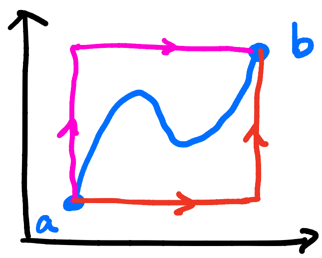
Chapter 3

Importance of State Functions

Learning Goals:

- Express state functions in terms of their variables using partial derivatives.
- Evaluate the dependence of H and U on variables such as T and V and T and P respectively.
- Quantify the difference between C_P and C_V.
- Understand the Joule-Thomson Experiment.



Partial Derivatives

Many quantities encountered in physical chemistry are functions of several variables. Consider 1 mol of an ideal gas. Then

$$P = f\begin{pmatrix} V \\ T \end{pmatrix} = \frac{RT}{V}$$

The change in P resulting from a change in V or T is proportional to the partial derivatives.

- If T is held constant in differentiation with respect to V:

$$\frac{\partial P}{\partial V} = \lim_{\Delta V \to 0} \frac{P\begin{pmatrix} V+\Delta V \\ T \end{pmatrix} - P\begin{pmatrix} V \\ T \end{pmatrix}}{\Delta V}$$

- If V is held constant in differentiation with respect to T:

$$\frac{\partial P}{\partial T} = \lim_{\Delta T \to 0} \frac{P\begin{pmatrix} V \\ T+\Delta T \end{pmatrix} - P\begin{pmatrix} V \\ T \end{pmatrix}}{\Delta T}$$

other notations:

$$\frac{\partial P}{\partial V} \Leftrightarrow P_V\begin{pmatrix} V \\ T \end{pmatrix}$$

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

all forms of partial derivatives are equivalent.

Question 3.0.1. *What is the change in P when the values of T and V both change?*

The differential dP determines the change in both V and T.

$$dP = \frac{\partial P}{\partial V} dV + \frac{\partial P}{\partial T} dT$$

Question 3.0.2. *Suppose this expression needs to be evaluated for a specific gas such as N_2. What quantities must be measured to obtain numerical values for $\frac{\partial P}{\partial T}$ and $\frac{\partial P}{\partial V}$?*

To be answered later on...

See page —

Before we tackle this, let's first learn about some mathematical properties of state functions.

3.1 Mathematical Properties of State Functions

Suppose a person is on a hill at a known altitude. How much will the altitude z change if the person moves a certain distance x to the right and y up?

$$dz = \underbrace{\frac{\partial z}{\partial x} dx}_{\text{change of } z \text{ when } x \text{ change.}} + \underbrace{\frac{\partial z}{\partial y} dy}_{\text{change of } z \text{ when } y \text{ changes.}}$$

Exact Differential

Definition 3.1.1 (Exact Differentials)**.** A differential ω of the form

$$\omega = f_1 \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} dx_1 + f_2 \;+ \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} dx_2 + \cdots + f_n \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} dx_n$$

is said to be *exact* if there exists a function f such that $\omega = df$.

where $f_1 = \frac{\partial f}{\partial x_1}$, $f_2 = \frac{\partial f}{\partial x_2}$, ..., $f_n = \frac{\partial f}{\partial x_n}$.

One can take second or higher derivatives with respect to either variable. For example, consider the ideal gas law $PV = nRT$. Compute the following partial derivatives.

- $\frac{\partial}{\partial T}\frac{\partial P}{\partial V} = \frac{\partial}{\partial T}\left(-\frac{nRT}{V^2}\right) = \boxed{-\frac{nR}{V^2} = \frac{\partial^2 P}{\partial T\,\partial V}}$
- $\frac{\partial}{\partial V}\frac{\partial P}{\partial T} = \frac{\partial}{\partial V}\left(\frac{nR}{V}\right) = \boxed{-\frac{nR}{V^2} = \frac{\partial^2 P}{\partial V\,\partial T}}$

So $\boxed{\frac{\partial^2 P}{\partial T\partial V} = \frac{\partial^2 P}{\partial V\partial T}}$.

For all state functions, the order in which the function is differentiated does not matter. The result is obtained.

One important theorem is used to determine whether a differential is exact or not. In other words, a differential is called exact if and only if it is a state function.

Theorem 3.1.2 (Clairaut's Theorem)**.** *Suppose f is defined on a region $R \subseteq \mathbb{R}^2$ that contains the point (x_0, y_0). If the functions $\frac{\partial^2 f}{\partial x \partial y}$ and $\frac{\partial^2 f}{\partial y \partial x}$ are continuous on R, then*

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

Theorem 3.1.2 is can be used to satisfy the following corollary.

Corollary 3.1.3. *Let u and v be functions of x and y, continuous, and have continuous first partial derivatives defined in a region*

$$R = \left\{ \begin{pmatrix} x \\ y \end{pmatrix} \in \mathbb{R}^2 : a < x < b, c < y < d \right\} \subseteq \mathbb{R}^2$$

$u = \frac{\partial f}{\partial x}$

Then a differential is called exact whenever

$$\boxed{\frac{\partial u}{\partial y} = \frac{\partial v}{\partial x} \Leftrightarrow \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}}$$

$v = \frac{\partial f}{\partial y}$.

must satisfy Clairaut's Theorem.

Question 3.1.4. *Determine whether $f\begin{pmatrix} x \\ y \end{pmatrix} = x^2y + x^2 + y^3$ is a state function. Justify your answer.*

Let $df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy$

$= (2xy + 2x)dx + (x^2 + 3y^2)dy$

Then $\frac{\partial^2 f}{\partial y \partial x} = 2x$ $\qquad \frac{\partial^2 f}{\partial x \partial y} = 2x$.

So $\frac{\partial^2 f}{\partial y\,\partial x} = \frac{\partial^2 f}{\partial x \partial y} \Rightarrow$ exact $\Rightarrow$ state.