

## **MME 231: Lecture 12**

# **Thermodynamic Variables and Relations**

Application of Thermodynamic Relations



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## **Today's Topics**

- Application of thermodynamic relations
  - ideal gases
  - solids and liquids
- Examples

## Application of Thermodynamic Relations to Ideal Gases

The equation of state for an ideal gas:

$$PV = nRT$$

### Universal gas constant

$$R = 1.98717 \text{ cal/K-mol} = 1.986 \text{ Btu/R-lb mol}$$

$$R = 10.73 \text{ ft}^3\text{-psia/R-lb mol} = 1545 \text{ ft-lb}_f\text{/R-lb mol}$$

$$R = 82.06 \text{ cm}^3\text{-atm/K-mol} = 83.14 \text{ cm}^3\text{-bar/K-mol}$$

$$R = 62356 \text{ cm}^3\text{-torr/K-mol} = 8314 \text{ cm}^3\text{-kPa/K-mol}$$

$$R = 0.082056 \text{ litre-atm/K-mol} = 0.7302 \text{ ft}^3\text{-atm/R-lb mol}$$

$$R = 0.082 \text{ m}^3\text{-bar/K-mol}$$

$$R = 8.31434 \text{ J/K-mol} = 8.31434 \text{ m}^3 \text{ Pa/K-mol}$$

$$PV = RT$$

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

$$\beta = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T = -\left(\frac{P}{RT}\right)\left(\frac{-RT}{P^2}\right) = \frac{1}{P}$$

$$C_P - \frac{TV\alpha^2}{\beta} = C_P - \frac{TVP}{T^2} = C_P - R$$

$$C_P - R = C_V$$

For monatomic gases:

$$C_V = 3R/2 \quad C_P = 5R/2$$

For diatomic gases:

$$C_V = 5R/2 \quad C_P = 7R/2$$

$$dU = (C_p - PV\alpha) dT + V(P\beta - T\alpha) dP$$

$$dU = (C_p - PV/T) dT + V(P/P - T/T) dP = (C_p - R) dT$$

$$dU = C_v dT$$

$$\Delta U = C_v (T_2 - T_1)$$

$$dH = C_p dT + V(1 - T\alpha) dP$$

$$dH = C_p dT + V(1 - T/T) dP$$

$$dH = C_p dT$$

$$\Delta H = C_p (T_2 - T_1)$$

#### Example 4.5

One mole of an ideal monatomic gas initially at temperature 298 K and occupying volume 10 litres is compressed reversibly and adiabatically to a final volume of 2 litres. Compute the final temperature of the system.

Here, the function is:  $T = T(S, V)$

For the function  $S = S(T, V)$ :  $dS = (C_v/T) dT + (\alpha/\beta) dV$

Then, for the function  $T = T(S, V)$ :  $dT = (T/C_v) dS - (T\alpha/\beta C_v) dV$

For adiabatic process,  $dS = 0$ . Thus,  $dT_S = -(T\alpha/\beta C_v) dV_S$

Now, for ideal gas,  $\alpha = 1/T$ ,  $\beta = 1/P$ . So,  $dT = -(P/C_v) dV$

Using  $PV = RT$ ,  $P = RT/V$ , and  $(dT/T) = -(R/C_v) (dV/V)$

$$(dT/T) = -(R/C_V) (dV/V)$$

Integrating between limits:

$$\ln (T_2/T_1) = -(R/C_V) \ln (V_2/V_1)$$

$$T_2 = T_1 (V_1/V_2)^{R/C_V}$$

$$T_2 = (298 \text{ K}) (10/2)^{2/3} = 871.36 \text{ K}$$

#### Given data

$$V_1 = 10 \text{ litre}$$

$$V_2 = 2 \text{ litre}$$

$$T_1 = 298 \text{ K}$$

$$C_V = 3R/2$$

## Application of Thermodynamic Relations to Solids and Liquids

- $\alpha$ ,  $\beta$  and  $C_p$  are functions of  $T$ ,  $P$  and  $X$ .
- For a given material, they are not strong functions of the state of the system.
- When **only an estimate** of the thermodynamic functions is sought,  $\alpha$ ,  $\beta$  and  $C_p$  **can be considered to be as constants**.
- For precise calculations, the **dependence upon  $P$  and  $T$  must be obtained** for these experimental variables  $\alpha$ ,  $\beta$  and  $C_p$ .

### Example 4.6

One mole of nickel initially at 300 K and 1 atm pressure is taken through two separate processes:

- (1) an isobaric change in temperature to 1000 K, and
- (2) an isothermal compression to 1000 atm.

Compare the change in enthalpy of nickel for these two processes.

Given data:

$$V (300 \text{ K}, 1 \text{ atm}) = 6.57 \text{ cc/mol}$$

$$\alpha = 40 \times 10^{-6} \text{ K}^{-1}$$

$$\beta = 1.5 \times 10^{-6} \text{ atm}^{-1}$$

$$C_p = 16.99 + 2.95 \times 10^{-2} T \text{ J/mol-K.}$$

### Answer:

$$H = H(T, P) \quad dH = C_p dT + V(1 - T\alpha) dP$$

#### Process 1 (Isobaric)

$$dH_p = C_p dT$$

$$\Delta H = \int_{300}^{1000} dH = \int_{300}^{1000} (16.99 + 2.95 \times 10^{-2} T) dT$$

$$\Delta H = 11893.0 + 13422.5 \text{ J/mol}$$

$$\Delta H = \mathbf{25315.5 \text{ J/mol}}$$

The second term on the right hand side of the equation arises from the temperature dependent contribution to the heat capacity.

If T dependency is ignored,  $C_p = 16.99$ , and then  $\Delta H = 11893.0 \text{ J/mol}$

$$H = H(T, P) \quad dH = C_p dT + V(1 - T\alpha) dP$$

### Process 2 (Isothermal)

$$dH_T = V(1 - T\alpha) dP_T$$

**Here  $V$  and  $\alpha$  depend upon pressure.**

**For an estimated calculation,**

- $V$  and  $\alpha$  both can be treated as pressure independent.

$$\Delta H = V(1 - T\alpha) [P_2 - P_1]$$

$$\Delta H = 6484.67 \text{ cc-atm/mol} = 657.0 \text{ J/mol}$$

**For an exact calculation,**

- the values of  $\alpha$  are within the range of  $10^{-6}$ , so that  $\alpha$  can be considered as constant.
- but, pressure dependency of  $V$  cannot be ignored.

$$dV = V\alpha dT - V\beta dP, \text{ and at constant } T$$

$$dV_T = -V\beta dP_T \text{ and integrating between the limits,}$$

$$\ln(V/V_0) = -\beta(P - P_0)$$

$$V/V_0 = \exp[-\beta(P - P_0)]$$

$$V \cong V_0[1 + \beta(P - P_0)]$$

Then the enthalpy change

$$dH = V_0[1 + \beta(P - P_0)](1 - T\alpha) dP$$

$$dH = V_0 \left[ 1 + \beta (P - P_0) \right] (1 - T\alpha) dP$$

Integrating,

$$\Delta H = V_0 (1 - T\alpha) \left[ P + \frac{\beta (P - P_0)^2}{2} \right]_1^{1000}$$

$$\Delta H = 657.0 + 0.07 \text{ J/mol}$$

Only 0.07 J/mol amount of enthalpy is added because of addition of the pressure variation of volume into the equation.

**For solids and liquids, energy changes associated with thermal influences tend to be much larger than those arising from mechanical influences.**

## **Problem Solving**

## **Next Class**

### **Lecture 13**

# **Equilibrium in Thermodynamic Systems**