EP 2827: Thermodynamics

Final Exam (100 marks, 3 hrs.)

March 15, 2019

Instructions

- Duration of the exam is 3 hours
- Use of books, class notes, laptops or phone is not allowed
- Use of a formula sheet is permitted (2 sides of an A4 sheet), however exchange of formula sheet is not permitted
- Please provide your answer in the blank space following/ next to the question in the exam paper itself
- Scratch papers for rough work should be included/attached at the back of the paper.

Problem No.	1	2	3	4	5	6	7	8	9	10	11	12	Total Score
Score													

1. Write down the four laws of thermodynamics. (No points for writing down the versions of the first and second law which you learned in high school e.g. conservation of energy as the first law or the Kelvin-Planck or Clausius versions of the second law). For the first and second law write down the mathematical versions in terms of infinitesimal work done, heat exchanged and change in internal energy (in the general case, not a pure hydrostatic system). State *both* versions of the third law taught in the class.

($2 + 4 + 4 + 4 = 14$ points)

Solution:

Zeroth law: Two bodies (say A and B) which are (simultaneously) in thermal equilibrium with a third body (say C), then they (A and B) are in thermal equilibrium with each other.

First law: The work done in taking a system from a state to another state by solely adiabatic processes (adiabatic means) is independent of the path. (Equivalently, *infinitesimal amount of adiabatic work done is an exact differential*

$$đW_{adiabatic} = dU$$

where U is a state function, the internal energy. For general processes, not necessarily adiabatic

$$\begin{aligned} dU &= đQ + đW \\ &= đQ + \sum_i Y_i dX_i \end{aligned}$$

where $đQ$ is the heat transferred to the system, and $đW = \sum_i Y_i dX_i$ is work done on the system - X_i's are generalized displacements and Y_i's are generalized forces.

Second law: In every open connected neighborhood of a point in the space of thermodynamic equilibrium states (say P), there always exist points which cannot be joined to P by purely *reversible adiabatic paths/processes.* (Equivalently, in the space of thermodynamic equilibrium states two reversible adiabatic (hyper)surfaces can never intersect). Reversible adiabatic (hyper)surfaces are characterized by constant values of the entropy, S and for two neighboring equilibrium states, the difference of entropies are related by,

$$TdS = dU - \sum_i Y_i dX_i.$$

Third law:

Planck Statement - As $T \to 0$, the contribution to the entropy of a system in thermodynamic equilibrium from each degree of freedom vanishes[1] in a differentiable way.

***Unattainability* statement** - One cannot lower the absolute temperature of a system to zero in a finite number of operations.

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[1] or equivalently the total entropy attains a limiting value independent of the process by which T is being made to approach zero.

2. Consider a composite system consisting of a nonmagnetic gas, a paramagnetic solid and a reversible cell separated by diathermic partitions.
(a) What are the thermodynamic coordinates for this composite system ?
(b) How many equations of state are there ?
(c) Write down the expression for $\text{đ}W$.

($1 + 1 + 1 = 3$ points)

Solution:
(a) $T, P, V, \mathcal{H}, M, \mathcal{E}, Z$
(b) 3
(c) $\text{đ}W = -PdV + \mu_0 \mathcal{H}\, dM + \mathcal{E}\, dZ.$

3. Complete the following sentences

A. In the Joule free expansion experiment, the initial and final states of the gas have identical Internal energy.

B. In the Joule-Kelvin throttling experiment, the initial and final states of the gas have identical enthalpy.

C. The Joule coefficient is defined by the expression, $\eta = \left(\frac{\partial T}{\partial V}\right)_U$.

D. The Joule-Kelvin coefficient is defined by the expression, $\mu = \left(\frac{\partial T}{\partial P}\right)_H$

($1 + 1 + 1 + 1 = 4$ points)

4. Complete the following sentences by indicating which state function increases or decreases

A. For an isolated system undergoing an irreversible process the entropy increases and the final equilibrium configuration has maximum entropy.

B. For a system undergoing a spontaneous isothermal process, the Helmholtz potential decreases and the final equilibrium configuration has minimum Helmholtz potential.

C. For a system undergoing a spontaneous process under isothermal and isobaric conditions, the Gibbs potential decreases and the final equilibrium configuration has minimum Gibbs potential.

D. The maximal amount of work that can be extracted out of a system under isothermal conditions is equal to the decrease in the Helmholtz free energy.

E. The maximal amount of work that can be extracted out of a system under isothermal and isobaric conditions is equal to the decrease in the Gibbs free energy.

