

PHYS 301: Thermodynamics and Statistical Mechanics
Solutions to Problem Set #15

Question 1: Maxwell's Relations

(a) Internal Energy, $E(S, V)$

The total differential of the internal energy $E(S, V)$ is mathematically given by:

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV \quad (1)$$

From the First Law of Thermodynamics, we also know that:

$$dE = TdS - PdV \quad (2)$$

By matching the coefficients of dS and dV , we can identify the first partial derivatives of E :

$$\left(\frac{\partial E}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial E}{\partial V}\right)_S = -P \quad (3)$$

Because the internal energy E is a well-behaved state function, its mixed second partial derivatives must be equal according to Schwarz's theorem:

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V} \quad (4)$$

Substituting our first derivatives into this equality yields:

$$\begin{aligned} \left[\frac{\partial}{\partial V} \left(\frac{\partial E}{\partial S}\right)_V\right]_S &= \left[\frac{\partial}{\partial S} \left(\frac{\partial E}{\partial V}\right)_S\right]_V \\ \left(\frac{\partial T}{\partial V}\right)_S &= \left(\frac{\partial(-P)}{\partial S}\right)_V \end{aligned} \quad (5)$$

Factoring out the negative sign completes the proof of the first Maxwell relation:

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \quad (6)$$

(b) Helmholtz Free Energy, $F(T, V)$

The Helmholtz free energy is defined as $F = E - TS$. Taking its total differential yields:

$$dF = dE - d(TS) = dE - TdS - SdT \quad (7)$$

Substitute the First Law ($dE = TdS - PdV$) into this expression:

$$dF = (TdS - PdV) - TdS - SdT \implies \boxed{dF = -SdT - PdV} \quad (8)$$

Because F is a function of T and V , its total differential can also be written generally as:

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \quad (9)$$

Matching coefficients gives:

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial F}{\partial V}\right)_T = -P \quad (10)$$

Using the equality of mixed partial derivatives for F :

$$\begin{aligned} \frac{\partial^2 F}{\partial V \partial T} &= \frac{\partial^2 F}{\partial T \partial V} \\ \left(\frac{\partial(-S)}{\partial V}\right)_T &= \left(\frac{\partial(-P)}{\partial T}\right)_V \\ -\left(\frac{\partial S}{\partial V}\right)_T &= -\left(\frac{\partial P}{\partial T}\right)_V \end{aligned} \quad (11)$$

Canceling the negative signs gives the second Maxwell relation:

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \quad (12)$$

(c) Gibbs Free Energy, $G(T, P)$

The Gibbs free energy is defined as $G = F + PV$. Taking its total differential yields:

$$dG = dF + d(PV) = dF + PdV + VdP \quad (13)$$

Substitute the relation for dF from part (b) ($dF = -SdT - PdV$):

$$dG = (-SdT - PdV) + PdV + VdP \implies \boxed{dG = -SdT + VdP} \quad (14)$$

Because G is a function of T and P , its total differential is generally:

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \quad (15)$$

Matching coefficients gives:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V \quad (16)$$

Using the equality of mixed partial derivatives for G :

$$\begin{aligned} \frac{\partial^2 G}{\partial P \partial T} &= \frac{\partial^2 G}{\partial T \partial P} \\ \left(\frac{\partial(-S)}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P \\ -\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P \end{aligned} \quad (17)$$

Multiplying both sides by -1 gives the third Maxwell relation:

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P} \quad (18)$$

(d) Enthalpy, $H(S, P)$

The enthalpy is defined as $H = E + PV$. Taking its total differential yields:

$$dH = dE + d(PV) = dE + PdV + VdP \quad (19)$$

Substitute the First Law ($dE = TdS - PdV$) into this expression:

$$dH = (TdS - PdV) + PdV + VdP \implies \boxed{dH = TdS + VdP} \quad (20)$$

Because H is a function of S and P , its total differential is generally:

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \quad (21)$$

Matching coefficients gives:

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_S = V \quad (22)$$

Using the equality of mixed partial derivatives for H :

$$\begin{aligned} \frac{\partial^2 H}{\partial P \partial S} &= \frac{\partial^2 H}{\partial S \partial P} \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \end{aligned} \quad (23)$$

This directly proves the fourth Maxwell relation:

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \quad (24)$$