

Some basic points in thermodynamics

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August 16, 2022

1 Always true

$$\Delta U = \Delta Q + \Delta W + \Delta(\text{chemical energy}) \quad (1)$$

$$= \Delta Q + \Delta W \quad \text{for closed system} \quad (2)$$

The chemical energy part is the energy associated with material moving into or out of the system, which does not happen for a closed system.

$$dU = TdS - pdV + \mu dN \quad \text{for } pV \text{ system} \quad (3)$$

$$= TdS - pdV \quad \text{for closed } pV \text{ system} \quad (4)$$

For closed system:

$$C_v \equiv \frac{dQ_v}{dT} = T \left(\frac{\partial S}{\partial T} \right)_v = \left(\frac{\partial U}{\partial T} \right)_v, \quad (5)$$

$$C_p \equiv \frac{dQ_p}{dT} = T \left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p. \quad (6)$$

$$\gamma \equiv \frac{C_p}{C_v} \quad (7)$$

2 Ideal gas

Definition: Boyle's law and $U = U(T)$.

In consequence:

$$pV = nRT, \quad \Delta U = \int C_v dT \quad (8)$$

So

$$C_p = C_v + p \left(\frac{\partial V}{\partial T} \right)_p = C_v + nR \quad (9)$$

and therefore

$$\gamma = 1 + \frac{nR}{C_v} \quad (10)$$

It is often assumed, but it is not necessarily true (for an ideal gas), that C_v is independent of temperature. If it is, then clearly so is C_p and γ . In this case, pV^γ is constant for an adiabatic process.

For a monatomic gas, one finds to very good approximation $C_v = (3/2)nR$ so then $\gamma = 5/3$.