

Heat capacities

Heat capacities are extensive properties: 100 g of water, for instance, has 100 times the heat capacity of 1 g of water (and therefore requires 100 times the energy as heat to bring about the same rise in temperature).

In general, the change in internal energy of a system is

$$dU = dq + dw$$

A system kept at constant volume can do no expansion work, so

$$dU = dq$$

We express this relation by writing $dU = dq_v$, where the subscript implies a change at constant volume. For a measurable change,

$$\Delta U = q_v$$

The heat capacity at constant volume is denoted C_v and is defined formally a

$$q_v = C_v \Delta T \quad \text{At constant volume}$$

Then

$$\Delta U = C_v \Delta T \quad \text{At constant volume}$$

The internal energy of a system increases when its temperature is raised. The increase depends on the conditions under which the heating takes place and for the present we suppose that the system has a constant volume.

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

The heat capacity of a perfect gas at constant volume depend on motional degrees of freedom A molecule has a certain number of motional degrees of

freedom, such as the ability to translate (the motion of its center of mass through space), rotate around its center of mass, or vibrate (as its bond lengths and angles change, leaving its center of mass unmoved).

1- Monatomic gas; translation only (such as He)

$$C_{V,m} = \frac{3}{2}R$$

2-linear molecule; translation and rotation only (such as CO₂, N₂)

$$C_{V,m} = \frac{5}{2}R$$

3- Nonlinear molecule; translation and rotation only (such as H₂O, CH₄)

$$C_{V,m} = 3R$$

The molar heat capacity at constant volume, $C_{V,m}$

$$C_V = n.C_{V,m}$$

Exercise// A sample consisting of 2.00 mol of perfect gas molecules, for which $C_{V,m}=5/2R$, initially at $P_1= 111$ kPa and $T_1 = 277$ K, is heated reversibly to 356 K at constant volume. Calculate the final pressure, ΔU , q , and w .

$$\Delta U = q + w$$

$$\Delta U = q_V \quad \text{at constant volume } w=0$$

$$\Delta U = q_V = nC_{V,m}\Delta T$$

$$\Delta U = (2\text{mol})\left(\frac{5}{2} \times 8.314\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\right)(356 - 277\text{K})$$

$$\Delta U = 3284\text{J} = 3.284\text{kJ} = q_V$$

Sample consisting of 3.00 mol of diatomic perfect gas molecules at 200 K is heated reversibly at constant volume to its temperature reaches 250 K. calculate q , w , ΔU .

Enthalpy

The enthalpy, H, is defined as

$$H = U + PV$$

*The change in enthalpy is equal to the energy supplied as heat at
Constant pressure (provided the system does no additional work)*

to measure enthalpy changes, however, is to use a differential scanning calorimeter (DSC). Changes in enthalpy and internal energy may also be measured by no calorimetric **methods**.

$$dH = dq_p$$

For a measurable change

$$\Delta H = q_p$$

Q) Provide the relation $\Delta H = q_p$ form the formula of first law of thermodynamics

$$dU = dq + dw$$

$$\Delta U = q_p + w$$

$$\Delta U = q_p + P\Delta V$$

$$q_p = \Delta U - P\Delta V$$

$$q_p = (U_2 - U_1) - (PV_2 - PV_1)$$

$$q_p = (U_2 + PV_2) - (U_1 + PV_1)$$

when

Since $P_2 = P_1 = P$

$$H = U + PV$$

$$\therefore q_p = H_2 - H_1 = \Delta H$$

The relation between enthalpy and internal energy of gas is:

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + nR\Delta T$$

The heat capacity at constant pressure is the **analogue** of the heat capacity at constant volume and is an extensive property.

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

The heat capacity at constant pressure is used to relate the change in enthalpy to a change in temperature. For infinitesimal changes of temperature

$$dH = C_p dT$$

For a measurable increase in temperature

$$\Delta H = C_p \Delta T$$

Because an increase in enthalpy can be equated with the energy supplied as heat at constant pressure.

$$q_P = C_p \Delta T$$

The molar heat capacity at constant volume, $C_{p,m}$

$$C_P = n.C_{p,m}$$

Then,

$$\Delta H = q_P = nC_{p,m} \Delta T$$

H.W) When 178 J of energy is supplied as heat to 1.9 mol of gas molecules at constant pressure, the temperature of the sample increases by 1.78 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

Q) When 2mol CO₂ is heated at a constant pressure of 1.25 atm, its Temperature increases from 250 K to 277 K. Given that the molar heat capacity of CO₂ (g) at constant pressure is 37.11 J K⁻¹ mol⁻¹, calculate q, ΔH, and ΔU.

$$\Delta H = q_P = nC_{p,m} \Delta T$$

$$\Delta H = (2mol)(37.11J.K^{-1}.mol^{-1})(277 - 250K)$$

$$\Delta H = 2004J$$

$$\Delta U = \Delta H - nR \Delta T$$

$$\Delta U = 2004 - ((2mol)(8.314J.K^{-1}.mol^{-1})(277 - 250K))$$

$$\Delta U = 2004 - 449J = 1555J$$

Q) When 3.0 mol O₂ is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. Given that the molar heat capacity of O₂ (g) at constant pressure is 29.4 J K⁻¹ mol⁻¹ calculate q, ΔH, and ΔU.

The relationship between C_p and C_v

In the isochoric case no work is done, so the heat fully converts into the internal energy U and the temperature increases. In the isobaric case, the system usually expands upon heating and a negative work is done on it. This leads to a smaller increase of U and thus smaller increase of the temperature. Consequently, for most materials C_p > C_v should be satisfied.

$$C_P - C_V = \left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V$$

$$H = U + PV$$

$$C_P - C_V = \left(\frac{\partial(U + PV)}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_P - C_V = \left(\frac{\partial U}{\partial T} \right)_P + \left(\frac{\partial(PV)}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V$$

when

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

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

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

Then

$$C_P - C_V = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial(PV)}{\partial T} \right)_P$$

At constant pressure

$$C_P - C_V = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

$$C_P - C_V = \left(\frac{\partial V}{\partial T} \right)_P \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right]$$

$$\left(\frac{\partial U}{\partial V} \right)_T = 0, \text{ and } \left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P}$$

$$C_P - C_V = \frac{nR}{P} [0 + P] = nR$$

It follows that the molar heat capacity of a perfect gas larger at constant pressure than at constant volume. Because the difference is highly significant and must be taken into account.

1- Monatomic gas; translation only (such as He)

$$C_{P,m} = C_{V,m} + R = \frac{3}{2}R + R = \frac{5}{2}R$$

2-linear molecule; translation and rotation only (such as O₂, N₂)

$$C_{P,m} = \frac{7}{2}R$$

3- Nonlinear molecule; translation and rotation only (such as H₂O, CH₄)

$$C_{P,m} = 4R$$

The molar heat capacity at constant pressure, $C_{V,m}$

$$C_P = n.C_{p,m}$$

EX/ When 3.0 mol O₂ (linear molecule) is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. calculate q , ΔH , and ΔU .

For linear molecule

$$C_{P,m} = \frac{7}{2}R = 29.4J.mol^{-1}.K^{-1}$$

$$C_P = n.C_{p,m} = (3mol)(29.4J.mol^{-1}.K^{-1}) = 88.2J.K^{-1}$$

$$q_P = \Delta H = C_p \Delta T = (88.2J.K^{-1})(285 - 260)K = 2205J$$

$$\Delta U = \Delta H - nR \Delta T$$

$$\Delta U = 2205J - [(3mol)(8.314J.mol^{-1}K^{-1})(285 - 260)K]$$

$$\Delta U = 1581.45J$$