

## 9.3: Differentials in Thermodynamics - State and Path Functions

Distinguishing between exact and inexact differentials has very important consequences in thermodynamics. We already mentioned thermodynamic variables such as the internal energy ( $U$ ), volume, pressure, and temperature, and you probably heard about entropy ( $S$ ) and free energy ( $G$ ). All these quantities can be used to specify the state of a system. They are properties of the current state of the system, and they do not depend on the way the system got to that state. For example, if you have a system consisting of 1 mol of He at 298 K and 1 atm, the system will have a given pressure, internal energy, entropy and free energy regardless of its history. You may have compressed the system from 2 atm, or heated the gas from 273 K. All this is irrelevant to specify the pressure, entropy, etc, because all these variables are what we call **state functions**. State functions depend only on the state of the system.

Other quantities such as work ( $w$ ) and heat ( $q$ ), on the other hand, are not state functions. There is no such a thing as an amount of work or heat in a system. The amounts of heat and work that "flow" during a process connecting specified initial and final states depend on how the process is carried out. Quantities that depend on the path followed between states are called **path functions**.

How is all this connected to differentials? Quantities whose values are independent of path are called state functions, and their differentials are exact ( $dP$ ,  $dV$ ,  $dG, dT...$ ). Quantities that depend on the path followed between states are called path functions, and their differentials are inexact ( $dw$ ,  $dq$ ). As we will discuss in a moment, when we integrate an exact differential the result depends only on the final and initial points, but not on the path chosen. However, when we integrate an inexact differential, the path will have a huge influence in the result, even if we start and end at the same points. We'll come back to this shortly.

Knowing that a differential is exact will help you derive equations and prove relationships when you study thermodynamics in your advanced physical chemistry courses. For example, you will learn that all the state functions we mentioned above are related through these equations:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Here, we introduced two new state functions we haven't talked about yet: the enthalpy ( $H$ ), and the Helmholtz free energy ( $A$ ). You will learn about what they mean physically in CHM 346, but for now, just accept the fact that they are state functions, just as the entropy and the free energy. Although we didn't write it explicitly,  $T$ ,  $P$ ,  $V$  and  $S$  are not constants. When we talked about gases, we learned that  $P$ ,  $V$  and  $T$  are not independent functions. If you change two of these variables you change the third, or in other words, you cannot independently vary the pressure, volume and temperature. The equation of state tells you how the three variables depend on each other. For one mole of gas, you can write the equation of state as a function  $P = P(V, T)$ , or as a function  $V = V(T, P)$ , or as a function  $T = T(P, V)$ . In the same way, you cannot independently change the pressure, volume, temperature and entropy of a system. If you modify the pressure and temperature, the volume and entropy will change as well. To make this clear, we can re-write the equations above as:

$$dU = T(S, V)dS - P(S, V)dV \quad (9.3.1)$$

$$dH = T(S, P)dS + V(S, P)dP \quad (9.3.2)$$

$$dA = -S(T, V)dT - P(T, V)dV \quad (9.3.3)$$

$$dG = -S(T, P)dT + V(T, P)dP \quad (9.3.4)$$

Because  $U$ ,  $H$ ,  $A$  and  $G$  are all state functions, their differentials are exact. We can derive a few relationships just from this fact.

For example, we see that  $G = G(T, P)$ , and because it's total differential, by definition, is:

$$dG = \left( \frac{\partial G}{\partial T} \right)_P dT + \left( \frac{\partial G}{\partial P} \right)_T dP \quad (9.3.5)$$

from Equations 9.3.4 and 9.3.5, we rapidly conclude that

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

and

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

With minimal math, we concluded that if we change the pressure of a system at constant temperature, the rate of change of the free energy equals the volume. At this point this does not mean a lot to you, but hopefully you can appreciate how knowing that  $G$  is a state function is enough for you to derive a thermodynamic relationship! We can take this even further. Because  $G$  is a state function,  $dG$  is exact, and therefore, from Equation 9.3.4:

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad (9.3.6)$$

We just derived one of the four Maxwell relations. You can derive the other three from Equations 9.3.1-9.3.3. Notice that once again, we derived this equation from the knowledge that  $G$  is a state function. Why are these equations useful? Let's see an example using Equation 9.3.6. We can integrate this expression with  $T$  constant to get:

$$\int_{P_1}^{P_2} dS = \Delta S = - \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP \text{ (constant } T\text{)}$$

This equation tells you that the change in entropy in a system can be calculated by integrating  $\left(\frac{\partial V}{\partial T}\right)_P$  data. This is extremely powerful, as we can easily measure temperature, pressure and volume in the lab, but we don't have an instrument that directly measures entropy!

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