Heat Capacities; Isobaric and Isochoric

When heat $q$ passes smoothly (reversibly) into a closed system from the surroundings, the temperature of the system increases (if there are no phase changes, e.g. liquid to vapour). The increase in temperature $\Delta T$ is related to heat $q$ using equation (a).

$$ q = C \cdot \Delta T \quad (a) $$

Heat capacity $C$ is an extensive property of a system whereas $\Delta T$ is the change in an intensive variable. For a given amount of heat, a more dramatic increase in temperature is produced the lower is the heat capacity $C$. Moreover as defined by equation (a) the heat capacity of a system is not a thermodynamic function of state because heat capacity describes a pathway accompanying a change in temperature. Hence, we define precisely the pathway taken by the system. Two important classes of heat capacities are (i) isobaric, $C_p$, and (ii) isochoric, $C_V$. Isochoric and isobaric heat capacities are related to the isobaric expansions $E_p$ and isothermal compression $K_T$ using equation (b) [1].

$$ C_V = C_p - T \cdot (E_p)^2 / K_T \quad (b) $$

Heat capacities and compressions are simply related [2].

$$ K_T / K_S = C_p / C_V \quad (c) $$

Footnotes

[1] According to a calculus operation, the dependences of entropy on temperature at constant volume and constant pressure are related.

$$ \frac{\partial S}{\partial T}_V = \left( \frac{\partial S}{\partial T}_p \right)_T - \left( \frac{\partial S}{\partial p}_T \right)_V \cdot \left( \frac{\partial V}{\partial T}_p \right)_T $$

A Maxwell equation requires that

$$ \frac{\partial S}{\partial p}_T = -\left( \frac{\partial V}{\partial T}_p \right)_T $$

Hence,

$$ \left( \frac{\partial S}{\partial T}_V \right)_V = \left( \frac{\partial S}{\partial p}_T \right)_V + \left( \frac{\partial V}{\partial T}_p \right)_T \cdot \left( \frac{\partial V}{\partial T}_p \right)_T $$
But the isobaric expansion, \( E_p = \left( \frac{\partial V}{\partial T} \right)_p \)

And the isothermal compression, \( K_T = -\left( \frac{\partial V}{\partial p} \right)_T \)

From the Gibbs–Helmholtz equation, \( C_V = T \cdot \left( \frac{\partial S}{\partial T} \right)_V \)

And \( C_p = T \cdot \left( \frac{\partial S}{\partial T} \right)_p \)

Then \( C_V = C_p - T \cdot (E_p)^2 / K_T \)

The latter equation is correct under the condition of either ‘at constant affinity A’ or ‘at constant composition’.

[2] The starting point is the following equation.

\[
\left( \frac{\partial V}{\partial p} \right)_T = -\left( \frac{\partial T}{\partial p} \right)_V \cdot \left( \frac{\partial V}{\partial T} \right)_p = -\left( \frac{\partial T}{\partial S} \right)_p \cdot \left( \frac{\partial V}{\partial p} \right)_V \cdot \left( \frac{\partial S}{\partial T} \right)_p
\]

\[
\left( \frac{\partial V}{\partial p} \right)_S = -\left( \frac{\partial S}{\partial p} \right)_V \cdot \left( \frac{\partial V}{\partial S} \right)_p = -\left( \frac{\partial T}{\partial S} \right)_p \cdot \left( \frac{\partial V}{\partial p} \right)_V \cdot \left( \frac{\partial S}{\partial T} \right)_V
\]

Then \( (\partial V / \partial p)_T / (\partial V / \partial p)_S = (\partial S / \partial T)_p / (\partial S / \partial T)_V \)

Hence, \( K_T / K_S = C_p / C_V \)