

1 Basic Concepts

Definitions:

- **System:** Any specified mass of material or piece(s) of equipment we wish to devote our attention to.
 - **closed:** No transfer of mass across the system boundaries.
 - **open:** Transfer of mass across the system boundaries is permitted.
- **Surroundings:** Anything that is not part of the system.
- **Properites:** A characteristic of the material that can be calculated or measured.
 - **extensive:** A property that is the sum of the values of each of the subsystems comprising the whole system. A property dependent on system size.
 - * Example: mass or volume.
 - **intensive:** A property whose value is not additive, and does not vary with system size.
 - * Example: temperature, pressure, density
 - **specific:** An intensive property that is obtained by dividing an extensive property by the total amount of process material.
 - * Example: A liquid where $V = 200 \text{ cm}^3$ and the mass = 200 g, then the specific volume $\hat{V} = 1 \text{ cm}^3/\text{g}$.
- **State:** A set of properites of the material at a point in time. The state of a system depends only on the system's intensive properties.

1.1 Work

The term “Work” is used widely in casual conversation, but in this context we refer to a specific definition. Work is a form of energy that represents a transfer of energy between the system

and surroundings. For a mechanical force:

$$W = \int_{state\ 1}^{state\ 2} F \cdot dl \quad (1)$$

where F is an external force in the direction of l acting on the system, or a system force acting on the surroundings.

The amount of work done by a system on its surroundings (or by the surroundings on the systems) is dependent upon the initial and final states of the system *and* the path taken to get from state 1 to state 2. For this reason, we say that work is a *path function*.

- **Path function:** A function whose final value is dependent on the path taken to get from the initial to final state.
 - Example: work, heat.
- **State function:** A function that is only dependent upon the initial and final states of the system.
 - Example: internal energy, enthalpy.

1.1.1 Illustration of work as a path function

An ideal gas at 300 K and 500 kPa is enclosed in a cylinder capped by a frictionless piston. The gas slowly expands from 0.1 m³ to 0.2 m³. Calculate the work done by the gas on the piston if:

- Path 1: expansion occurs at constant pressure ($p = 500$ kPa)
- Path 2: expansion occurs at constant temperature ($T = 300$ K)

$$W = \int_{V_1}^{V_2} \frac{F}{A} \cdot A dl = \int_{V_1}^{V_2} p dV \quad (2)$$

Path 1

$$\begin{aligned} W &= \int_{V_1}^{V_2} p dV = p(V_2 - V_1) \\ &= 5.00 \times 10^5 \text{ kPa} (0.2 \text{ m}^3 - 0.1 \text{ m}^3) = 50 \text{ kJ} \end{aligned} \quad (3)$$

Remember $1 \text{ J} = 1 \text{ N}\cdot\text{m}$.

Path 2

$$\begin{aligned} W &= \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV \\ &= nRT \ln(V_2/V_1) \end{aligned} \quad (4)$$

$$n = \frac{PV}{RT} = \frac{(5.0 \times 10^5 \text{ Pa})(0.1 \text{ m}^3)}{(300 \text{ K})(8.314 \text{ Pa m}^3/\text{mol K})} = 20.0 \text{ mol} \quad (5)$$

$$W = (20.0 \text{ mol})(8.314 \text{ Pa m}^3/\text{mol K})(300 \text{ K}) \ln(0.2/0.1) = 34.57 \text{ kJ} \quad (6)$$

1.2 Heat

- **Heat (Q):** The part of the total energy flow across a system boundary that is caused by a temperature difference between the system and its surroundings. Heat, like work, is a *path function*.

1.3 Kinetic Energy

- **Kinetic energy (KE):** The energy a system possesses because of a velocity difference between it and its surroundings at rest.

$$KE = \frac{1}{2}mv^2 \quad (7)$$

where m is the mass of the object and v is the object's velocity relative to the reference state.

1.3.1 Example: Calculation of Kinetic Energy

Water is pumped from a storage tank into a 4.0 cm ID tube at a rate of $0.001 \text{ m}^3/\text{s}$. What is the kinetic energy of the water?

