

16.1: Expressions for Heat Capacity

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 $\stackrel{\text{def}}{=} dq/dT$. 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 dq/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: $dU = dq$. We can replace dq by dU and write C_V as a partial derivative:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (16.1.1)$$

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 .

16.1.1 does not require the condition $dw' = 0$ (no nonexpansion work), 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 $\overline{C}_V \stackrel{\text{def}}{=} C_V/n$. \overline{C}_V 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 16.1.1 can be simplified to

$$C_V = \frac{dU}{dT} \quad (16.1.2)$$

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

The **heat capacity at constant pressure**, C_P , is the ratio dq/dT for a process in a closed system with a constant, uniform pressure and with expansion work only. Under these conditions, the heat dq is equal to the enthalpy change dH , and we obtain a relation analogous to 16.1.1:

$$C_P = \left(\frac{\partial H}{\partial T} \right)_p \quad (16.1.3)$$

C_P is an extensive state function. For a phase containing a pure substance, the **molar heat capacity at constant pressure** is $\overline{C}_P \stackrel{\text{def}}{=} C_P/n$, an intensive property.

Since the enthalpy of a fixed amount of an ideal gas depends only on T , we can write a relation analogous to 16.1.2

$$C_p = \frac{dH}{dT} \quad (16.1.4)$$

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