

11.2: Total Differential of the Internal Energy

One Component, Closed Systems

Consider a closed system of one chemical component (e.g., a pure substance) in a single homogeneous phase. The only kind of work is expansion work, with V as the work variable. This kind of system has *two* independent variables. During a *reversible* process in this system, the heat is $dq = TdS$, the work is $dw = -PdV$, and an infinitesimal internal energy change is given by

$$dU = TdS - PdV \quad (11.2.1)$$

The appearance of the intensive variables T and P in 11.2.1 implies, of course, that the temperature and pressure are uniform throughout the system during the process. If they were not uniform, the phase would not be homogeneous and there would be more than two independent variables. The temperature and pressure are strictly uniform only if the process is reversible; it is not necessary to include “reversible” as one of the conditions of validity.

A real process approaches a reversible process in the limit of infinite slowness. For all practical purposes, therefore, we may apply 11.2.1 to a process obeying the conditions of validity and taking place so slowly that the temperature and pressure remain essentially uniform—that is, for a process in which the system stays very close to thermal and mechanical equilibrium.

Because the system under consideration has two independent variables, 11.2.1 is an expression for the total differential of U with S and V as the independent variables. In general, an expression for the differential dX of a state function X is a total differential if

1. it is a valid expression for dX consistent with the physical nature of the system and any conditions and constraints;
2. it is a sum with the same number of terms as the number of independent variables;
3. each term of the sum is a function of state functions multiplied by the differential of one of the independent variables.

Note that the work coordinate of any kind of dissipative work—work without a reversible limit—cannot appear in the expression for a total differential, because it is not a state function.

We may identify the coefficient of each term in an expression for the total differential of a state function as a partial derivative of the function. We identify the coefficients on the right side of 11.2.1 as follows:

$$T = \left(\frac{\partial U}{\partial S} \right)_V \quad (11.2.2)$$

$$-P = \left(\frac{\partial U}{\partial V} \right)_S \quad (11.2.3)$$

One Component, Open Systems

Now let us consider some of the ways a system might have more than two independent variables. Suppose the system has one phase and one substance, with expansion work only, and is *open* so that the amount N of the substance can vary. Such a system has three independent variables. Let us write the formal expression for the total differential of U with S , V , and N as the three independent variables:

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V,N} dS + \left(\frac{\partial U}{\partial V} \right)_{S,N} dV + \left(\frac{\partial U}{\partial N} \right)_{S,V} dN \quad (11.2.4)$$

We have seen above that if the system is *closed*, the partial derivatives are $(\partial U / \partial S)_V = T$ and $(\partial U / \partial V)_S = -P$. Since both of these partial derivatives are for a closed system in which N is constant, they are the same as the first two partial derivatives on the right side of 11.2.4

The quantity given by the third partial derivative, $(\partial U / \partial N)_{S,V}$, is represented by the symbol μ (mu). This quantity is an intensive state function called the **chemical potential**.

With these substitutions, 11.2.4 becomes

$$dU = TdS - PdV + \mu dN \quad (11.2.5)$$

and this is a valid expression for the total differential of U under the given conditions.

Multiple Component, Open Systems

If a system contains a mixture of M different substances in a single phase, and the system is open so that the amount of each substance can vary independently, there are $2 + M$ independent variables and the total differential of U can be written

$$dU = TdS - PdV + \sum_{i=1}^M \mu_i dN_i \quad (11.2.6)$$

The coefficient μ_i is the chemical potential of substance i . We identify it as the partial derivative $(\partial U / \partial N_i)_{S, V, N_{j \neq i}}$.

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