



## Thermodynamic Axioms

### First Law of Thermodynamics

Postulates the existence of a state variable Internal Energy ( $U$ ) with a total differential  $dU$

$$dU = dq + dw$$

Units: J

In a thermodynamic process where only reversible pressure-volume work is done

$$dU = dq - pdV$$

### Second Law of Thermodynamics

Postulates the existence of a state variable Entropy ( $S$ ) with a total differential

$$dS = \frac{dq}{T} \quad [\text{reversible process}] \quad dS > \frac{dq}{T} \quad [\text{irreversible process}]$$

Units: J/K

*Note:* Entropy is a measure of disorder in a system. Lower degree of order leads to a higher entropy. It follows from the second law that perpetuum mobile of the second kind is impossible – machine, which spontaneously converts thermal energy into mechanical work without any heat loss.

### Third Law of Thermodynamics

Entropy of a pure compound in its most stable crystalline form at temperature 0 K is zero

$$\lim_{T \rightarrow 0} S = 0$$

This postulate provides an absolute reference for the determination of entropy. The entropy determined relative to this point is the absolute entropy. It follows from the third law that it is impossible to reach temperature 0 K by any finite number of processes.

## Additional Thermodynamic Variables

### Enthalpy

$$H = U + PV$$

### Helmholtz Energy

$$F = U - TS$$

### Gibbs Energy

$$G = H - TS$$

Units  $H, F, G$ : J

### Heat capacity

$$C_v = \left( \frac{dq}{dT} \right)_v = \left( \frac{dU}{dT} \right)_v$$

$$C_p = \left( \frac{dq}{dT} \right)_p = \left( \frac{dH}{dT} \right)_p$$

Units: J/K

### Fugacity

$$f = p^\circ \exp \left( \frac{G_m(T, p) - G_m^\circ(T, p^\circ)}{RT} \right)$$

$p^\circ = 101325$  Pa is a standard pressure,  $G_m(T, p)$  molar Gibbs energy,  $G_m^\circ(T, p^\circ)$  molar Gibbs energy of system in ideal gas standard state at the same temperature (properties of ideal gas are pressure-independent and stated at standard pressure). The units of fugacity are the same as of pressure.

### Gibbs Fundamental Equations

$$\begin{aligned}dU &= TdS - pdV \\dF &= -SdT - pdV\end{aligned}$$

$$\begin{aligned}dH &= TdS + Vdp \\dG &= -SdT + Vdp\end{aligned}$$

### Maxwell Relations

$$\begin{aligned}\left(\frac{dT}{dV}\right)_S &= -\left(\frac{dp}{dS}\right)_V & \left(\frac{dT}{dp}\right)_S &= \left(\frac{dV}{dS}\right)_p \\ \left(\frac{dp}{dT}\right)_V &= \left(\frac{dS}{dV}\right)_T & \left(\frac{dV}{dT}\right)_p &= -\left(\frac{dS}{dp}\right)_T\end{aligned}$$

### T, V and T, p Dependence of Thermodynamic Functions

$$\begin{aligned}dS &= \frac{C_v}{T} dT + \left(\frac{dp}{dT}\right)_V dV = \frac{C_p}{T} dT - \left(\frac{dV}{dT}\right)_p dp \\ dU &= C_v dT + \left[ T \left(\frac{dp}{dT}\right)_V - p \right] dV & dH &= C_p dT + \left[ V - T \left(\frac{dV}{dT}\right)_p \right] dp\end{aligned}$$

### Calculation of Thermodynamic Properties Using State Functions

The change in a thermodynamic property between states **1** and **2** can be obtained by integration of the above equations, e.g.

$$U(T_2, V_2) = U(T_1, V_1) + \int_{T_1}^{T_2} [C_v]_{V_1} dT + \int_{V_1}^{V_2} \left[ T \left(\frac{dp}{dT}\right)_V - p \right] dV$$

(lower index in integrals denote which variable is kept constant in integration). Generally the procedure is: from state **1** to ideal gas at  $T_1$  – to ideal gas at  $T_2$  – to state **2**.

$$\begin{aligned}U(T_2, V_2) &= U(T_1, V_1) + \int_{V_1}^{\infty} \left[ T \left(\frac{dp}{dT}\right)_V - p \right]_{T_1} dV + \int_{T_1}^{T_2} C_v^\circ dT + \int_{\infty}^{V_2} \left[ T \left(\frac{dp}{dT}\right)_V - p \right]_{T_2} dV \\ H(T_2, p_2) &= H(T_1, p_1) + \int_{p_1}^0 \left[ V - T \left(\frac{dV}{dT}\right)_p \right]_{T_1} dp + \int_{T_1}^{T_2} C_p^\circ dT + \int_0^{p_2} \left[ V - T \left(\frac{dV}{dT}\right)_p \right]_{T_2} dp \\ S(T_2, p_2) &= S(T_1, p_1) + \int_{p_1}^0 \left[ \frac{nR}{p} - \left(\frac{dV}{dT}\right)_p \right]_{T_1} dp + \int_{T_1}^{T_2} \frac{C_p^\circ}{T} dT - nR \ln \frac{p_2}{p_1} + \int_0^{p_2} \left[ \frac{nR}{p} - \left(\frac{dV}{dT}\right)_p \right]_{T_2} dp \\ F(T_2, V_2) &= F(T_1, V_1) + [U(T_2, V_2) - T_2 \cdot S(T_2, V_2)] - [U(T_1, V_1) - T_1 \cdot S(T_1, V_1)] \\ G(T_2, p_2) &= G(T_1, p_1) + [H(T_2, p_2) - T_2 \cdot S(T_2, p_2)] - [H(T_1, p_1) - T_1 \cdot S(T_1, p_1)] \\ f(T, p) &= p \exp \left( \int_0^p \left[ \frac{z-1}{p} \right] dp \right) = \frac{RT}{V_m} \exp \left( z - 1 - \int_{\infty}^{V_m} \left[ \frac{z-1}{V_m} \right] dV_m \right)\end{aligned}$$

The input for calculations are an equation-of-state valid in the whole range from the initial to final state, heat capacity (only in the ideal gas standard state), and entropy at the initial state **1**.

**Homework 1:** Calculate the change in  $U$ ,  $H$ ,  $G$ ,  $F$  of one mole of gaseous (oxygen; nitrogen; sulfur dioxide; argon; chlorine; nitrous oxide; hydrogen; methane) between states  $T_1 = 298$  K,  $p_1 = 0,1$  MPa and  $T_2 = 500$  K,  $p_2 = 10$  MPa. Assume ideal gas behavior (equation-of-state  $pV = nRT$ ).