State Functions

A state function is a property whose value does not depend on the path taken to reach that specific value. In contrast, functions that depend on the path from two values are called path functions. Both path and state functions are often encountered in thermodynamics.

Introduction

Whenever compounds or chemical reactions are discussed, one of the first things mentioned is the state of the specific molecule or compound. "State" refers to temperature, pressure, and the amount and type of substance present. Once the state has been established, state functions can be defined. State functions are values that depend on the state of the substance, and not on how that state was reached. For example, density is a state function, because a substance's density is not affected by how the substance is obtained. Consider a quantity of H\textsubscript{2}O: it does not matter whether that H\textsubscript{2}O is obtained from the tap, from a well, or from a bottle, because as long as all three are in the same state, they have the same density. When deciding whether a certain property is a state function or not, keep this rule in mind: is this property or value affected by the path or way taken to establish it? If the answer is no, then it is a state function, but if the answer is yes, then it is not a state function.

Mathematics of State Functions

Another way to think of state functions is as integrals. Integrals depend on only three things: the function, the lower limit and the upper limit. Similarly, state functions depend on three things: the property, the initial value, and the final value. In other words, integrals illustrate how state functions depend only on the final and initial value and not on the object's history or the path taken to get from the initial to the final value.

Here is an example of the integral of enthalpy, \((H)\), where \(t_0\) represents the initial state and \(t_1\) represents the final state.

\[
\int_{t_o}^{t_1} H(t) \, dt = H(t_1)-H(t_o)
\]

This is equivalent to a familiar definition of enthalpy:
\[ \Delta H = H_{\text{final}} - H_{\text{initial}} \]

As represented by the solution to the integral, enthalpy is a state function because it only depends on the initial and final conditions, and not on the path taken to establish these conditions. Therefore, the integral of state functions can be taken using only two values: the final and initial values. On the other hand, multiple integrals and multiple limits of integration are required to take the integral of a path function. If an integral of a certain property can be calculated using just the property and its initial and final value, the property is a state function.

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**State Functions vs. Path Functions**

State functions are defined by comparing them to path functions. As stated before, a state function is a property whose value does not depend on the path taken to reach that specific function or value. In essence, if something is not a path function, it is probably a state function. To better understand state functions, first define path functions and then compare path and state functions.

Path functions are functions that depend on the path taken to reach that specific value. For example, suppose you have $1000 in your savings account. Suppose you want to deposit some money to this account. The amount you deposit is a path function because it is dependent upon the path taken to obtain that money. In other words, the amount of money you will deposit in your savings account is dependent upon the path or way taken to obtain that money. If you work as a CEO of a company for a week versus working at a gas station for a week, you would receive two different amounts of money at the end of the week. Thus, a path function is a property or value that is dependent on the path taken to establish that value.

State functions do not depend on the path taken. Using the same example, suppose you have $1000 in your savings account. You withdraw $500 from your savings account. It does not matter whether you withdraw the $500 in one shot or whether you do so at a rate of $50. At the end when you receive your monthly statement, you will notice a net withdrawal of $500 and will see your resulting balance as $500. Thus, the bank balance is a state function because it does not depend on the path or way taken to withdraw or deposit money. In the end whether you do so in one lump or in multiple transactions, your bank balance will stay the same. The figure below illustrates state functions in the form of enthalpy:
Figure 1: Two different paths from same initial and final states results in the state variables values

In this figure, two different steps are shown to form \(\text{NaCl}_\text{(s)}\).

**Path one**: The first path takes only a single step with an enthalpy of formation of -411 kJ/mol:

\[\text{Na}^+_{(g)} + \text{Cl}^-_{(g)} \rightarrow \text{NaCl}_{(s)}\]

**Path two**: The second path takes five steps to form \(\text{NaCl}_\text{(s)}\)

1. \[\text{Na}_{(s)} + \frac{1}{2} \text{Cl}_{(g)} \rightarrow \text{Na}_{(g)} + \frac{1}{2} \text{Cl}_{(g)} \text{ (1: sublimation)}\]
2. \[\text{Na}_{(g)} + \frac{1}{2} \text{Cl}_{(g)} \rightarrow \text{Na}_{(g)} + \text{Cl}_{(g)} \text{ (2: atomization)}\]
3. \[\text{Na}_{(g)} + \text{Cl}_{(g)} \rightarrow \text{Na}^+_{(g)} + \text{Cl}^-_{(g)} \text{ (3: ionization)}\]
4. \[\text{Na}^+_{(g)} + \text{Cl}^-_{(g)} \rightarrow \text{NaCl}_{(s)} \text{ (5: lattice formation)}\]

When enthalpies of all these steps are added, the enthalpy of formation of \(\text{NaCl}_\text{(s)}\) is still -411 kJ/mol. This is a perfect example of a state function: no matter which path is taken to form \(\text{NaCl}_\text{(s)}\), it results the same enthalpy of formation of -411 kJ/mol.
Table 1: Summary of differences between state and path functions

