

## 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  $\delta q$  by  $dU$  and write  $C_V$  as a partial derivative:

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

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

$$C_V = \frac{dU}{dT} \quad (5.6.2) \quad (\text{closed system, ideal gas})$$

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  $\delta q$  is equal to the enthalpy change  $dH$  (Eq. 5.3.7), and we obtain a relation analogous to Eq. 5.6.1:

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

$C_p$  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:

$$C_p = \frac{dH}{dT} \quad (5.6.4) \quad (\text{closed system, ideal gas})$$

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