this the material is Paramagnetic and below it is Antiferromagnetic (anti-parallel arrangement). From the same data if we plot the specific heat capacity,  $C_p$ , there is a discontinuity at  $T_n$ . As expected.

- Liquid Helium

If we plot the specific heat against against temperature, again there is a discontinuity again, see **Fig Two**.

On this plot the liquid Helium (LHe) phase one (LHeI) is normal liquid. LHeII is a superfluid, there is no viscosity and infinite thermal conductivity. The maximum of the plot is known as the

"lambda point".

If we now make a PT plot for this second order change. See **Fig Three**. Along the type 2 phase transition we have,

$$\begin{aligned} dP/dT &= (C_{p1} - C_{p2}) / (Tv(\hat{a}_1 - \hat{a}_2)) \\ &= (\hat{a}_1 - \hat{a}_2) / (k_1 - k_2) \end{aligned}$$

These are known as Ahrenfest equations.

**End of course, thank you for reading !**