MME 231: Lecture 11

Thermodynamic Variables and Relations

General Procedure to Obtain Thermodynamic Relations

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Today's Topics

- The general strategy to obtain thermodynamic relations
- The general procedure to obtain thermodynamic relations
- Examples

General Strategy for Deriving Thermodynamic Relations

❶ Identify the properties of the system about which the information is given.
➨ Independent variables

❷ Identify the property of the system about which one is seeking information.
➨ Dependent variable

❸ Find or derive a relationship between the sought and the given variables.
➨ The generic form of this relation Z = Z (X, Y)
➨ Contains quantities such as α, β, C_P, etc.

❹ Obtain values for these quantities.
➨ Tabulated data (books, databases, experiments)

❺ Substitute values into relationship and carry out mathematical operations.
➨ Get a value for the dependent variable

Step three is critical.

❑ To develop a general procedure for deriving such a relation

- Choose **T** and **P** as the independent variables
- Express all state variables as functions of **T** and **P**: **Z = Z (T, P)**
- Convert this function to the required function: **Z = Z (X, Y)**

State Functions	Combined Law
Equation of State Variables (T, P, V)	dU = TdS – PdV
Energy Functions (U, H, F, G)	dH = TdS + VdP
Entropy Function, S	dF = - SdT - PdV
	dG = - SdT + VdP

- Express **V** and **S** as functions of **T** and **P**:

V = V (T, P)

S = S (T, P)

Expressing V as a function of T and P

$V = V(T, P)$

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

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

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

$$\mathbf{dV = V\alpha\, dT - V\beta\, dP}$$

Expressing S as a function of T and P

$S = S(T, P)$

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

Since $\delta Q_{rev} = TdS$

For a constant P process,

$\delta Q_{rev, P} = TdS_P = C_P\, dT_P$

$(\partial S/\partial T)_P = C_P/T$

From Maxwell relation,

$(\partial S/\partial P)_T = -(\partial V/\partial T)_P = -V\alpha$

$$\mathbf{dS = \left(\frac{C_P}{T}\right) dT - V\alpha\, dP}$$

TABLE 4.2
Thermodynamic state functions expressed in terms of the independent variables T and P

$V = V(T, P)$:		$dV = V\alpha dT - V\beta dP$
$S = S(T, P)$:		$dS = (C_P/T)\,dT - V\alpha dP$
$U = U(T, P)$:	$dU = TdS - PdV$	$dU = (C_P - PV\alpha)dT + V(P\beta - T\alpha)dP$
$H = H(T, P)$:	$dH = TdS + VdP$	$dH = C_P dT + V(1 - T\alpha)dP$
$F = F(T, P)$:	$dF = - SdT - PdV$	$dF = -(S + PV\alpha)dT + PV\beta dP$
$G = G(T, P)$:	$dG = - SdT + VdP$	$dG = - SdT + VdP$

The coefficients in these differential equations contain the following factors:

- ❑ **T** and **P** (the independent variables specified in any application)
- ❑ α, β and C_P (the experimental variables to be available in tables or data bases)
- ❑ **S** and **V** (can be evaluated as functions of T and P, given the value of α, β and C_P)

General Procedure to Obtain Thermodynamic Relations

1. Identify the variables: $Z = Z(X, Y)$

2. Write the differential form: $dZ = M\,dX + N\,dY$

3. Use Table 4.2 to express dX and dY in terms of the variables dT and dP:
$dZ = M[X_T\,dT + X_P\,dP] + N[Y_T\,dT + Y_P\,dP]$

4. Collecting terms:
$dZ = [M X_T + N Y_T]\,dT + [M X_P + N Y_P]\,dP$

5. Obtain Z = Z (T, P) from Table 4.2:
$dZ = Z_T\,dT + Z_P\,dP$

6. Equating the like terms for the function Z = Z (T, P):
$M X_T + N Y_T = Z_T$ (4.37a)
$M X_P + N Y_P = Z_P$ (4.37b)

7. Solving Eq.(4.37) will result expressions for M and N

Check Units

Energy (**PV**)
Entropy (**PV/T**)
Heat capacity (**PV/T**)
α (**1/T**)
β (**1/P**)

Example 4.3

Relate the entropy of a system to its temperature and volume.

1. $S = S(T, V)$
2. $dS = M\,dT + N\,dV$
3. Using Table 4.2: $dS = M\,dT + N\,(V\alpha\,dT - V\beta\,dP)$
4. $dS = M\,dT + NV\alpha\,dT - NV\beta\,dP = (M + NV\alpha)\,dT - NV\beta\,dP$
5. From Table 4.2: $dS = [C_P/T]dT - V\alpha\,dP$
6. Comparing coefficients:

   $M + NV\alpha = C_P/T\ ; \quad -NV\beta = -V\alpha$
7. Solve this pair of equations for M and N:

   $M = \frac{1}{T}\left(C_P - \frac{TV\alpha^2}{\beta}\right)$ and $N = \frac{\alpha}{\beta}$

$$S = S(T, V) : \quad dS = \frac{1}{T}\left(C_P - \frac{TV\alpha^2}{\beta}\right)dT + \frac{\alpha}{\beta}\,dV$$

Example

Find the relationship needed to compute the change in Gibbs free energy when the initial and final states are specified by their pressure and volume.

$$G = G(P, V) \qquad dG = \left(V - \frac{S\beta}{\alpha}\right)dP - \frac{S}{V\alpha}\,dV$$

Example 4.4

Derive an expression for the increase in temperature for process in which the volume of the system is changed at constant entropy.

$$T = T(V, S) \qquad dT_S = -\frac{T\alpha}{C_V\beta}\,dV_S$$

Next Class

Lecture 12

Thermodynamic Variables and Relations

Applications of thermodynamic relations

Rashid/ Ch#4