Lecture-22

The Thermodynamic Web

* Thermodynamic state of a system can be characterized by its properties. our goal is to develop mathematical expressions through which we can relate the properties of a system to one another and to forms in which data are typically reported.

* Three distinct categories of thermodynamic properties:

→ Measured properties.
→ Fundamental properties.
→ Derived properties.

* **Measured properties:** are those properties that are directly accessible from measurements in the lab.
Pressure, volume, Temperature, composition

* **Fundamental properties:**
observations of nature led us to the two laws of thermodynamics. In formulating these laws, we introduced two new properties:

U (From conservation of energy)
S (from directionality of nature)

Since internal energy and entropy come from the two fundamental postulates of thermodynamics, we call them fundamental properties.

We will develop a web of property relationships whereby we can relate the thermodynamic properties we need to solve problems to properties we can measure in the lab. we want to relate fundamental and derived thermodynamic properties such as U, S, H, A and G, to things we can measure, such as measured properties P, V, T or to quantities for which measured data are typically reported, for example

C_p, C_v, β and K.

we limit our present discussion to constant compositions systems. The state postulate says that for systems of constant composition, values of two independent, intensive properties completely constrain the state of the system. Mathematically, the change in any intensive thermodynamic property of interest, z, can be written in terms of partial derivatives of the two independent intensive properties,

x and y, as follows:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \longrightarrow (1)$$

These properties cannot be measured directly.

* ~~Dervied~~ Derived properties: These cannot be measured in the lab, nor are they properties directly fundamental to the postulates that govern thermodynamics; they are merely some specific combination of the above two types of properties that are defined out of convenience. Consider, for example, enthalpy:

$$H = U + PV$$

Helmholtz energy : $A = U - TS$

Gibbs energy : $G = H - TS$

Fundamental Property Relations:

First law of thermodynamics,

$$dQ + dW = dU \longrightarrow (2)$$

Second law of thermodynamics,

$$dQ = Tds \longrightarrow (3)$$

[closed system undergoing a reversible process]

From (2) & (3),

$$dU = Tds + dW$$

$$\Rightarrow \boxed{dU = Tds - PdV} \longrightarrow (4)$$

Enthalpy is defined as:

$$H = U + PV$$

$$\Rightarrow dH = dU + PdV + Vdp$$

Using eq^n. (4),

$$dH = (Tds - PdV) + PdV + Vdp$$

$$\Rightarrow \boxed{dH = Tds + Vdp} \longrightarrow (5)$$

Helmholtz energy, $A = U - TS$

$$\Rightarrow dA = dU - TdS - SdT$$

using eq^n. (4),

$$dA = (TdS - PdV) - TdS - SdT$$

$$\boxed{dA = -PdV - SdT} \longrightarrow (6)$$

Gibbs energy, $G = H - TS$

$$dG = dH - TdS - SdT$$

using eq^n. (5),

$$dG = (TdS + Vdp) - TdS - SdT$$

$$\boxed{dG = Vdp - SdT} \longrightarrow (7)$$

Equations (4), (5), (6) & (7) are known as the fundamental property relations. These equations can be applied to any process; reversible or irreversible.

Lecture-23

From eq^n. (1),

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

or, $$\boxed{dz = M dx + N dy} \longrightarrow (8)$$

where, $M = \left(\frac{\partial z}{\partial x}\right)_y$ and $N = \left(\frac{\partial z}{\partial y}\right)_x$

Then, $$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y \partial x} \text{ and } \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}$$

The order of differentiation in mixed second derivatives is immaterial and thus,

$$\boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y} \longrightarrow (9)$$

Therefore, using (8) and (9) with eq^n. (4),

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \longrightarrow (10)$$

From eq^n. (5),

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \longrightarrow (11)$$

From eq^n. (6),

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

From eq^n. (7),

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \longrightarrow (13)$$

Equations (10), (11), (12) & (13) are Known as Maxwell's equations.

Other Useful Mathematical Relations:

$$\left(\frac{\partial Z}{\partial x}\right)_a = \left(\frac{\partial Z}{\partial y}\right)_a \left(\frac{\partial Y}{\partial x}\right)_a \longrightarrow (14)$$

↳ chain Rule.

