MME 231: Lecture 10

# Thermodynamic Variables and Relations

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# Today's Topics

■ Thermodynamic relations derived from the Laws of Thermodynamics

■ Definitions in thermodynamics
  ❖ **The energy functions**
  ❖ **Experimental variables**

■ Coefficient relations and Maxwell relations

■ Examples

# How to Tackle a Thermodynamic Problem ?

❑ To solve practical problems requires

**finding or deriving the relationships between the sought (dependent) variables and the given (independent) variables of the type:**

$$Z = Z(X, Y, ....)$$

❑ Steps in solving practical problems:

❶ **Identify which system properties are given (X, Y, ....)**

❷ **Identify which system property you want to find (Z)**

❸ **Establish the relationship that connect the sought and given properties**

$$Z = Z(X, Y, ...)$$

❹ **Find required materials properties**

❺ **Perform calculation**

# Relations Derived from the Laws of Thermodynamics

The first law:
$$dU = \delta Q + \delta W + \delta W'$$

Reversible heat absorbed by the system:
$$\delta Q_{rev} = TdS$$

Reversible mechanical work done on the system:
$$\delta W_{rev} = -P\,dV$$

Combined statement of the first and second laws:
$$dU = TdS - PdV + \delta W'$$

# Definitions in Thermodynamics

### Energy Functions

❑ Enthalpy, **H**
❑ Helmholtz Free Energy, **F**
❑ Gibbs Free Energy, **G**

### Experimental Variables

❑ Coefficient of Thermal Expansion, $\alpha$
❑ Coefficient of Compressibility, $\beta$
❑ Heat Capacity, $C_P$

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# Enthalpy   or   The Heat Content

**Definition:**   $\boxed{H \equiv U + PV}$

$dH = dU + PdV + VdP$

$dH = [\,TdS - PdV + \delta W'\,] + PdV + VdP$

$dH = TdS + VdP + \delta W'$

For isobaric processes in simple systems ($\delta W' = 0$),

$dH_P = TdS_P = \delta Q_{rev,\,P}$

That is why, enthalpy is often noted as
the **heat content** of the system

## Helmholtz Free Energy  or  The Work Function

**Definition:**  $\boxed{F \equiv U - TS}$

$dF = dU - TdS - SdT$

$dF = [\,TdS - PdV + \delta W'\,] - TdS - SdT$

$dF = -SdT - PdV + \delta W'$

For isothermal processes,

$dF_T = -PdV_T + \delta W'_T = \delta W_T + \delta W'_T$

$$dF_T = \delta W_{tot\,,T}$$

So. F is often called the **Work Function**

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## Gibbs Free Energy, G

**Definition:**  $\boxed{G \equiv H - TS}$

$dG = dU - TdS - SdT$

$dG = [TdS + VdP + \delta W'] - TdS - SdT$

$dG = -SdT + VdP + \delta W'$

For isothermal and isobaric processes,

$$dG_{T,\,P} = \delta W'_{T,\,P}$$

## The Four Combined Statements

$$dU = TdS - PdV + \delta W'$$

$$dH = TdS + VdP + \delta W'$$

$$dF = -SdT - PdV + \delta W'$$

$$dG = -SdT + VdP + \delta W'$$

## The Experimental Variables

**Coefficient of
Thermal Expansion, $\alpha$**

Change in volume of material
with temperature at constant P

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

**Coefficient of
Compressibility, $\beta$**

Change in volume of material
with pressure at constant T

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

● These coefficients depend not only on material composition,
but also on temperature and pressure of the system.

## Heat Capacity

● Heat required (Q) to bring about a certain temperature change ($\Delta T$)

$$C = \frac{Q_{rev}}{\Delta T} \quad \text{and} \quad C = \frac{\delta Q_{rev}}{dT}$$

● The concept of heat capacity is only used when the system produces a finite temperature change (i.e. $\Delta T \neq 0$)

**A material melts at constant temperature.**

**Thus, for this isothermal process, heat capacity cannot be considered.**

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● Like heat, heat capacity is a **process variable**.

$$C_P = \left( \frac{\delta Q_{rev}}{\partial T} \right)_P \quad \text{or,} \quad \delta Q_{rev,P} = C_P \, dT_P$$

$$C_V = \left( \frac{\delta Q_{rev}}{\partial T} \right)_V \quad \text{or,} \quad \delta Q_{rev,V} = C_V \, dT_V$$

● Heat capacity is an **extensive** variable.

**Specific heat capacity (heat capacity per gram of substance at constant P) and molar heat capacity (heat capacity per mole of substance at constant P or V) are also used. Thus, for example, $C_P = n \, c_P$.**

● Generally, for a given material, $C_P > C_V$. Why?