($1 + 1 + 1 + 1 + 1 = 5$ points)

5. **Increase of boiling point with pressure:** Consider the situation when a liquid boils to form gaseous vapor. Treat the vapor as an ideal gas and show that the boiling curve is given by the equation,

$$\ln\frac{P}{P_0} = \frac{l}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

Thus if $P > P_0$, then $T > T_0$ i.e. the boiling point temperature T at pressure P is higher than the boiling point temperature T_0 at a lower pressure, P_0. Here l is the molar latent heat of vaporization. (Hint: Use the Clausius-Clapeyron equation for first order phase transitions and neglect the molar volume of the liquid compared to the molar volume of the gas).

(3 points)

Solution:

We begin from the Clausius-Clapeyron equation for the liquid-gas phase transition,

$$\frac{dP}{dT} = \frac{l}{T\left(v_g - v_l\right)}$$

where l is the molar latent heat of vaporization, v_g and v_l are the molar volumes in the gas phase and liquid phase respectively. Since the distance of separation of the molecules is far larger than the separation of molecules in the liquid phase, we have $v_g >> v_l$ and we can approximate $v_g - v_l \approx v_g$. Thus we have,

$$\begin{aligned}\frac{dP}{dT} &= \frac{l}{T\left(v_g - v_l\right)} \\ &\approx \frac{l}{Tv_g}.\end{aligned}$$

Then using the ideal gas law for the vapor, $Pv_g = RT$, we have,

$$\begin{aligned}\frac{dP}{dT} &= \frac{l}{T\left(RT/P\right)} \\ &= \frac{l}{R}\left(\frac{P}{T^2}\right) \\ \Rightarrow \frac{dP}{P} &= \frac{l}{R}\frac{dT}{T^2} \\ \Rightarrow \ln\frac{P}{P_0} &= -\frac{l}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right).\end{aligned}$$

Here we have used the boundary condition $P(T_0) = T_0$ to fix

6. Derive the *enthalpy equations* for a hydrostatic system

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

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T$$

(3 + 3 = 6 points)

Solution:

We start with the second law in terms of enthalpy change

$$dH = TdS + VdP. \tag{1}$$

Dividing both sides by dP with T held fixed, we get,

$$\left.\frac{dH}{dP}\right|_{T\text{ fixed}} = T\left.\frac{dS}{dP}\right|_{T\text{ fixed}} + V,$$

or,

$$\left(\frac{\partial H}{\partial P}\right)_T = T\underline{\left(\frac{\partial S}{\partial P}\right)_T} + V$$

and then using the Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ to replace the underlined term in the rhs , we get,

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

This is the first enthalpy equation.

Next we divide both sides (1) by dV with T held fixed and obtain,

$$\left.\frac{dH}{dV}\right|_{T\text{ fixed}} = T\left.\frac{dS}{dV}\right|_{T\text{ fixed}} + V\left.\frac{dP}{dV}\right|_{T\text{ fixed}},$$

or,

$$\left(\frac{\partial H}{\partial V}\right)_T = T\underline{\left(\frac{\partial S}{\partial V}\right)_T} + V\left(\frac{\partial P}{\partial V}\right)_T.$$

Then we use the Maxwell relation, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ to replace the underlined term in the rhs of the above equation to obtain,

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T.$$

This is the second enthalpy equation.

7. For a hydrostatic system, starting from the first Maxwell relation, namely,

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

derive the other three Maxwell relations using properties of multi-variable differential calculus.

(3 + 3 + 3 = 9 points)

Solution:

Second Maxwell relation from the first:

$$\begin{aligned}
\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V, \\
\Rightarrow \left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V, \\
\Rightarrow \left(\frac{\partial T}{\partial P}\right)_S &= \frac{-\left(\frac{\partial P}{\partial S}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_S} \\
&= -\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial V}{\partial P}\right)_S \\
&= -\underbrace{\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial V}{\partial P}\right)_S \left(\frac{\partial S}{\partial V}\right)_P}_{=-1} \left(\frac{\partial V}{\partial S}\right)_P \\
\Rightarrow \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P.
\end{aligned}$$

Third Maxwell relation from the first:

$$\begin{aligned}
\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \\
\Rightarrow \frac{\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_V}{\left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_V} &= -\left(\frac{\partial P}{\partial S}\right)_V \\
\Rightarrow \frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} &= \left(\frac{\partial P}{\partial S}\right)_V \\
\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V \\
\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V.
\end{aligned}$$

Fourth Maxwell relation from the first:

This is best done in two steps, first derive the second Maxwell relation from the first and then in turn derive the fourth from the second. The first step has been done before, so we just show the second step i.e. starting from the second

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

$$\Rightarrow\Rightarrow \underbrace{\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P}_{=-1} \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial V}{\partial S}\right)_P$$

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

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

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

Hence proved.

