2.8 Enthalpy and heat capacity at constant pressure

- When heating a system, typically the volume V increases. Thus often it is more simple to conduct processes at constant p to get the interrelation between the heat q and a state function.
- To analyze e.g. reaction products we can spontaneously create our system while it is thermally insulated, but in constant mechanical contact with a "volume bath" at pressure p. For example, we could create our system inside a thermally insulated chamber with one movable wall where the external pressure is fixed at p.

In both cases in addition to the internal energy U of the system, we must also perform work pV in order to make room for the expanding system. The thermodynamic discussion of such systems needs the introduction of enthalpy H:

$$\begin{aligned} H &= U + pV \\ \Rightarrow dH &= dU + d(pV) \\ &= \delta q - pdV + pdV + V dp = \delta q + V dp = \delta q_p \end{aligned} \tag{2.20}$$

so $\Delta H = q_p$ is the heat for systems under isobaric expansion.

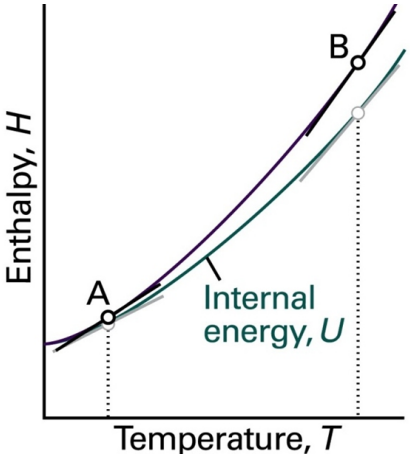

Figure 2.4: Schematic representation of enthalpy H and inner energy U vs. temperature T.

- The enthalpy is important for chemistry, it describes reactions in an open container.
- For solids and liquids: $\Delta H \approx \Delta U$.
- Completely analogous to Eq. (2.8) we find the exact differential

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \tag{2.21}$$

- Consequently the heat capacity for isobaric processes is

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT = C_p dT \tag{2.22}$$

- The perfect gas has no interactions. Thus, no change of T in the course of chemical reactions (no caloric effect) is expected, i.e. $\Delta_r T$: Change of T during a reaction ≈ 0. As a consequence

$$\begin{aligned} \Delta_r H &= \Delta_r U + \Delta_r(pV) \\ &= \Delta_r U + \Delta_r(n\,R\,T) \\ &= \Delta_r U + n\,R\Delta_r T + R\,T\Delta_r n \approx \Delta_r U + R\,T\Delta_r n \end{aligned} \tag{2.23}$$

As illustrated in Fig. 2.4 generally $C_P > C_V$ since at constant volume all of the heat added is solely used to raise the temperature.
Several experimental approaches exist with similar working principles as the adiabatic bomb calorimeter:

- Differential Scanning Calorimetry (DSC):
  Here a well defined heating rate $\alpha = \Delta T/t$ is enforced and basically the heating power is monitored.
- Differential thermal analysis (DTA) / Thermo-gravimetry (TG):
  Simultaneous measurement of Δm and ΔT.