- Step 1, determine the linear velocity of the water

$$v = \dot{V}/A = \frac{0.001 \text{ m}^3/\text{s}}{\pi(0.02)^2 \text{ m}^2} = 0.795 \text{ m/s} \quad (8)$$

- Step 2, find the mass flow rate of water

$$\rho = m/V; \rho\dot{V} = \dot{m}; (1000 \text{ kg/m}^3)(0.001 \text{ m}^3/\text{s}) = 1.0 \text{ kg/s} \quad (9)$$

- Step 3, calculate the kinetic energy

$$KE = \frac{1}{2}\dot{m}v^2 = \frac{1}{2}(1.0 \text{ kg/s})(0.795 \text{ m/s})^2 = 0.316 \text{ J/s} \quad (10)$$

- check units

- $1 \text{ N} = \text{kg} \cdot \text{m/s}^2$

- $1 \text{ J} = \text{N} \cdot \text{m}$

- Therefore: $(\text{kg} \cdot \text{m/s}^2)(\text{m/s}) = \text{N} \cdot \text{m/s} = \text{J/s}$

1.4 Potential Energy

- **Potential Energy (PE):** The energy a system possesses because of forces exerted on its mass by gravitational or electromagnetic fields with respect to a reference surface.

$$PE = mgh \quad (11)$$

where h is the distance from the reference surface, m is the mass of the object and g is the acceleration due to gravity (9.807 m/s^2).

1.4.1 Example: Calculation of Potential Energy

Water is pumped from one reservoir to a second reservoir 10 m above the water level of the first. What is the increase in the potential energy of the water per kg of water moved (the increase in the specific PE of the water)?

$$PE = mgh = (9.80 \text{ m/s}^2)(10\text{m}) = 98.0 \text{ J/kg} \quad (12)$$

1.5 Internal Energy

- **Internal Energy (U):** A macroscopic measure of the molecular, atomic and subatomic energies contained within a fluid. Cannot be measured, but is instead calculated from other variables that can be measured, such as pressure, temperature and volume.
- U is a state function. From the Gibbs phase rule we know for a one component, one phase system that specifying two intensive variables will define U .
- \hat{U} is commonly defined in terms of T and \hat{V}

$$\hat{U} = f(T, \hat{V}) \quad (13)$$

- Taking the derivative yields

$$d\hat{U} = \left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}} dT + \left(\frac{\partial \hat{U}}{\partial \hat{V}}\right)_T d\hat{V} \quad (14)$$

- Note:

$$C_v = \left(\frac{\partial \hat{U}}{\partial T}\right)_V ; \left(\frac{\partial \hat{U}}{\partial \hat{V}}\right)_T \approx 0 \quad (15)$$

- Therefore, changes in \hat{U} can be calculated by integration of equation 14.

$$\hat{U}_2 - \hat{U}_1 = \int_{T_1}^{T_2} C_v dT \quad (16)$$

1.6 Enthalpy

- **Enthalpy (H):** Enthalpy, like U , is a state function and is defined:

$$H = U + pV \quad (17)$$

- for a one component, one phase system:

$$H = f(T, p) \quad (18)$$

- Taking the derivative yields:

$$d\hat{H} = \left(\frac{\partial \hat{H}}{\partial T}\right)_p dT + \left(\frac{\partial \hat{H}}{\partial p}\right)_T dp \quad (19)$$

- Note:

$$C_p = \left(\frac{\partial \hat{H}}{\partial T} \right)_p ; \left(\frac{\partial \hat{H}}{\partial p} \right)_T \approx 0 \quad (20)$$

- Therefore, changes in \hat{H} can be calculated by integration of equation 19.

$$\hat{H}_2 - \hat{H}_1 = \int_{T_1}^{T_2} C_p dT \quad (21)$$

Again, we note that the absolute values of both U and H cannot be calculated directly. Only *differences* in U or H relative to a reference state may be calculated.

2 Heat Capacities

Definitions:

- **Sensible heat:** The heat that must be transferred to raise or lower the temperature of a substance(s).

$$Q = \Delta U \quad (\text{closed system}) \quad (22)$$

$$\dot{Q} = \Delta \dot{H} \quad (\text{open system}) \quad (23)$$

- **Latent heat:** The specific enthalpy change associated with a phase transition (e.g. liquid-vapor) of a substance at constant T and P .
 - **Heat of vaporization** ($\Delta \hat{H}_v$): The specific enthalpy difference between the liquid and vapor forms of a substance at a given T and P .
 - **Heat of fusion** ($\Delta \hat{H}_m$): The specific enthalpy difference between the solid and liquid forms of a substance at a given T and P .
 - **NOTE:** Both $\Delta \hat{H}_v$ and $\Delta \hat{H}_m$ are strong functions of T , but only weak functions of P .
- Knowing the sensible heat and the latent heat, it is possible to determine the change in internal energy (ΔU , closed system), or the enthalpy (ΔH , open system).
- The determination of ΔU for a system that does not undergo a phase transition is straightforward.

$$\hat{U}_2 - \hat{U}_1 = \int_{T_1}^{T_2} C_v dT \quad (24)$$

- This equation is valid under the following conditions:
 - Exact for ideal gases
 - A good approximation for liquids and solids
 - Only valid for a non-ideal gas if $V = \text{constant}$.