8. **Thermodynamics of Blackbody radiation:** Consider EM waves (radiation) trapped inside a container with perfectly absorbing walls at temperature T (walls in turn radiate back). This is a hydrostatic system because EM radiation applies pressure on the absorbing surface due to transfer of momentum. From EM theory the pressure of the radiation on the walls of the cavity is given by,

$$P = \frac{1}{3}u$$

where $u = U/V$ is the (internal) energy density of the radiation. Further, experiments reveal that the internal energy density is purely a function of T, i.e.

$$u = u(T).$$

Using these two inputs, and applying thermodynamics, show the following

A. the internal energy (density) is

$$u = a\,T^4.$$

This is the Stefan-Boltzmann law.

B. the entropy density ($s \equiv S/V$) is given by

$$s = \frac{4}{3}a\,T^3.$$

C. the Gibbs potential $G = 0$. (This implies the chemical potential of photons, $\mu = \frac{G}{N}$ is zero!)

D. $C_p = \infty$.

$(3 + 2 + 1 + 1 = 7$ points$)$

Solution:

A. We substitute,

$$U = u(T)\,V, \quad P = \frac{1}{3}u(T)$$

in the first internal energy equation for a hydrostatic system,

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

to get,

$$u = \frac{T}{3}\frac{du}{dT} - \frac{1}{3}u,$$

or,

$$\frac{du}{dT} = 4\frac{u}{T}.$$

This can be easily integrated to give,

$$u = a\,T^4.$$

B. Next we use the Euler relation,

$$U = TS - PV,$$

and divide both sides by V to get,

$$u = T\,s - P,$$

or,

$$s = \frac{u+P}{T}.$$

Since for radiation, $P = (1/3)u$, we get,

$$s = \frac{4}{3}\frac{u}{T}.$$

Substituting, $u = a\,T^4$ we get,

$$s = \frac{4}{3}a\,T^3.$$

C. From the Euler relation, $U = TS - PV$, it is obvious that,

$$G = U - TS + PV = 0!$$

D. By definition,

$$C_P = \left(\frac{đQ}{dT}\right)_{P \text{ fixed}}.$$

But here $P = \frac{1}{3}u = \frac{a}{3}T^4$. This means $dT|_{P \text{ fixed}} = 0$! Thus the vanishing denominator in the above expression gives $C_P = \infty$.

9. Show that for an ideal gas C_V and C_P are purely functions of T. (Hint: Regard C_V as a function of independent variables T, V and then show $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$. Next regard $C_P = C_P(T, P)$ and repeat the same logic).

(4 + 4 = 8 points)

Solution: Regarding C_V is a function of two independent variables V, T, we will show $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$. Since $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$ we have,

$$\begin{aligned}\left(\frac{\partial C_V}{\partial V}\right)_T &= T\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T \\ &= T\left(\frac{\partial}{\partial T}\underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{=\left(\frac{\partial P}{\partial T}\right)_V}\right)_V \\ &= T\left(\frac{\partial^2 P}{\partial T^2}\right)_V .\end{aligned}$$

Here in going from the first to second step we have interchanged order of derivatives and in going from the second to third we have used the third Maxwell relation. Now, for an ideal gas

$$\begin{aligned}P &= nRT/V, \\ \Rightarrow \left(\frac{\partial^2 P}{\partial T^2}\right)_V &= 0.\end{aligned}$$

Thus, $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$ i.e. C_V is independent of V and purely a function of T.

Next, regarding C_P as a function of two independent variables T, P, we will show $\left(\frac{\partial C_P}{\partial V}\right)_T = 0$. Since $C_P = T\left(\frac{\partial S}{\partial T}\right)_P$ we have,

$$\begin{aligned}\left(\frac{\partial C_P}{\partial P}\right)_T &= T\left(\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right)_T \\ &= T\left(\frac{\partial}{\partial T}\underbrace{\left(\frac{\partial S}{\partial P}\right)_T}_{=\left(\frac{\partial V}{\partial T}\right)_P}\right)_P \\ &= T\left(\frac{\partial^2 V}{\partial T^2}\right)_P .\end{aligned}$$

For an ideal gas

$$\begin{aligned}V &= nRT/P, \\ \Rightarrow \left(\frac{\partial^2 V}{\partial T^2}\right)_P &= 0.\end{aligned}$$

Thus, $\left(\frac{\partial C_P}{\partial P}\right)_T = 0$ i.e. C_P is independent of P and purely a function of T.

10. If we start with n_0 moles of NH_3 dissociates according to the reaction,

$$\mathrm{NH_3} \leftrightharpoons \frac{1}{2}\mathrm{N_2} + \frac{3}{2}\mathrm{H_2}.$$

Show that at equilibrium,

$$K = \frac{\sqrt{27}}{4}\frac{\epsilon^2}{1-\epsilon^2}P,$$

where ϵ is the degree of dissociation at equilibrium (fraction of NH_3 dissociated).

