

5.6: Expressions for Heat Capacity

As explained in Sec. 3.1.5, the heat capacity of a closed system is defined as the ratio of an infinitesimal quantity of heat transferred across the boundary under specified conditions and the resulting infinitesimal temperature change: heat capacity $\stackrel{\text{def}}{=} \delta q / dT$. The heat capacities of isochoric (constant volume) and isobaric (constant pressure) processes are of particular interest.

The **heat capacity at constant volume**, C_V , is the ratio $\delta q / dT$ for a process in a closed constant-volume system with no nonexpansion work—that is, no work at all. The first law shows that under these conditions the internal energy change equals the heat: $dU = \delta q$ (Eq. 5.3.9). We can replace δq by dU and write C_V as a partial derivative:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (5.6.1)$$

(closed system)

If the closed system has more than two independent variables, additional conditions are needed to define C_V unambiguously. For instance, if the system is a gas mixture in which reaction can occur, we might specify that the system remains in reaction equilibrium as T changes at constant V .

Equation 5.6.1 does not require the condition $\delta w' = 0$, because all quantities appearing in the equation are *state* functions whose relations to one another are fixed by the nature of the system and not by the path. Thus, if heat transfer into the system at constant V causes U to increase at a certain rate with respect to T , and this rate is defined as C_V , the performance of electrical work on the system at constant V will cause the same rate of increase of U with respect to T and can equally well be used to evaluate C_V .

Note that C_V is a state function whose value depends on the state of the system—that is, on T , V , and any additional independent variables. C_V is an *extensive* property: the combination of two identical phases has twice the value of C_V that one of the phases has by itself.

For a phase containing a pure substance, the **molar heat capacity at constant volume** is defined by $C_{V,m} \stackrel{\text{def}}{=} C_V / n$. $C_{V,m}$ is an *intensive* property.

If the system is an ideal gas, its internal energy depends only on T , regardless of whether V is constant, and Eq. 5.6.1 can be simplified to

$$C_V = \frac{dU}{dT} \quad (5.6.2)$$

(closed system, ideal gas)

Thus the internal energy change of an ideal gas is given by $dU = C_V dT$, as mentioned earlier in Sec. 3.5.3.

The **heat capacity at constant pressure**, C_p , is the ratio $\delta q / dT$ for a process in a closed system with a constant, uniform pressure and with expansion work only. Under these conditions, the heat δq is equal to the enthalpy change dH (Eq. 5.3.7), and we obtain a relation analogous to Eq. 5.6.1:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (5.6.3)$$

(closed system)

C_p is an extensive state function. For a phase containing a pure substance, the **molar heat capacity at constant pressure** is $C_{p,m} = C_p / n$, an intensive property.

Since the enthalpy of a fixed amount of an ideal gas depends only on T (Prob. 5.1), we can write a relation analogous to Eq. 5.6.2:

$$C_p = \frac{dH}{dT} \quad (5.6.4)$$

(closed system, ideal gas)

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