- We can write a similar expression for ΔH :

$$\hat{H}_2 - \hat{H}_1 = \int_{T_1}^{T_2} C_p dT \quad (25)$$

- This equation is valid under the following conditions:

- Exact for ideal gases
- Only valid for a non-ideal gas if $P = \text{constant}$.
- For liquids or solids:

$$\hat{H}_2 - \hat{H}_1 = \hat{V}\Delta P + \int_{T_1}^{T_2} C_p dT \quad (26)$$

However, the $\hat{V}\Delta P$ term in the above equation is usually negligible compared to the second term.

- C_p and C_v are related to each other in the following way:

- For liquids and solids $C_p \approx C_v$
- Ideal gases $C_p = C_v + R$

2.1 Example of a ΔU Calculation from C_v .

1 mol of liquid cyclohexane is stored in a covered beaker at 1 atm and 20 °C. Calculate the energy input required to heat the cyclohexane to 60 °C.

- For a closed system, the energy balance becomes:

$$Q = n\Delta\hat{U} \quad (27)$$

- ΔU may be calculated from integration of 14. $C_p \approx C_v$ for liquid cyclohexane, taken from Table B.2 [kJ/(mol °C)]is:

$$C_v = 94.140 \times 10^{-3} + 49.62 \times 10^{-5}T - 31.90 \times 10^{-8}T^2 + 80.63 \times 10^{-12}T^3 \quad (28)$$

- Integration of 28 yields:

$$\begin{aligned}\Delta\hat{U} = & 94.140 \times 10^{-3}(T_2 - T_1) \\ & + \frac{49.62 \times 10^{-5}}{2}(T_2^2 - T_1^2) \\ & - \frac{31.90 \times 10^{-8}}{3}(T_2^3 - T_1^3) \\ & + \frac{80.63 \times 10^{-12}}{4}(T_2^4 - T_1^4)\end{aligned}\tag{29}$$

$$\Delta\hat{U} = 4.582 \text{ kJ/mol}\tag{30}$$

- Since $Q = n\Delta\hat{U}$, $Q = (1.0 \text{ mol})(4.582 \text{ kJ/mol}) = 4.582 \text{ kJ}$

If the fluid undergoes a change of phase (solid to liquid, liquid to vapor, etc), a more complex procedure to calculate the amount of heat required.

2.2 Hypothetical Process Paths

Suppose we wish to calculate the heat required to turn solid phenol at 25°C and 1 atm to vapor at 300 °C at 3 atm.

$$\Delta\hat{H} = \hat{H}(\text{vapor}, 300^\circ\text{C}, 1 \text{ atm}) - \hat{H}(\text{solid}, 25^\circ\text{C}, 3 \text{ atm})\tag{31}$$

- Problem - we don't know \hat{H} for each state.
- Fortunately \hat{H} is a state function, so it doesn't matter what path we take to get from point A to point B.
- $\Delta\hat{H}$ can be evaluated by constructing a convenient alternate path.

The change in the enthalpy for the process is simply the sum of the enthalpy changes for each leg of the hypothetical process path.

$$\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2 + \Delta\hat{H}_3 + \Delta\hat{H}_4 + \Delta\hat{H}_5 + \Delta\hat{H}_6\tag{32}$$