(4 points)

Solution:

At equilibrium, in terms of ϵ, the number of moles of various species are,

$$n_{\mathrm{NH_3}} = n_0(1-\epsilon),$$

$$n_{\mathrm{N_2}} = \frac{n_0\epsilon}{2},$$

$$n_{\mathrm{H_2}} = \frac{3n_0\epsilon}{2}.$$

The total number of moles are, $n = n_0(1+\epsilon)$. So the mole fractions at equilibrium are,

$$x_{\mathrm{NH_3}} = \frac{1-\epsilon}{1+\epsilon}, \qquad x_{\mathrm{N_2}} = \frac{\epsilon}{2(1+\epsilon)}, \qquad x_{\mathrm{H_2}} = \frac{3\epsilon}{2(1+\epsilon)}.$$

The stoichiometric coefficients are,

$$\nu_{\mathrm{NH_3}} = -1, \qquad \nu_{\mathrm{N_2}} = \frac{1}{2}, \qquad \nu_{\mathrm{H_2}} = \frac{3}{2}$$

The law of mass action,

$$(x_{\mathrm{H_2}})^{\nu_{\mathrm{H_2}}} \quad (x_{\mathrm{N_2}})^{\nu_{\mathrm{N_2}}} \quad (x_{\mathrm{NH_3}})^{\nu_{\mathrm{NH_3}}} \; P^{(\nu_{\mathrm{NH_3}}+\nu_{\mathrm{N_2}}+\nu_{\mathrm{H_2}})} = K,$$

or,

$$\left(\frac{3\epsilon}{2(1+\epsilon)}\right)^{3/2}\left(\frac{\epsilon}{2(1+\epsilon)}\right)^{1/2}\left(\frac{1-\epsilon}{1+\epsilon}\right)^{-1} P^{\left(-1+\frac{1}{2}+\frac{3}{2}\right)} = K$$

or,

$$3^{3/2}\left(\frac{\epsilon}{2(1+\epsilon)}\right)^{2}\left(\frac{1+\epsilon}{1-\epsilon}\right)P = K,$$

or,

$$\frac{\sqrt{27}}{4}\frac{\epsilon^2}{1-\epsilon^2}P = K.$$

11. A very small amount of sugar is dissolved in water, and the solution is in equilibrium with pure water vapor.

(a) Show that the equation of phase equilibrium is,

$$g''' = g'' + RT\ \ln(1-x)$$

where g''' is the molar Gibbs potential of water vapor and, g'' is the molar Gibbs function of pure liquid water, and x is the mole fraction of the sugar in solution.
(b) For an infinitesimal change in concentration, x, at constant temperature. show that

$$\left(v''' - v''\right) dP = RTd\ \ln\left(1-x\right).$$

(c) Assume that vapor behaves like an ideal gas and regard v'' as constant (since the molar volume of in liquid phase is many orders of magnitude less than in gaseous phase and its change can be neglected). Find the relation expressing the change in vapor pressure due to dissolving sugar, i.e. from $x = 0, P = P(0)$to final state, $x = x$, $P = P(x)$

$$\ln\frac{P(x)}{P(0)} = \ln(1-x) + \frac{v''}{RT}\left[P(x) - P(0)\right].$$

(d) Justify that the last term can be dropped and then show that you obtain the experimentally observed result known as ***Raoult's law***

$$P(x) = P(0)\left(1-x\right)$$

$(2+3+3+2 = 10$ points)

Solution:

(a) The vapor phase can be taken to be an ideal gas in pure (unmixed state), while the liquid phase can be assumed to be a gaseous mixture of the solute (sugar) and the mixture. We know for chemical equilibrium the chemical potentials of water in the two phases must be equal,

$$\mu''' = \mu''$$

And we also know that in the pure state the chemical potential is equal to the (molar) Gibbs potential,

$$\mu''' = g'''$$

while in the mixture state, the chemical potential is equal to the *partial* Gibbs potential (molar),

$$\mu'' = \overset{''}{g}_{H_2O}.$$

The expression for the partial Gibbs potential is,

$$\overset{''}{g}_{H_2O} = RT\left(\phi_{H_2O} + \ln P_{H_2O}\right)$$

where ϕ_{H_2O} is some pure function of T and P_{H_2O} is the partial pressure of water in the solution. If x is the mole fraction of the sugar solution, $P_{H_2O} = (1-x)P$ where Ps the total pressure