<table>
<thead>
<tr>
<th>State Function</th>
<th>Path Function</th>
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</thead>
<tbody>
<tr>
<td>Independent of path taken to establish property or value.</td>
<td>Dependent on path taken to establish property or value.</td>
</tr>
<tr>
<td>Can integrate using final and initial values.</td>
<td>Need multiple integrals and limits of integration in order to integrate.</td>
</tr>
<tr>
<td>Multiple steps result in same value.</td>
<td>Multiple steps result in different value.</td>
</tr>
<tr>
<td>Based on established state of system (temperature, pressure, amount, and identity of system).</td>
<td>Based on how state of system was established.</td>
</tr>
<tr>
<td>Normally represented by an uppercase letter.</td>
<td>Normally represented by a lowercase letter.</td>
</tr>
</tbody>
</table>

1The last comparison made is a generalization that does not necessarily hold for all aspects and calculations involved in chemistry.

**Analogy**

The main point to remember when trying to identify a state function is to determine whether the path taken to reach the function affects the value. The analogy below illustrates how to tell whether a certain property is a state function.

Every morning, millions of people must decide how to reach their offices. Some opt for taking the stairs, whereas others take the elevator. In this situation, Δy, or change in vertical position is the same whether a person take the stairs or the elevator. The distance from the office lobby to the office stays the same, irrespective of the path taken to get to your office. As a result, Δy is a state function because its value is independent of the path taken to establish its value.

In the same situation, time, or Δt, is not a state function. If someone takes the longer way of getting to the office (climbing the stairs), Δt would be greater, whereas Δt would be smaller if the elevator is taken. In this analogy, Δt is not a state function because its value is dependent on the path.

**Applications**

State functions are commonly encountered in thermodynamics; many of the equations involved with thermodynamics, such as \(\Delta U\) and \(\Delta H\), are state functions. Additionally, state functions are crucial in thermodynamics because they make calculations simple and allow one to calculate data that could otherwise only be obtained through experiments.
More specifically, state functions facilitate the use of Hess's Law, which allows the manipulation (addition, subtraction, multiply etc.) of the enthalpies of half reactions when adding multiple half reactions to form a full reaction. Hess's Law is dependent upon the fact that enthalpy is a state function. If enthalpy was not a state function, Hess's Law would be much more complicated, because the enthalpies of half reactions could not be added. Instead, several additional calculations would be required. Furthermore, state functions and Hess's Law helps one calculate the enthalpy of complex reactions without having to actually replicate these reactions in a laboratory. All that is required is to write out and sum the enthalpy of the half reactions or of the hypothetical steps leading to the chemical reaction. State functions are also encountered in many other equations involved with thermodynamics such as internal energy (\(\Delta U\)), Gibb's free energy, enthalpy, and entropy.

Problems

1. In terms of what we have discussed in this module, is going from the 1st floor of Sproul hall, to the 9th floor of Sproul hall, the same thing as going from the 1st floor of Sproul hall, to the 3rd floor, to the 5th floor, to the 9th floor of Sproul hall?
2. Is \(\Delta U\) a state function?
3. Is temperature a state function?
4. Is volume a state function? (prove with an example)
5. Although pressure and volume are state functions, why is work (which is often expressed as \(-P\Delta V\)) not a state function?

Solutions

1. Yes, because the question describes a state function. Your position is dependent only on the final and initial position, which are respectively 9th floor of Sproul and 1st floor of Sproul, and not on the path or way taken to get there.
2. The formula for \(\Delta U\) is, \(\Delta U = U_{\text{final}} - U_{\text{initial}}\). The formula of \(\Delta U\) itself proves that it is a state function because \(\Delta U\) is only dependent on \(U_{\text{final}}\) and \(U_{\text{initial}}\). In other words, \(\Delta U\) is not affected by the path taken to establish its values. This is the definition of a state function and as a result, \(\Delta U\) is a state function.
3. Temperature is a state function as it is one of the values used to define the state of an object. Furthermore, temperature is dependent on the final and initial values, not on the path taken to establish the values.
4. Volume is a state function because volume is only dependent on the final and initial values and not on the path taken to establish those values. Any example that shows this statement in function is acceptable. Here's an acceptable answer: Imagine a balloon is inflated until a certain volume. If inflated in multiple steps or in a single step, it will still attain the same volume at the end. As a result, volume is a state function because it is not dependent on the object's path or history.
5. The reason work is not a state function depends on the definition of work rather than the formula of work. The definition of work is moving an object against a force. Thus, in essence, the definition of work states that work depends on its history or path it takes because the movement of an object is dependent upon the path taken to execute that movement (i.e. running vs. walking). Therefore, if an object is dependent on its history or on the path it takes, the resulting value or property is not a state function. Even though pressure and volume are state functions, the definition of work illustrates why work is not a state function.
References


Outside Links

1. http://www.chemistry.ohio-state.edu/~woodward/ch121/ch5_law.htm

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