Temperature Dependence of Enthalpy Changes:

The enthalpy changes for chemical reaction can be deduced for a range of temperature.

For a chemical equation:

Reactants \(\rightarrow\) Products

The enthalpy change for the reaction can be written as:

\[
\Delta H = \Delta H_{\text{prod}} - \Delta H_{\text{react}}
\]

Where the product and reactants enthalpies imply the sum of the molar enthalpies of the products and reactants in given chemical equation.

The derivative with respect to temperature is given as:

\[
[\partial (\Delta H)/\partial T]_P = [\partial (\Delta H_{\text{prod}})/\partial T]_P - [\partial (\Delta H_{\text{react}})/\partial T]_P
\]

We can write this using heat-capacity terms:

\[
[\partial (\Delta H)/\partial T]_P = (C_p)_{\text{prod}} - (C_p)_{\text{react}} = \Delta C_p
\]

Where \((C_p)_{\text{prod}}\) and \((C_p)_{\text{react}}\) imply the sum of the heat capacities of the product and reactant species.
Integrated Enthalpy-of-reaction Results:

\[
\begin{align*}
T_2 & \quad \int_{T_1}^{T_2} \left[ \frac{\partial (\Delta H)}{\partial T} \right]_P = \Delta H_{T_2} - \Delta H_{T_1} \\
& = \int_{T_1}^{T_2} \Delta C_p \, dT
\end{align*}
\]

Since,

\[C_p = a + bT + (C/T^2)\]

Thus, we have

\[
\begin{align*}
\Delta H_{T_2} - \Delta H_{T_1} &= \int_{T_1}^{T_2} \Delta C_p \, dT \\
&= \Delta a \, (T_2 - T_1) + (1/2)(\Delta b)(T_2^2 - T_1^2) - (\Delta c)[(1/T_2) - (1/T_1)]
\end{align*}
\]

Using this equation we can calculate the enthalpy change at one temperature from the enthalpy change at another temperature.

A more general expression for temperature dependence of the reaction enthalpy change is obtained by developing an indefinite integral.

Thus, we get

\[
\Delta H_T = \int \Delta C_p \, dT + \text{const.}
\]
And

\[ \Delta H_T = \Delta a \, T + (1/2)(\Delta b)(T^2) - (\Delta c) \, (1/T) + \text{const} \]

The constant term is evaluated by using the enthalpy change for the reaction at 25\(^0\)C.

After calculating the constant term, the equation can be used to calculate the enthalpy change at any other temperature.

Problem 1:

Calculate the enthalpy change for the industrially important shift-conversion reaction CO (g) + H\(_2\)O (g) --\(\rightarrow\) CO\(_2\) (g) + H\(_2\) (g) at 1500 K.

Standard enthalpies of formation of CO (g), H\(_2\)O (g), CO\(_2\) (g), H\(_2\) (g) are -110.52, -241.82, -393.51 and 0 kJmol\(^{-1}\) respectively.

\[
\text{CO} (g) + \text{H}_2\text{O} (g) \rightarrow \text{CO}_2 (g) + \text{H}_2 (g)
\]

\[ \Delta H^0_f = -110.52 \quad -241.82 \quad -393.51 \quad 0 \]

therefore enthalpy change for the reaction is

\[ \Delta H^0_{298} = -41.17 \text{ kJmol}^{-1} \]

Also, from table 3.1

\[
\begin{array}{cccccc}
\text{CO} (g) + \text{H}_2\text{O} (g) \rightarrow \text{CO}_2 (g) + \text{H}_2 (g) \\
a \text{ terms} & 28.41 & 30.54 & 44.22 & 27.28 & \Delta a = 12.55 \\
b \text{ terms} & 0.00410 & 0.01029 & 0.00879 & 0.00326 & \Delta b = -2.34 \times 10^{-3} \\
c \text{ terms} & -46,000 & 0 & -862,000 & 50,000 & \Delta b = -7.66 \times 10^5
\end{array}
\]
We have
\[ \Delta H^0_T = \Delta a T + (1/2)(\Delta b)(T^2) - (\Delta c) (1/T) + \text{const} \]

------------ (1)

\[ = 12.55 T + (1/2)(-2.34 \times 10^{-3})(T^2) -(-7.66 \times 10^5) (1/T) + \text{const} \]

------------ (2)

