

PHYS 328

HOMEWORK #9

Solutions

1. Given that

$$\int_0^{\infty} e^{-ax} \sin kx \, dx = \frac{k}{a^2 + k^2}$$

find :

$$\int_0^{\infty} x e^{-ax} \sin kx \, dx \quad \text{and} \quad \int_0^{\infty} x e^{-ax} \cos kx \, dx$$

Solution : We find the first integral by differentiating our original integral with respect to a :

$$\frac{d}{da} \int_0^{\infty} e^{-ax} \sin kx \, dx = \int_0^{\infty} \frac{d}{da} (e^{-ax} \sin kx \, dx) = \int_0^{\infty} -x e^{-ax} \sin kx \, dx$$

Differentiating the RHS give :

$$\frac{d}{da} \left(\frac{k}{a^2 + k^2} \right) = \frac{-2ak}{(a^2 + k^2)^2}$$

Equating the two expressions yields the solution :

$$\int_0^{\infty} x e^{-ax} \sin kx \, dx = \frac{2ak}{(a^2 + k^2)^2}$$

For the second integral, differentiate our original integral with respect to k and obtain :

$$\frac{d}{dk} \int_0^{\infty} e^{-ax} \sin kx \, dx = \int_0^{\infty} x e^{-ax} \cos kx \, dx = \frac{d}{dk} \left(\frac{k}{a^2 + k^2} \right) = \frac{(a^2 + k^2) - k(2k)}{(a^2 + k^2)^2} = \frac{a^2 - k^2}{(a^2 + k^2)^2}$$

Verifying with Mathematica :

```
In[6]:= Integrate[{x Exp[-a x] Sin[k x], x Exp[-a x] Cos[k x]}, {x, 0, ∞}]
```

```
Out[6]= {ConditionalExpression[ $\frac{2ak}{(a^2 + k^2)^2}$ , Abs[Im[k]] < Re[a]],  
ConditionalExpression[ $\frac{(a - k)(a + k)}{(a^2 + k^2)^2}$ , k ∈ Reals && Re[a] > 0]}
```

2. Derive the equations 5.23 and 5.24 :

Solution : We begin by writing the thermodynamic identity as we derived it in Ch. 3 :

$$dU = T dS - P dV + \mu dN$$

Next, we write our definition of G :

$$G = U - TS + PV$$

Taking the total derivative of G :

$$dG = dU - T dS - S dT + P dV + V dP$$

Substitute our expression for dU into the equation directly above :

$$dG = (T dS - P dV + \mu dN) - T dS - S dT + P dV + V dP = -S dT + V dP + \mu dN$$

Taking partial derivatives yields :

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S; \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V; \quad \left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu$$

3. Deriving Maxwell relations :

Solutions : These relations are the result of the interchangeability of the order of differentiation for multi - valued functions, in other words :

$$\frac{\partial}{\partial x} \frac{\partial f}{\partial y} = \frac{\partial}{\partial y} \frac{\partial f}{\partial x}$$

We can show our first relation by starting with :

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S$$

We know that the expression in parenthesis on the left is just T, and from the thermodynamic identity :

$$dU = T dS - P dV + \mu dN$$

we get that $\partial U/\partial V = -P$ if we hold S and N constant. Therefore, substituting this new relationship into the right hand side gives us :

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

showing the relationship indicated.

Now let's find analogous relationships for H, F, and G.

Enthalpy : Holding N constant (and we will hold N constant throughout), the thermodynamic identity for H is :

$$dH = T dS + V dP$$

$$\text{so that } \left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V$$

Taking the mixed partial derivatives, we get :

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

Helmholtz Free Energy :

We start with

$$dF = -S dT - P dV \Rightarrow \left(\frac{\partial F}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial F}{\partial V}\right)_S = -P$$

Thus, we write the mixed partials :

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

Gibbs Free Energy :

$$dG = -S dT + V dP \Rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

Thus, we can construct the mixed partials :

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

4. Stability of calcite vs. aragonite :

Solution : We use the data from the back of the text to find that :

Phase	ΔG at surface	V at surface
calcite	-1128.8 kJ	$3.693 \times 10^{-5} \text{ m}^3$
aragonite	-1127.8 kJ	$3.415 \times 10^{-5} \text{ m}^3$

a) We know that the more stable phase will be the one with the lower value of ΔG , so that calcite is more stable at the surface of the Earth. Aragonite will become more stable when its value of ΔG becomes less than the value of calcite. We can find the pressure when this occurs by using the expression derived from the thermodynamic identity for G (See question 2 above) :

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V$$

Integrating this relationship yields :

$$G \approx V \Delta P + G_0$$

where G_0 is the surface value. We realize that since calcite has a larger volume at the surface than aragonite, the Gibbs Free Energy of calcite will increase faster than $G(\text{aragonite})$. We also see from the table that calcite is more stable by 1000J at the surface, so we need to find the depth at which the change in G due to increasing P exceeds 1000J, or when:

$$V_{\text{calcite}} \Delta P = 1000 \text{ J} + V_{\text{aragonite}} \Delta P \Rightarrow \Delta P = \frac{1000 \text{ J}}{V_{\text{calcite}} - V_{\text{aragonite}}} = \frac{1000 \text{ J}}{2.788 \times 10^{-6} \text{ m}^3} = 3.610^9 \text{ Pa}$$

It is customary in geophysics to express pressure in units of kbar, with 1 bar = 10^5 Pa , so this pressure is equivalent to approximately 36 kbar. We can estimate the depth at which this transition occurs using the equation of for pressure:

$$P = \rho g h$$

and the density of aragonite is approximately 3000 kg/m^3 . Thus, this depth of this transition is approximately:

$$h = \frac{3.6 \times 10^9 \text{ Pa}}{3000 \text{ kg/m}^3 \cdot 9.8 \text{ m/s}^2} = 1.22 \times 10^5 \text{ m or } 122 \text{ km (somewhere in the upper crust).}$$

5. Thermodynamics of a quantum harmonic oscillator :

This question shows how using the partition function can aid in determining the thermodynamic properties of a system. The partition function for a single quantum harmonic oscillator is :

$$Z = \frac{1}{1 - e^{-\beta\epsilon}}$$

where $\beta = 1/kT$ and ϵ is the spacing between quantum levels. The Helmholtz Free Energy of N particles is simply :

$$F = -NkT \ln Z = -NkT \ln(1 - e^{-\beta\epsilon})^{-1} = NkT \ln(1 - e^{-\beta\epsilon})$$

We can use one of the expressions we derived in class to find the entropy of a system of N quantum oscillators:

$$S = -\left(\frac{\partial F}{\partial T}\right)_N$$

Using this expression, we obtain:

$$\begin{aligned} S &= \frac{-\partial}{\partial T} (NkT \ln(1 - e^{-\epsilon/kT})) = -Nk \ln(1 - e^{-\epsilon/kT}) - \frac{NkT}{1 - e^{-\epsilon/kT}} \left(+e^{-\epsilon/kT} \cdot \left(\frac{-\epsilon}{kT^2}\right) \right) = \\ &= -Nk \ln(1 - e^{-\epsilon/kT}) + \frac{\epsilon N e^{-\epsilon/kT}}{(1 - e^{-\epsilon/kT})} \cdot \frac{1}{T} \end{aligned}$$