$$\begin{aligned}\overset{''}{g}_{H_2O} &= RT\left(\phi_{H_2O} + \ln\left[\left(1-x\right)P\right]\right)\\ &= RT\left(\phi_{H_2O} + \ln P + \ln\left(1-x\right)\right)\\ &= g'' + RT\ \ln(1-x),\end{aligned}$$

where $g'' = RT\,(\phi_{H_2O} + \ln P)$ is the Gibbs potential of pure water, i.e. if the sugar concentration vanishes, $x = 0$. Thus, at equilibrium we have,

$$g''' = g'' + RT\ \ln(1-x)\,.$$

(b) For an infinitesimal change in the concentration at unchanged temperature, one has,

$$dg'''_T - dg''_T = RT\,d\left[\ln(1-x)\right]$$

where the subscript means fixed T. But, according to second law,

$$dg = -sdT + vdP \implies dg_T = vdP.$$

Thus for infinitesimal change in concentration we get,

$$\left(v''' - v''\right)dP = RT\,d\left[\ln(1-x)\right].$$

(c) Integrating the above equation holding v' approximately constant, and taking ideal gas equation of state for vapor i.e. $v''' = RT/P$,

$$\int_{P_0}^{P(x)} \frac{RT}{P}\,dP - v'' \int_{P_0}^{P(x)} dP = RT \int_{x=0}^{x} d\left[\ln(1-x)\right],$$

or,

$$RT\ \ln\frac{P(x)}{P_0} - v''\left(P(x) - P_0\right) = RT\ \ln(1-x)\,,$$

or,

$$\ln\frac{P(x)}{P_0} = \ln(1-x) + \frac{v''}{RT}\left[P(x) - P_0\right].$$

(d) Using the ideal gas law for the vapor state,

$$\frac{v''}{RT}\left[P(x) - P_0\right] = \frac{v''}{v'''}\left[1 - \frac{P_0}{P(x)}\right]$$

Now the quantity $1 - P_0/P(x)$ is an order 1 quantity but since the molar volume in gaseous phase is way larger than the molar volume in the liquid phase,

$$\frac{v''}{v'''}\left[1 - \frac{P_0}{P(x)}\right] \ll 1$$

and can be ignored. Thus we have the equation,

$$\ln\frac{P(x)}{P_0} = \ln(1-x)$$

or,

$$P(x) = P_0(1-x).$$

12. For a paramagnetic system with coordinates $(T,\mathcal{H},M)$ starting from the mathematical form of the second law, obtain the following:

A. Maxwell relations

$$\left(\frac{\partial T}{\partial M}\right)_S = \mu_0\left(\frac{\partial \mathcal{H}}{\partial S}\right)_M,$$

$$\left(\frac{\partial T}{\partial \mathcal{H}}\right)_S = -\mu_0\left(\frac{\partial M}{\partial S}\right)_{\mathcal{H}},$$

$$\left(\frac{\partial S}{\partial M}\right)_T = -\mu_0\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M,$$

$$\left(\frac{\partial S}{\partial \mathcal{H}}\right)_T = \mu_0\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}$$

B. The TdS equations

$$TdS = C_M dT - \mu_0 T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M dM,$$

$$TdS = C_{\mathcal{H}} dT + \mu_0 T\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} d\mathcal{H},$$

$$TdS = C_{\mathcal{H}}\left(\frac{\partial T}{\partial M}\right)_{\mathcal{H}} dM + C_M\left(\frac{\partial T}{\partial \mathcal{H}}\right)_M d\mathcal{H}.$$

C. The heat capacity equations,

$$C_{\mathcal{H}} - C_M = \mu_0\frac{TM\alpha^2}{\chi}$$

$$\frac{C_{\mathcal{H}}}{C_M} = \frac{\chi}{\chi_S}$$

where we have introduced the response functions, thermal magnetizability $\alpha = \frac{1}{M}\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}$ and $\chi \equiv \frac{1}{M}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_T$ is the isothermal magnetic susceptibility and $\chi_S \equiv \frac{1}{M}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_S$ is the isentropic (adiabatic) magnetic susceptibility.

D. Internal energy equations,

$$\left(\frac{\partial U}{\partial M}\right)_T = \mu_0\left[\mathcal{H} - T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M\right],$$

$$\left(\frac{\partial U}{\partial \mathcal{H}}\right)_T = \mu_0\left[\mathcal{H}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_T + T\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}\right].$$

E. An ideal paramagnet is one which obeys Curie's law, namely, $M = C_c\frac{\mathcal{H}}{T}$ where C_c is the Curie constant. Show that for an ideal paramagnet,

$$C_{\mathcal{H}} - C_M = \mu_0\frac{M^2}{C_C}$$

and $U = U(T)$ i.e. the internal energy is purely a function of temperature.