With \( \Delta H^0_{298.15} = -41,170 \text{ J mol}^{-1} \) and \( T = 298.15 \text{ K} \)

We get the

\text{Const} = -47,380 \text{ J mol}^{-1}

Substituting the value for constant in equation (2)
\[ \Delta H^0_T = 12.55 T + (1/2)(-2.34 \times 10^{-3})(T^2) -(-7.66 \times 10^5) (1/T) -47,380 \text{ J mol}^{-1} \]

For \( T = 1500 \text{ K} \)

\[ \Delta H^0_{1500} = -30.68 \text{ kJ mol}^{-1} \]
Molecular Basis of Heat Capacities:

The Molar Heat Capacity $C_p$ of monoatomic gases:

Using the classical kinetic-molecular theory and the quantum-mechanical theory, the molar thermal internal energy due to translational motion is equal to $(3/2) \, R T$

\[
C_v = \left( \frac{\partial U}{\partial T} \right)_v = \frac{3}{2} R = 12.47 \text{ J} \text{ K}^{-1} \text{ mol}^{-1}
\]

\[
C_p = \left( \frac{\partial H}{\partial T} \right)_p = \frac{5}{2} R = 20.78 \text{ J} \text{ K}^{-1} \text{ mol}^{-1}
\]

Cp for Gases Composed of Diatomic Molecules:

Linear Molecules:

Linear Diatomic molecules have 3 translational degrees of freedom, 2 rotational degrees of freedom, and 1 vibrational degree of freedom.

The translational motion gives thermal energy of $(1/2)RT$ per degree of freedom.

\[
(U - U_0)_{trans} = \frac{3}{2} \, R T
\]

The heat-capacity contribution for translational motion is

\[
C_{trans} = \frac{\partial (U - U_0)_{trans}}{\partial T} = \frac{3}{2} \, R
\]

The rotational motion gives thermal energy of $(1/2)RT$ per degree of freedom.
\[ (U - U_0)_{\text{rot}} = (2/2)RT = RT \]

The heat-capacity contribution for rotational motion is

\[ C_{\text{rot}} = \frac{\partial (U - U_0)_{\text{rot}}}{\partial T} = R \]

The vibrational motion gives thermal energy of \( RT \left[ \frac{x}{(e^x - 1)} \right] \) per degree of freedom where \( x = \frac{\Delta \varepsilon_{\text{vib}}}{kT} \).

\[ (U - U_0)_{\text{vib}} = RT \left[ \frac{x}{(e^x - 1)} \right] \quad \text{where} \quad x = \frac{\Delta \varepsilon_{\text{vib}}}{kT} \]

The heat-capacity contribution for vibrational motion is

\[ C_{\text{vib}} = \frac{\partial (U - U_0)_{\text{rot}}}{\partial T} = R x^2 e^x / (e^x - 1)^2 \]

The total heat capacity contribution for linear diatomic molecules (1 mole of ideal gas) is given as:

\[ C_v = C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}} \]

\[ = (3/2) R + R + R x^2 e^x / (e^x - 1)^2 \quad \text{where} \quad x = \frac{\Delta \varepsilon_{\text{vib}}}{kT} \]

\[ = (5/2) R + C_{\text{vib}} \]

And

\[ C_p = C_v + R \]

\[ = (5/2) R + C_{\text{vib}} + R \]
\[= (7/2) \, R + C_{\text{vib}}\]

\[= 29.10 \, \text{J K}^{-1} \, \text{mol}^{-1} + C_{\text{vib}}\]

Non-linear molecules:

For non-linear molecules there are 3 rotational degrees of freedom, giving rotational heat-capacity contribution as \((3/2)R\) and \((3n-6)\) vibrational degrees of freedom, giving vibrational heat-capacity contribution as \(C_{\text{vib}}\).

Thus

The total heat capacity contribution for non-linear diatomic molecules (1 mole of ideal gas) is given as:

\[C_v = C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}}\]

\[= (3/2) \, R \, + \, (3/2)R \, + \, R \, \frac{x^2 \, e^x}{(e^x - 1)^2} \quad \text{where} \quad x = (\Delta \epsilon_{\text{vib}} / kT)\]

\[= 3 \, R \, + \, C_{\text{vib}}\]

And

\[C_p = C_v + R\]

\[= 3 \, R \, + \, C_{\text{vib}} \, + \, R\]

\[= 4 \, R \, + \, C_{\text{vib}}\]

\[= 33.26 \, \text{J K}^{-1} \, \text{mol}^{-1} + C_{\text{vib}}\]
**Thermal Enthalpy:**

Thermal enthalpy means the enthalpy that a sample has as a result of quantum states with energies greater than the lowest-energy, or ground, state being occupied.