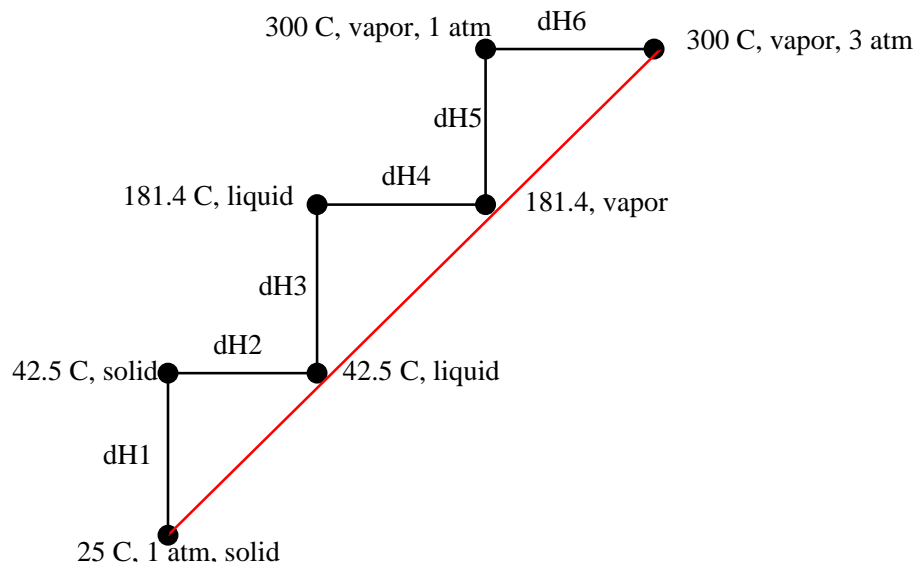


Figure 1: Hypothetical process path for the vaporization of Phenol. Red line denotes actual path, black line denotes the hypothetical process path.

2.3 Example of $\Delta\hat{H}$ Calculation

100 mol of liquid hexane at 25 ° C and 7 bar is vaporized and heated to 300 ° C at constant pressure.

Step 1, collect data

- From table B.1, $\Delta\hat{H}_v = 28.85$ kJ/mol at 69 °C.
- Find $T_{boil}(7 \text{ bar})$.

$$\log p^* = \left(6.88555 - \frac{1175.817}{T + 224.867} \right) \quad (33)$$

- Solve for T , $T_{boil} = 144$ °C.

Since $T_{boil} \neq T_{n-boil}$, we need to construct a hypothetical process path to get from the initial to final states. The change in enthalpy for this process is given by:

$$\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2 + \Delta\hat{H}_3 \quad (34)$$

Step 2, determine the $\Delta\hat{H}$ values for each leg of our hypothetical process.

$$\Delta\hat{H}_1 = \hat{V}\Delta P + \int_{25}^{69} 216.3 \times 10^{-3} dT \quad (35)$$

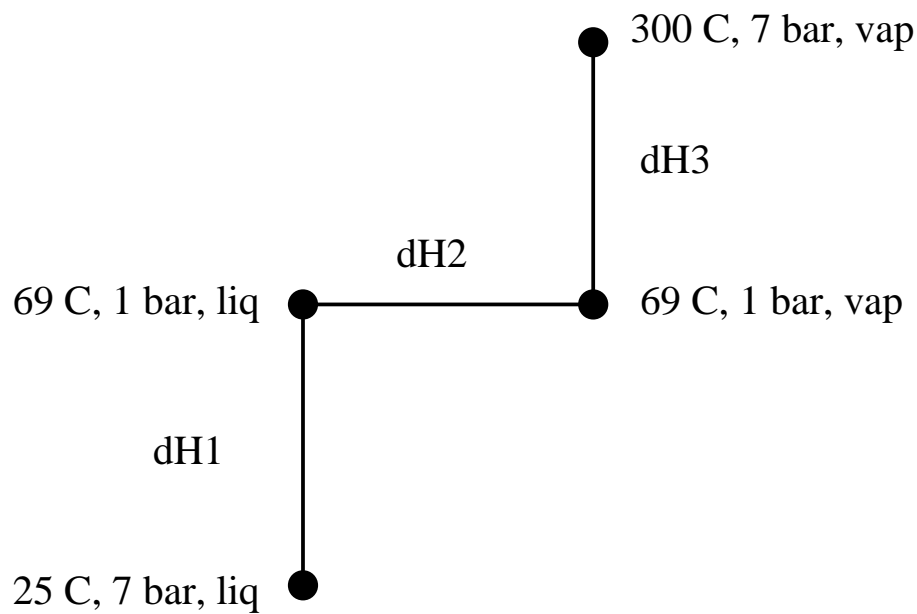


Figure 2: Hypothetical process path for the vaporization of Hexane.