$(8 + 6 + 4 + 4 + 5 = 27$ points)

Solution:

(A) Maxwell relations: The second law for the paramagnet is,

$$dU = TdS + \mu_0 \mathcal{H} dM \tag{2}$$

In the entropy representation, $U = U(S, M)$ and,

$$dU = \left(\frac{\partial U}{\partial S}\right)_M dS + \left(\frac{\partial U}{\partial M}\right)_S dM$$

So we have,

$$\left(\frac{\partial U}{\partial S}\right)_M = T, \quad \left(\frac{\partial U}{\partial M}\right)_S = \mu_0 \mathcal{H}.$$

Equating the mixed second derivatives of U,

$$\left(\frac{\partial}{\partial M}\left(\frac{\partial U}{\partial S}\right)_M\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial M}\right)_S\right)_M$$

we get the first Maxwell relation,

$$\left(\frac{\partial T}{\partial M}\right)_S = \mu_0 \left(\frac{\partial \mathcal{H}}{\partial S}\right)_M. \tag{3}$$

Next we Legendre transform the internal energy, $U(S, M)$ to a new state function, magnetic enthalpy $E(S, \mathcal{H}) = U - \mu_0 \mathcal{H} M$. The second law (2) for this function looks like,

$$dE = TdS - \mu_0 M \, d\mathcal{H}.$$

This implies,

$$\left(\frac{\partial E}{\partial S}\right)_{\mathcal{H}} = T, \qquad \left(\frac{\partial E}{\partial \mathcal{H}}\right)_S = -\mu_0 M.$$

Again, equating second derivatives,

$$\left(\frac{\partial}{\partial \mathcal{H}}\left(\frac{\partial E}{\partial S}\right)_{\mathcal{H}}\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial E}{\partial \mathcal{H}}\right)_S\right)_{\mathcal{H}}$$

we get,

$$\left(\frac{\partial T}{\partial \mathcal{H}}\right)_S = -\mu_0 \left(\frac{\partial M}{\partial S}\right)_{\mathcal{H}}. \tag{4}$$

Next, we Legendre transform the internal energy $U(S, M)$ again but this time wrt to the variable S and construct the state function, the Helmholtz potential, $F(T, M) = U - TS$. The second law (2) for F looks like,

$$dF = -SdT + \mu_0 \mathcal{H} dM.$$

This implies,

$$\left(\frac{\partial F}{\partial T}\right)_M = -S, \qquad \left(\frac{\partial F}{\partial M}\right)_T = \mu_0 \mathcal{H}.$$

Again, equating second derivatives,

$$\left(\frac{\partial}{\partial M}\left(\frac{\partial F}{\partial T}\right)_M\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial M}\right)_T\right)_M$$

we get,

$$\left(\frac{\partial S}{\partial M}\right)_T = -\mu_0 \left(\frac{\partial \mathcal{H}}{\partial T}\right)_M. \tag{5}$$

Finally, we Legendre transform the internal energy $U(S, M)$ *simultaneously* wrt S as well as M, to construct the new state function, namely the Gibbs potential, $G(T, \mathcal{H}) = U - TS - \mu_0\mathcal{H}M$. The second law (2) for this function looks like,

$$dG = -SdT - \mu_0 M\, d\mathcal{H}.$$

This implies,

$$\left(\frac{\partial G}{\partial T}\right)_{\mathcal{H}} = -S, \qquad \left(\frac{\partial G}{\partial \mathcal{H}}\right)_T = -\mu_0 M.$$

Equating second derivatives,

$$\left(\frac{\partial}{\partial \mathcal{H}}\left(\frac{\partial G}{\partial T}\right)_{\mathcal{H}}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial \mathcal{H}}\right)_T\right)_{\mathcal{H}}$$

we get,

$$\left(\frac{\partial S}{\partial \mathcal{H}}\right)_T = \mu_0 \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}. \tag{6}$$

(**B**) TdS **equations:** For the first equation, we regard $S = S(T, M)$. Then the differential of S,

$$dS = \left(\frac{\partial S}{\partial T}\right)_M dT + \left(\frac{\partial S}{\partial M}\right)_T dM,$$

or,

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

Now we substitute, $T\left(\frac{\partial S}{\partial T}\right)_M = C_M$ and from the third Maxwell relation, $\left(\frac{\partial S}{\partial M}\right)_T = -\mu_0\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M$ to obtain,

$$TdS = C_M dT - \mu_0 T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M dM. \tag{7}$$

This is the first TdS equation. For the second TdS equation, we regard $S = S(T, \mathcal{H})$. Then,

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_{\mathcal{H}} dT + T\left(\frac{\partial S}{\partial \mathcal{H}}\right)_T d\mathcal{H}$$