At 0 K, only the lowest energy states are occupied and the thermal energy is zero.

The thermal enthalpy at other temperatures can be expressed as

\[
H^0_T - H^0_0 = \int_0^T C^0 p \, dT
\]

Generally all the thermodynamic properties are expressed with reference to 25°C or 298 K.

\[
H^0_T - H^0_0 = (H^0_T - H^0_{298}) + (H^0_{298} - H^0_0)
\]

\[
(H^0_T - H^0_{298}) = (H^0_T - H^0_0) - (H^0_{298} - H^0_0)
\]

\[
= (H^0_T - H^0_0) + (H^0_0 - H^0_{298})
\]
Problem 2: Calculate the thermal contribution $U - U_0$ to the internal energy and $H - H_0$ to the enthalpy of Cl$_2$ at 298 and at 1000K. Assume ideal-gas behavior, and used the vibrational energy level spacing of $1.10 \times 10^{-20}$ J per molecule.

$$(U - U_0)_{\text{trans}} = (3/2) \, RT$$

$$(U - U_0)_{\text{rot}} = RT$$

$$(U - U_0)_{\text{vib}} = RT \left[ \frac{x}{(e^x - 1)} \right]$$

where $x = \frac{\Delta \varepsilon_{\text{vib}}}{kT}$

At 298 K

$x = \frac{\Delta \varepsilon_{\text{vib}}}{kT} = \frac{(1.10 \times 10^{-20})}{(1.381 \times 10^{-23} \, \text{JK}^{-1} \, 298 \, \text{K})}$

$= \frac{(1.10 \times 10^3)}{(1.381 \times 298)} = 2.67$

$\left[ \frac{x}{(e^x - 1)} \right] = \frac{2.67}{(14.43 - 1)} = 0.198$

At 1000 K

$x = \frac{\Delta \varepsilon_{\text{vib}}}{kT} = \frac{(1.10 \times 10^{-20})}{(1.381 \times 10^{-23} \, \text{JK}^{-1} \, 1000 \, \text{K})}$

$= \frac{(1.10 \times 10^3)}{(1.381 \times 1000)} = 0.797$

$\left[ \frac{x}{(e^x - 1)} \right] = \frac{0.797}{(2.218 - 1)} = 0.654$

Now,

$$(U - U_0) = (U - U_0)_{\text{trans}} + (U - U_0)_{\text{rot}} + (U - U_0)_{\text{vib}}$$

$$= (3/2) \, RT + RT + RT \left[ \frac{x}{(e^x - 1)} \right]$$
At 298 K

\[(U - U_0) = (3/2) RT + RT + RT 0.198\]

\[= 2.69 \text{ RT}\]

\[= (2.69) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K})\]

\[= 6684.48 \text{ J mol}^{-1} = 6.68 \text{ kJ mol}^{-1}.\]

At 1000 K

\[(U - U_0) = (3/2) RT + RT + RT 0.654\]

\[= 3.15 \text{ RT}\]

\[= (3.15) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (1000 \text{ K})\]

\[= 26189.10 \text{ J mol}^{-1} = 26.18 \text{ kJ mol}^{-1}.\]

Now,

\[(H - H_0) = (U - U_0) + RT\]

AT 298 K

\[(H - H_0) = (U - U_0) + RT \quad = 6684.48 \text{ J mol}^{-1} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K})\]

\[= 6684.48 \text{ J mol}^{-1} + 2477.57 \text{ J mol}^{-1} = 9162.05 \text{ J mol}^{-1} = 9.16 \text{ kJ mol}^{-1}\]

AT 1000 K

\[(H - H_0) = (U - U_0) + RT \quad = 26189.10 \text{ J mol}^{-1} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (1000 \text{ K})\]

\[= 26189.10 \text{ J mol}^{-1} + 8314.00 \text{ J mol}^{-1} = 34503.10 \text{ J mol}^{-1} = 34.5 \text{ kJ mol}^{-1}\]