- $\rho = 0.659 \text{ g/cm}^3$, $\hat{V} = 1/\rho = 1.517 \times 10^{-3} \text{ m}^3/\text{kg}$.
- $100 \text{ mol} \times 86.17 \text{ g/mol} = 8617 \text{ g}$ or $8.617 \times 10^{-3} \text{ kg}$

$$\begin{aligned} \Delta H_1 = & (8.617) \times (1.517 \times 10^{-3})(1.01325 - 7.0) \\ & \times (1.01325 \times 10^5) \\ & + 100(0.2163(69 - 25)) \end{aligned} \quad (36)$$

$$\Delta H_1 = -0.0785 \text{ kJ/h} + 951.7 \text{ kJ/h} \quad (37)$$

$$\Delta H_2 = (100)(28.85) = 2885 \text{ kJ/h} \quad (38)$$

$$\begin{aligned} \Delta H_3 = & \int_{69}^{300} 137.44 \times 10^{-3} + 40.85 \times 10^{-5}T \\ & + 23.92 \times 10^{-8}T^2 + 57.66 \times 10^{-12}T^3 \quad dT \end{aligned} \quad (39)$$

$$\Delta H_3 = 4714.85 \text{ kJ/h} \quad (40)$$

Sum values of ΔH determined above:

$$\Delta H = -0.0785 + 951.7 + 2885 + 4714.8 = 8551 \text{ kJ/h} \quad (41)$$

2.4 Estimation of Latent Heats

- Trouton's Rule:

$$\begin{aligned}\Delta\hat{H}_v &\approx 0.088T_b \text{ (non - polar fluids)} \\ &\approx 0.109T_b \text{ (water, low MW alcohols)}\end{aligned}\quad (42)$$

– where $\Delta\hat{H}_v = [\text{kJ/mol}]$ and $T_b = [\text{K}]$.

- For greater accuracy, one should use **Chen's equation**

$$\Delta\hat{H}_v = \frac{T_b[0.0331(T_b/T_c) - 0.0327 + 0.0297 \log P_c]}{1.07 - (T_b/T_c)}\quad (43)$$

– where $\Delta\hat{H}_v = [\text{kJ/mol}]$, $T_b, T_c = [\text{K}]$ and $P_c = [\text{atm}]$.

- If $\Delta\hat{H}_v$ is known for one temperature, **Watson's Correlation** can be used to predict $\Delta\hat{H}_v$ at a different temperature

$$\Delta\hat{H}_v(T_2) = \Delta\hat{H}_v(T_1) \left(\frac{T_c - T_2}{T_c - T_1} \right)^{0.38}\quad (44)$$

- The following relationships can be used to predict heats of fusion ($\Delta\hat{H}_m$) when experimental data is not available

$$\begin{aligned}\Delta\hat{H}_m &\approx 0.0092T_m \text{ (metallic elements)} \\ &\approx 0.0025T_m \text{ (inorganic compounds)} \\ &\approx 0.050T_m \text{ (organic compounds)}\end{aligned}\quad (45)$$

3 Energy Balances on Closed Systems

Remember, a *closed* system is one where there is no transfer of material across the system boundary. In this case, the general balance equation becomes:

$$\text{accumulation} = \text{input} - \text{output}\quad (46)$$

or

$$\begin{aligned}\text{final system energy} - \text{initial system energy} = \\ \text{net energy transferred to system}\end{aligned}\quad (47)$$

- initial system energy

$$U_i + KE_i + PE_i \quad (48)$$

- final system energy

$$U_f + KE_f + PE_f \quad (49)$$

- energy transferred

$$Q + W \quad (50)$$

- Combining the above equations we can write the energy balance for a closed system

$$\Delta U + \Delta KE + \Delta PE = Q + W \quad (51)$$

- **NOTES:**

- U depends almost entirely on chemical composition, temperature, and phase (gas, solid, liquid) of the system materials.
- For a closed system with no ΔT , phase changes or chemical reactions, $\Delta U \approx 0$
- If the system is not accelerating or decelerating ($v = 0$), $\Delta KE = 0$.
- If the system is not rising or falling, $\Delta PE = 0$.
- If the system and its surroundings are at the same temperature, or the system is perfectly insulated, $Q = 0$. This kind of process is referred to as **adiabatic**.
- If there are no moving parts, electrical currents or radiation at the system boundary, $W = 0$.

4 Energy Balances for Open Systems

In an *open* system, mass is allowed to cross the system boundaries. The general balance equation in this case becomes simply:

$$\text{input} = \text{output}$$

and

$$\Delta H + \Delta KE + \Delta PE = Q + W \quad (52)$$