● The value of heat capacity changes with temperature, pressure and composition of the system.

● Almost all heat capacity measurements are generally made at 1 atm pressure i.e., at constant pressure.

● Temperature dependence of constant-pressure heat capacity, $C_P$, is usually expressed by the relation

$$C_P(T) = a + bT + cT^{-2}$$

where a, b, c are constants

● If $\alpha$, $\beta$, and $C_P$ are known for any simple system (for which $\delta W' = 0$)

   ❖ **Changes of all the state functions can be computed** for any arbitrary process through which the system may be taken

   ❖ **No additional information is required**.

# The Coefficient Relations

**The function:**

$Z = Z (X, Y)$

**$dZ = MdX + NdY$**

**Coefficient Relations:**

$M (X,Y) = (\partial Z/\partial X)_Y$

$N (X,Y) = (\partial Z/\partial Y)_X$

**Combined Statements**

$dU = TdS - PdV$

$dH = TdS + VdP$

$dF = -SdT - PdV$

$dG = -SdT + VdP$

**Coefficient Relations**

$T = (\partial U/\partial S)_V$ ;  $-P = (\partial U/\partial V)_S$

$T = (\partial H/\partial S)_P$ ;  $V = (\partial H/\partial P)_S$

$-S = (\partial F/\partial T)_V$ ;  $-P = (\partial F/\partial V)_T$

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

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# The Maxwell Relations

$Z = Z (X, Y)$     $M = (\partial Z/\partial X)_Y$

**$dZ = MdX + NdY$**     $N = (\partial Z/\partial Y)_X$

**Maxwell Relation:**

$(\partial M/\partial Y)_X = (\partial N/\partial X)_Y$

**Combined Statements**

$dU = TdS - PdV$

$dH = TdS + VdP$

$dF = -SdT - PdV$

$dG = -SdT + VdP$

**Maxwell Relations**

$(\partial T/\partial V)_S = - (\partial P/\partial S)_V$

$(\partial T/\partial P)_S = (\partial V/\partial S)_P$

$(\partial S/\partial V)_T = (\partial P/\partial T)_V$

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

It is important to specify explicitly

not only the variables in the **numerator** and **denominator** of each partial derivative

but also **the variable that is being held constant**, indicated in the subscript outside the parentheses of the partial derivative.

$$\left(\frac{\partial H}{\partial T}\right)_P \quad \text{and} \quad \left(\frac{\partial H}{\partial T}\right)_V$$

are not equal to each other

# The Transformation Formula

**Z = Z (X, Y)**

$dZ = (\partial Z/\partial X)_Y \, dX + (\partial Z/\partial Y)_X \, dY$

For an incremental change in state at constant Z:

$dZ = 0 = (\partial Z/\partial X)_Y \, dX_Z + (\partial Z/\partial Y)_X \, dY_Z$

$(\partial Z/\partial X)_Y \, dX_Z = - (\partial Z/\partial Y)_X \, dY_Z$

$(\partial Z/\partial X)_Y \cdot (\partial X/\partial Y)_Z = - (\partial Z/\partial Y)_X$

$(\partial Z/\partial X)_Y \cdot (\partial X/\partial Y)_Z \cdot (\partial Y/\partial Z)_X = - 1$

**$(\partial X/\partial Y)_Z \cdot (\partial Y/\partial Z)_X \cdot (\partial Z/\partial X)_Y = - 1$**

**Example 4.2**
Show that heat is not a state variable.

Using the first law, for $\delta W' = 0$,
$dU = \delta Q - PdV$
$\delta Q = dU + PdV$

For the function $U = U(P,V)$:
$dU = (\partial U/\partial P)_V\, dP + (\partial U/\partial V)_P\, dV$

$\delta Q = (\partial U/\partial P)_V\, dP + (\partial U/\partial V)_P\, dV + PdV$
$\delta Q = (\partial U/\partial P)_V\, dP + [(\partial U/\partial V)_P + P]\, dV$

If $Q = Q(P, V)$ were to be a state function, Maxwell relation must be valid.

$$(\partial/\partial V)\left[(\partial U/\partial P)_V\right]_P = (\partial/\partial P)\left[(\partial U/\partial V)_P + P\right]_V$$

$$\left(\frac{\partial^2 U}{\partial V . \partial P}\right)_{V,\,P} = \left(\frac{\partial^2 U}{\partial P . \partial V}\right)_{P,\,V} + \left(\frac{\partial P}{\partial P}\right)_V$$

But this requires that
$(\partial P/\partial P)_V = 0$
which is never true.

Thus, heat is not a state variable.

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# Next Class

## Lecture 11
# Thermodynamic Variables and Relations
**General Procedure to Obtain Thermodynamic Relations**
**Rashid/ Ch#4**