~~Derivative inversion allows us to flip partial derivatives~~

$$\cancel{\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\;}}$$

Again, $\quad dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy$

Taking partial derivative of each term with respect to x ~~and~~ at constant z, we get:

$$\left(\frac{\partial Z}{\partial x}\right)_Z = \left(\frac{\partial Z}{\partial x}\right)_y \underset{\downarrow(1)}{\left(\frac{\partial x}{\partial x}\right)_Z} + \left(\frac{\partial Z}{\partial y}\right)_x \left(\frac{\partial Y}{\partial x}\right)_Z$$

$$\searrow 0 = \left(\frac{\partial Z}{\partial x}\right)_y + \left(\frac{\partial Z}{\partial Y}\right)_x \left(\frac{\partial Y}{\partial x}\right)_Z$$

$$\Rightarrow \left(\frac{\partial Z}{\partial Y}\right)_x \left(\frac{\partial Y}{\partial x}\right)_Z = -\left(\frac{\partial Z}{\partial x}\right)_y$$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial z}{\partial y}\right)_x = -1} \longrightarrow (15)$$

$$\downarrow$$

<u>cyclic Relation</u>

Heat capacity at constant volume,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

using $dU = TdS - PdV$, we get-

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

$$= T\left(\frac{\partial S}{\partial T}\right)_V - P\underset{\substack{\downarrow \\ 0}}{\left(\frac{\partial V}{\partial T}\right)_V}$$

$$\Rightarrow C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}} \longrightarrow (16)$$

Heat capacity at constant pressure,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

using, $dH = TdS + Vdp$

$$\Rightarrow \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p + V\underset{\substack{\downarrow \\ 0}}{\left(\frac{\partial p}{\partial T}\right)_p}$$

$$\Rightarrow \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

$$\Rightarrow \quad \boxed{\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}} \longrightarrow (17)$$

$$x = x(y,z)$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$z = z(x,y)$$

similarly, $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y \left[\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy\right]$$

$$= \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\cancel{\partial x}}{\cancel{\partial z}}\right)_y \left(\frac{\cancel{\partial z}}{\cancel{\partial x}}\right)_y dx + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\cancel{dx} = \left(\frac{\partial x}{\partial y}\right)_z dy + \cancel{dx} + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = 0$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1} \longrightarrow (15)$$

$\downarrow$

<u>cyclic Relation.</u>

E.g. Among the thermodynamic variables P, V and T, the following relation holds good.

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1.$$

Lecture-24

Calculation of fundamental and derived properties using Equations of state and other measured quantities:

Relation of ds in terms of independent properties T and V and independent properties T and p:

$$s = s(T,V)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_V dT + \left(\frac{\partial s}{\partial V}\right)_T dV$$

from, eq^n. (16), $\left(\frac{\partial s}{\partial T}\right)_V = \frac{C_V}{T}$

and eq^n. (12), $\left(\frac{\partial s}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$\Rightarrow \boxed{ds = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV} \longrightarrow (18)$$

On integration,

$$\boxed{\Delta s = \int \frac{C_V}{T} dT + \int \left(\frac{\partial P}{\partial T}\right)_V dV} \longrightarrow (19)$$

Again, $s = s(T,P)$

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

From, eq^n. (17), $\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_P}{T}$

and, $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

$$\Rightarrow \boxed{ds = \frac{C_p}{T}dT - \left(\frac{\partial v}{\partial T}\right)_p dp} \longrightarrow (20)$$

On integration,

$$\boxed{\Delta s = \int \frac{C_p}{T}dT - \int\left(\frac{\partial v}{\partial T}\right)_p dp} \longrightarrow (21)$$

Relation of du in terms of independent properties T and V:

$$U = U(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

since, $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

and $dU = TdS - PdV$

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

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

from eq^n (12), $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

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

Thus, $\boxed{dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV} \longrightarrow (22)$

on integration, $\boxed{\Delta U = \int C_V dT + \int\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV} \longrightarrow (23)$

$$H = H(T, P)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dp$$

Since, $C_p = \left(\frac{\partial H}{\partial T}\right)_P$

and, $dH = Tds + vdp$ [Eq^n. 5]

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

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

Since, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ [Eq^n. (13)]

Thus, $\boxed{dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dp}$ → (24)

For ideal gas, $PV = RT$

$\Rightarrow V = \frac{RT}{P}$

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

Thus, from eq^n. (24), $dH = C_p dT + \underbrace{\left[V - \frac{RT}{P}\right]}_{0} dp$

$\boxed{dH = C_p dT}$ → (25)

only for ideal gas.

