BPT-201 (semester II)
THERMAL PHYSICS............ Credits: 4
Topic: Thermodynamics of paramagnetic salt

Dr Neelam Srivastava
Department of Physics (MMV Section)
Banaras Hindu University
neelamsrivastava_bhu@yahoo.co.in
neel@bhu.ac.in

Back Ground

- All the thermodynamic equations which you have learned till now (applied to compressible substance) are applicable to many other systems/process.

S. No.	system	Thermodynamic variable	Parametric form of equation of state
1.	Hydrostatic or chemical	P,V,T	$f(P,V,T)=0$
2.	Stretched wire or elastic systems	L,F,T	$f(L,F,T)=0$
3.	Surface Film	A,S,T	$f(A,S,T)=0$
4.	Electric Cell	Z,E,T	$f(Z,E,T)=0$
5.	Magnetic System	M,H,T	$f(M,H,T)=0$

- How to get different thermodynamical equations for different systems
- For that you have to identify the force and work giving parameters. In case of magnetic systems H is force and M is work giving parameter
- Then you have to identify the relation between the two parameters.
- For example as P increases the V decreases but in magnetic materials if H increases M also increases
- i.e. Since for hydrostatic systems $TdS=dU+PdV$

  so for magnetic material it will be $TdS=dU-HdM$

  Take care of -ve sign before HdM

Thermodynamic equation

- Let us start considering M and T as independent variables
- Then U=U(M, T) and so $dU = \left(\frac{\partial U}{\partial M}\right)_T dM + \left(\frac{\partial U}{\partial T}\right)_M dT$ ....(A)
- The first law of thermodynamics for paramagnetic materials is given as dU -HdM=TdS
- Dividing this equation by dM and applying constant temperature condition and using Maxwell's relation $\left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_M$
- We will get $\left(\frac{\partial U}{\partial M}\right)_T = -T\left(\frac{\partial H}{\partial T}\right)_M + H$ .... (B)
- Remember the first energy equation for compressible system which says $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

i.e. equation 'B' gives the 1st energy equation for paramagnetic salts. Note the changes in -ve and +ve signs which are according to what we discussed in previous slide

- Using equation 'A' and the first law equation TdS=dU-HdM, we can get

$$TdS = \left(\frac{\partial U}{\partial M}\right)_T dM + \left(\frac{\partial U}{\partial T}\right)_M dT - HdM$$

- or $$TdS = \left(\left(\frac{\partial U}{\partial M}\right)_T - H\right)dM + \left(\frac{\partial U}{\partial T}\right)_M dT$$
- Or using equation 'B' from previous slide we get

$$TdS = -T\left(\frac{\partial H}{\partial T}\right)_M dM + \left(\frac{\partial U}{\partial T}\right)_M dT$$

- We know $\left(\frac{\partial U}{\partial T}\right)_M$ gives C_M (specific heat at constant magnetization)
- So we get $TdS = -T\left(\frac{\partial H}{\partial T}\right)_M dM + C_M dT$ ....(C)
- Comparing it with 1st TdS equation for compressible systems i.e. $TdS = +T\left(\frac{\partial P}{\partial T}\right)_V dV + C_V dT$
- We get that equation 'C' gives the 1st TdS equation for paramagnetic materials (take care of +ve and -ve signs)

- Similarly we can get second energy and TdS equations for magnetic materials.
- Here we will start assuming T and H as independent variables i.e. U=U (T,H) and will get
- $dU = \left(\frac{\partial U}{\partial H}\right)_T dH + \left(\frac{\partial U}{\partial T}\right)_H dT$ ....(D)
- Dividing the first law equation i.e. TdS=dU-HdM by dH and applying the constant temperature condition
- We get $\left(\frac{\partial U}{\partial H}\right)_T = T\left(\frac{\partial S}{\partial H}\right)_T + H\left(\frac{\partial M}{\partial H}\right)_T$ ....(E)
- Then using Maxwell's equation for paramagnetic salt
- We get $\left(\frac{\partial U}{\partial H}\right)_T = T\left(\frac{\partial M}{\partial T}\right)_H + H\left(\frac{\partial M}{\partial H}\right)_T$ ......(F) this is second energy equation for paramagnetic materials

- For second TdS equation let us start from S=S(T,H)

- So we get $dS = \left(\frac{\partial S}{\partial H}\right)_T dH + \left(\frac{\partial S}{\partial T}\right)_H dT$ ....(F)
- Or $TdS = T\left(\frac{\partial S}{\partial H}\right)_T dH + T\left(\frac{\partial S}{\partial T}\right)_H dT$
- Using Maxwell's equation $\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$
- Considering that specific heat at constant field is given by $T\left(\frac{\partial S}{\partial T}\right)_H = C_H$
- We get $TdS = T\left(\frac{\partial M}{\partial T}\right)_H dH + C_H dT$ ....(G)
- Equation 'G' gives the second TdS equation for paramagnetic salts.

Let us analyze these equations for material following curie's Law

- Paramagnetic materials following Curie's law, satisfy a relation M=CH/T where 'C' is a constant.
- Using Curie's Law we get $\frac{C}{T} = \left(\frac{\partial M}{\partial H}\right)_T$ and $-\frac{CH}{T^2} = \left(\frac{\partial M}{\partial T}\right)_H$
- Putting these relation in energy equations $\left(\frac{\partial U}{\partial H}\right)_T = T\left(\frac{\partial M}{\partial T}\right)_H + H\left(\frac{\partial M}{\partial H}\right)_T$
- We get $\left(\frac{\partial U}{\partial H}\right)_T = H\frac{C}{T} - T\frac{CH}{T^2} = 0$
- Similarly using 1st energy equation $\left(\frac{\partial U}{\partial M}\right)_T = -T\left(\frac{\partial H}{\partial T}\right)_M + H$
- and $\frac{M}{C} = \left(\frac{\partial H}{\partial T}\right)_M$ from Curie's law
- we get $\left(\frac{\partial U}{\partial M}\right)_T = H - T\frac{M}{C} = 0$

- These two equations indicates : For magnetic materials following Curie's law, the internal energy is independent of M and H and depends upon temperature only. A case similar to ideal gas.
- Equation 'D' and 'G' show the dependence of magnetic properties on temperature, the effect known as 'magnetocaloric effect'
- Since the experimental experience says that $\left(\frac{\partial M}{\partial T}\right)_H$ is always negative. Hence from equation 'G' we get that for an isothermal procedure the drop in magnetic field will result in decrease in temperature and the same phenomenon is used in adiabatic demagnetization