By definition, $C_{\mathcal{H}} = T\left(\frac{\partial S}{\partial T}\right)_{\mathcal{H}}$ and from the fourth Maxwell relation, $\left(\frac{\partial S}{\partial \mathcal{H}}\right)_T = \mu_0\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}$. Substituting these in the previous equation, we get,

$$TdS = C_{\mathcal{H}} dT + \mu_0 T\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} d\mathcal{H}. \tag{8}$$

To get the third TdS equation, we regard, $S = S(\mathcal{H}, M)$. Then the differential of S is given by,

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial \mathcal{H}}\right)_M d\mathcal{H} + \left(\frac{\partial S}{\partial M}\right)_{\mathcal{H}} dM \\ &= \left(\frac{\partial S}{\partial T}\cdot\frac{\partial T}{\partial \mathcal{H}}\right)_M d\mathcal{H} + \left(\frac{\partial S}{\partial T}\frac{\partial T}{\partial M}\right)_{\mathcal{H}} dM \\ &= \left(\frac{\partial S}{\partial T}\right)_M \left(\frac{\partial T}{\partial \mathcal{H}}\right)_M d\mathcal{H} + \left(\frac{\partial S}{\partial T}\right)_{\mathcal{H}} \left(\frac{\partial T}{\partial M}\right)_{\mathcal{H}} dM \end{aligned}$$

or,

$$\begin{aligned} TdS &= T\left(\frac{\partial S}{\partial T}\right)_M \left(\frac{\partial T}{\partial \mathcal{H}}\right)_M d\mathcal{H} + T\left(\frac{\partial S}{\partial T}\right)_{\mathcal{H}} \left(\frac{\partial T}{\partial M}\right)_{\mathcal{H}} dM \\ &= C_M \left(\frac{\partial T}{\partial \mathcal{H}}\right)_M d\mathcal{H} + C_{\mathcal{H}} \left(\frac{\partial T}{\partial M}\right)_{\mathcal{H}} dM. \end{aligned} \tag{9}$$

(C) Heat Capacity equations: First we use the definition of thermal magnetizability, $\alpha = \frac{1}{M}\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}$ and isothermal magnetic susceptibility, $\chi = \frac{1}{M}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_T$ to obtain the result,

$$\begin{aligned} \left(\frac{\partial T}{\partial \mathcal{H}}\right)_M \left(\frac{\partial \mathcal{H}}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} &= -1 \\ \implies \left(\frac{\partial T}{\partial \mathcal{H}}\right)_M &= -\frac{\left(\frac{\partial M}{\partial \mathcal{H}}\right)_T}{\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}} \\ &= -\frac{\chi}{\alpha}. \end{aligned}$$

Thus,

$$\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} = \alpha M, \left(\frac{\partial T}{\partial \mathcal{H}}\right)_M = -\frac{\chi}{\alpha}. \tag{10}$$

Next, equating both sides of the first and second TdS equations, we get,

$$C_M dT - \mu_0 T \left(\frac{\partial \mathcal{H}}{\partial T}\right)_M dM = C_{\mathcal{H}} dT + \mu_0 T \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} d\mathcal{H},$$

rearranging which we get,

$$C_{\mathcal{H}} - C_M = -\mu_0 T \left(\frac{\partial \mathcal{H}}{\partial T}\right)_M \frac{dM}{dT} - \mu_0 T \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} \frac{d\mathcal{H}}{dT}.$$

For constant $\mathcal{H}$, this becomes,

$$C_{\mathcal{H}} - C_M = -\mu_0 T \left(\frac{\partial \mathcal{H}}{\partial T}\right)_M \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}$$

Using the relations (10) this becomes,

$$C_{\mathcal{H}} - C_M = \frac{\mu_0 \alpha^2 M}{\chi}. \tag{11}$$

This is the first heat capacity equation.
From third TdS equation (9) we get using the relations (10),

$$TdS = -\frac{\chi C_M}{\alpha} d\mathcal{H} + \frac{C_{\mathcal{H}}}{M\alpha} dM.$$

For an isentropic process, $dS = 0$ and this equation becomes,

$$0 = -\frac{\chi C_M}{\alpha} d\mathcal{H}_S + \frac{C_{\mathcal{H}}}{M\alpha} dM_S,$$

rearranging which we get,

$$\frac{C_{\mathcal{H}}}{C_M} = \frac{\chi}{\frac{1}{M}\left(dM_S/d\mathcal{H}_S\right)} = \frac{\chi}{\frac{1}{M}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_S} = \frac{\chi}{\chi_S}. \tag{12}$$

This is the second heat capacity equation.