Since, volume expansivity,

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \boxed{\left(\frac{\partial V}{\partial T}\right)_P = \beta V}$$

↳ (26)

and, isothermal compressibility,

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \Rightarrow \boxed{\left(\frac{\partial V}{\partial P}\right)_T = -KV}$$

↳ (27)

From Eq^n. (13), $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

using eq^n. (26), we get-

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\beta V} \longrightarrow (28)$$

Since, $dH = TdS + VdP$ [Eq^n. 5]

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

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

$$= V + T(-\beta V) \quad \underline{\text{using Eq}^n\text{. (28)}}$$

$$= V - \beta T V$$

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_T = (1-\beta T)V} \longrightarrow (29)$$

From eq^n. (24),

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp$$

using Eq^n. (26),

$$\left(\frac{\partial V}{\partial T}\right)_p = \beta V$$

$$dH = C_p dT + [V - T\beta V] dp$$

$$\boxed{dH = C_p dT + (1 - \beta T) V dp} \longrightarrow (30)$$

From Eq^n. (20),

$$dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_p dp$$

using Eq^n. (26),

$$\left(\frac{\partial V}{\partial T}\right)_p = \beta V$$

$$\boxed{dS = C_p \frac{dT}{T} - \beta V dp} \longrightarrow (31)$$

Internal Energy as a Function of P:

$$U = H - PV$$

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

$$= \underbrace{(1-\beta T)V}_{\text{Eq}^n.\ (29)} - P(\underset{\substack{\uparrow \\ \text{Eq}^n.\ (27)}}{-KV}) - V$$

$$= V - \beta TV + KPV - V$$

$$= KPV - \beta TV$$

$$\boxed{\left(\frac{\partial U}{\partial P}\right)_T = (KP - \beta T)V} \longrightarrow (32)$$

* The equations, incorporating 'β' and 'K', although general, are usually applied only to liquids. Because 'β' and 'V' are weak functions of pressure for liquids, they are usually assumed constant.

If $V = V(T, P)$

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

Using Eq^n. (26) & (27),

$$dV = \beta V dT - K V dp$$

$$\Rightarrow \frac{dV}{V} = \beta dT - K dp$$

At constant volume,

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{K}} \longrightarrow (33)$$

From eq^n. (22),

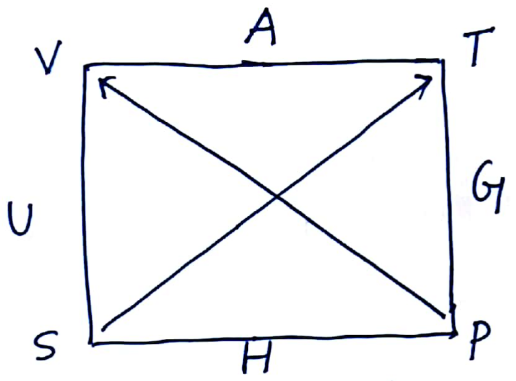
$$\boxed{dU = C_V dT + \left(\frac{\beta}{K} T - P\right) dV} \longrightarrow (34)$$

From eq^n. (18),

$$\boxed{dS = \frac{C_V}{T} dT + \frac{\beta}{K} dV} \longrightarrow (35)$$

Thermodynamic Mnemonic diagram Lecture-25

- A number of the most useful Maxwell relations can be remembered conveniently in terms of a simple mnemonic diagram. The diagram was presented by Max Born [1954 Nobel prize in physics].



Thermodynamic potential: A, G, H, U.

- Mnemonic diagram consists of a square with arrows pointing upward along the two diagonals.
- The sides are labelled with the four common thermodynamic potentials A, G, H and U, in alphabetical order clockwise around the diagram, the helmholtz potential at the top.
- The two corners at the left are labelled with 'V' and 'S' and the two corners at the right are labelled with 'T' and 'P'.

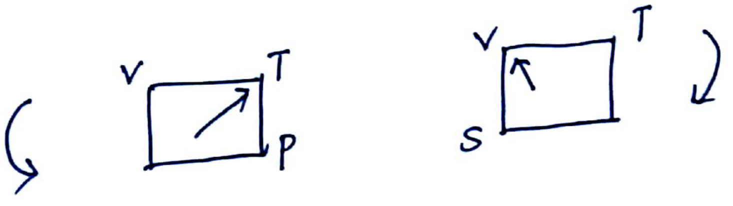
- Each of the four thermodynamic potentials appearing on the square is flanked by independent variables.
- 'U' is a function of 'V' and 'S'.
  'A' is a function of 'V' and 'T'.
  'G' is a function of 'T' and 'p'.
  'H' is a function of 'S' and 'p'.
- In the differential expression for each of the potentials, in terms of the differentials of its variables, the associated algebraic sign is indicated by the diagonal arrow.
- An arrow pointing away from a variable implies a positive coefficient, whereas an arrow pointing toward a variable implies negative coefficient.
- Based on the above scheme, we can write the following equations:

$$\left.\begin{aligned} dU &= PdV - Tds \\ dA &= -PdV - SdT \\ dG &= -SdT + Vdp \\ dH &= Tds + Vdp \end{aligned}\right\} \text{Fundamental property Relations.}$$

- Finally the Maxwell relations can be read from the diagram. We then deal only with the corners of the diagram.

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

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



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

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

Question: One mole of propane gas is to be expanded from $0.001 m^3$ to $0.04 m^3$ while in contact with a heating bath at 100 °C. The expansion is not reversible. The heat extracted from the bath is 600 J. Using the vander waals equation of state, determine the work for the expansion.

Solution: To find the work, we apply the first law;

$$\Delta U = Q + W \longrightarrow (1)$$

Since we know, $Q = 600 J$, we just need to find ΔU.

From the problem, we find that information about temp. (T) and volume (V) is given. Thus, we start with:

$$U = U(T,V)$$

$$\Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \longrightarrow (2)$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \longrightarrow (3)$$

From property relations, we have-

$$dU = TdS - PdV$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T \rightarrow (4)$$

From Maxwell relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \longrightarrow (5)$$

using eqⁿ. (5) in eqⁿ. (4), we get-

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \longrightarrow (6)$$

using eqⁿ. (3) and eqⁿ. (6) in eqⁿ. (2),

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

On Integration,

$$\Delta U = \underbrace{\int C_V dT}_{0 \text{ (as temp. is constant)}} + \int\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

$$\Delta U = \int\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \longrightarrow (7)$$

From the van der waals equations, we have

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} \longrightarrow (8)$$

using eqⁿ. (8) in eqⁿ. (7), we get-

$$\Delta U = \int\left[\frac{RT}{V-b} - P\right] dV$$

~~using eqⁿ.~~

$$= \int\left[\frac{RT}{V-b} - \left\{\frac{RT}{V-b} - \frac{a}{V^2}\right\}\right] dV$$

$$\Delta U = \int_{v_i}^{v_f} \frac{a}{v^2}\, dV = a\int_{v_i}^{v_f} v^{-2}\, dv = -a\left(\frac{1}{v}\right)_{v_i}^{v_f}$$

Since, $a = \frac{27}{64}\,\frac{R^2 T_c^2}{P_c}$

For propane, $T_c = 369.8\ K$

$P_c = 42.48\ bar$

$$\therefore a = \frac{27}{64}\,\frac{(83.14\ cm^3\, bar\, mol^{-1} K^{-1})^2 (369.8\ K)^2}{(42.48\ bar)}$$

$$= 9.4\times10^6\ \frac{cm^6\, bar^{\cancel{2}}\, mol^{-2}\, \cancel{K^{2}}\, \cancel{K^{2}}}{\cancel{bar}}$$

$$\therefore a = 9.4\times10^6\ \frac{cm^6\, bar}{mol^2}$$

Thus, $\Delta U = -9.4\times10^6\ \frac{cm^6\, bar}{mol^2}\left[\frac{1}{v_f} - \frac{1}{v_i}\right]$

$v_i = 0.001\ m^3/mol$

$v_f = 0.04\ m^3/mol$

$$= -9.4\times10^6\ \frac{cm^6\, bar}{mol^{\cancel{2}}}\left[\frac{1}{0.04} - \frac{1}{0.001}\right]\frac{\cancel{mol}}{m3}$$

$$= 9165\times10^6 \times \frac{\cancel{(10^{-6}\, m^{3})}^{2}(10^5\ N/m^2)}{(mol)\,(m^3)} \times (10^{-12}\ m^6)$$

$$\boxed{\Delta U = 916\ J/mol.}$$ ~~solution~~

Thus, from (1),

$W = \Delta U - Q = 916 - 600$

$\boxed{W = 316\ J/mol}$ solution