(D). Internal energy equations: The second law once again,

$$dU = TdS + \mu_0 \mathcal{H}\, dM$$

Dividing both sides by dM while holding T constant we get,

$$\left(\frac{\partial U}{\partial M}\right)_T = \underline{T\left(\frac{\partial S}{\partial M}\right)_T} + \mu_0 \mathcal{H}.$$

Using the third Maxwell equation (5) to replace the underlined term, we get,

$$\left(\frac{\partial U}{\partial M}\right)_T = \mu_0 \left[\mathcal{H} - T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M\right].$$

This is the first internal energy equation. Next we divide both sides the second law for the paramagnet by $d\mathcal{H}$ and hold T constant to get,

$$\left(\frac{\partial U}{\partial \mathcal{H}}\right)_T = \underline{T\left(\frac{\partial S}{\partial \mathcal{H}}\right)_T} + \mu_0 \mathcal{H}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_T.$$

Now we use the fourth Maxwell equation to replace the underlined term to get,

$$\left(\frac{\partial U}{\partial \mathcal{H}}\right)_T = \mu_0 \left[T\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} + \mathcal{H}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_T\right].$$

This is second internal energy equation.
Alternate method: Using the first TdS equation (7) to replace the TdS term we get,

$$dU = C_M dT + \mu_0 \left[\mathcal{H} - T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M\right] dM$$

But since we can regard, $U = U(T, M)$, we can also write,

$$dU = \left(\frac{\partial U}{\partial T}\right)_M dT + \left(\frac{\partial U}{\partial M}\right)_T dM.$$

Comparing the two expressions for dU, we get,

$$\left(\frac{\partial U}{\partial M}\right)_T = \mu_0 \left[\mathcal{H} - T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M\right].$$

Similarly using the second TdS equation (8) to replace the TdS term in the second law, we get,

$$dU = C_{\mathcal{H}} dT + \mu_0 T\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} d\mathcal{H} + \mu_0 \mathcal{H}\, dM$$

Further since we can regard $M = M(T, \mathcal{H})$, we can replace,

$$dM = \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} dT + \left(\frac{\partial M}{\partial \mathcal{H}}\right)_T d\mathcal{H}$$

and obtain,

$$dU = \left[C_{\mathcal{H}} + \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}\right] dT + \mu_0 \left[T\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} + \mathcal{H}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_T\right] d\mathcal{H}.$$

Regarding $U = U(T, \mathcal{H})$ we get, $dU = \left(\frac{\partial U}{\partial T}\right)_{\mathcal{H}} dT + \left(\frac{\partial U}{\partial \mathcal{H}}\right)_T d\mathcal{H}$. Comparing both expressions we get,

$$\left(\frac{\partial U}{\partial \mathcal{H}}\right)_T = \mu_0 \left[T\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} + \mathcal{H}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_T\right].$$

(E). Using the equation of state for an ideal paramagnet, $M = C_C \frac{\mathcal{H}}{T}$, we compute, $\alpha = \frac{1}{M}\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} = -C_C \frac{\mathcal{H}}{MT^2} = -\frac{1}{T}$, and $\chi = \frac{1}{M}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_T = \frac{C_C}{MT}$. Using these expressions for α and χ in the RHS of the first heat capacity equation (11) gives,

$$C_{\mathcal{H}} - C_M = \frac{M^2}{C_C}.$$

Next, using the first internal energy equation,

$$\begin{aligned}\left(\frac{\partial U}{\partial M}\right)_T &= \mu_0 \left[\mathcal{H} - T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M\right] \\ &= \mu_0 \left[\mathcal{H} - T\frac{\partial}{\partial T}\left(\frac{MT}{C_C}\right)_M\right] \\ &= \mu_0 \left[\mathcal{H} - \frac{TM}{C}\right] \\ &= 0.\end{aligned}$$

Then using the second internal energy equation,

$$\begin{aligned}\left(\frac{\partial U}{\partial \mathcal{H}}\right)_T &= \mu_0 \left[T\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} + \mathcal{H}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_T\right] \\ &= \mu_0 \left[T\left(\frac{\partial\left(C_C\mathcal{H}/T\right)}{\partial T}\right)_{\mathcal{H}} + \mathcal{H}\left(\frac{\partial\left(C_C\mathcal{H}/T\right)}{\partial \mathcal{H}}\right)_T\right] \\ &= \mu_0 \left[-\frac{C_C\mathcal{H}}{T} + (C_C\mathcal{H}/T)\right] \\ &= 0.\end{aligned}$$

Since both $\frac{\partial U}{\partial M} = 0$, and $\frac{\partial U}{\partial \mathcal{H}} = 0$, i.e. the internal energy is independent of $M, \mathcal{H}$. It then follows that $U = U(T)$.