

Chapter 3:: Mathematical properties of state functions

Jerry Wu (217545898)

February 13, 2023

Mathematical properties of state functions

Motivation

We want to be able to express state functions as variables and partial derivatives. From there we can model stuff like internal energy and enthalpy in terms of P , V , and P interchangeably. We can also do the following::

- Quantify the difference between C_P and C_V
- Understand the Joule-Thomson experiment.

Consider 1mol of an ideal gas::

$$P = f(V, T) = \frac{RT}{V}$$

When we assume $T \equiv \text{const}$,

$$\frac{\partial P}{\partial V}_T = \lim_{\Delta V \rightarrow 0} \frac{P(V + \Delta V, T) - P(V, T)}{\Delta V} = -\frac{RT}{V^2}$$

When we assume $V \equiv \text{const}$,

$$\frac{\partial P}{\partial T}_V = \lim_{\Delta T \rightarrow 0} \frac{P(V, T + \Delta T) - P(V, T)}{\Delta T} = \frac{R}{V}$$

So the total change in pressure (dP) can be expressed as::

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

In general,

$$dz = \frac{\partial z}{\partial x_y} dx + \frac{\partial z}{\partial y_x} dy$$

by principle of vector addition.

The cyclic rule

$$\frac{\partial P}{\partial V_T} \frac{\partial V}{\partial T_P} \frac{\partial T}{\partial P_V} = -1 \implies \frac{\partial P}{\partial T_v} = -\frac{\partial P}{\partial V_T} \frac{\partial V}{\partial T_P} = -\frac{\frac{\partial V}{\partial T_P}}{\frac{\partial V}{\partial P_T}} = \frac{\alpha}{\kappa_T}$$

The expansion coefficient for isobaric volumetric thermal is::

$$\alpha = \frac{1}{V} \frac{\partial V}{\partial T_P}$$

Isothermal compressibility::

$$\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P_T}$$

So we have that

$$dP = \frac{\alpha}{\kappa_T} dT - \frac{1}{\kappa_T V} dV$$

and the total change is expressed as::

$$\Delta P = \int_{T_i}^{T_f} \frac{\alpha}{\kappa_T} dT - \int_{V_i}^{V_f} \frac{1}{\kappa_T V} dV \approx \frac{\alpha}{\kappa_T} \Delta T - \frac{1}{\kappa_T} \ln\left(\frac{V_f}{V_i}\right)$$

Example 1

You have accidentally arrived at the end of the range of an ethanol-in-glass thermometer so that the entire volume of the glass capillary is filled. By how much will the pressure in the capillary increase if the temperature is increased by another 10.0°C ? $\alpha_{\text{glass}} = 2E - 5(^{\circ}\text{C})^{-1}$, $\alpha_{\text{ethanol}} = 11.2E - 4(^{\circ}\text{C})^{-1}$, $\kappa_{T,\text{ethanol}} = 11.0E - 5(\text{bar})^{-1}$. Will the thermometer survive the experiment?

$$\Delta P = \int_{T_i}^{T_f} \frac{\alpha_{ethanol}}{\kappa_{T,ethanol}} dT - \int_{V_i}^{V_f} \frac{1}{\kappa_{T,ethanol} V} dV \approx \frac{\alpha_{ethanol}}{\kappa_{T,ethanol}} (T_f - T_i) - \frac{1}{\kappa_{T,ethanol}} \ln\left(\frac{V_f}{V_i}\right)$$

So ΔP becomes::

$$\Delta P = \frac{\alpha_{ethanol}}{\kappa_{T,ethanol}} \ln\left(\frac{V_i(1 + \alpha_{glass}\Delta T)}{V_i}\right) = 100bar$$

So no, the glass will not survive the experiment.

Dependence of U on V and T

Internal energy on a fixed amount of substance is a function of P , V , and T .

$$U = f(P, V) = f(V, T) = f(T, P)$$

We are most interested in the one with volume and temperature.

$$dU = \frac{\partial U}{\partial T}_V dT + \frac{\partial U}{\partial V}_T dV$$

So how can numerical values for $\frac{\partial U}{\partial T}_V$ and $\frac{\partial U}{\partial V}_T$ be obtained?

$$dq - P_{external}dV = \frac{\partial U}{\partial T}_V dT + \frac{\partial U}{\partial V}_T dV$$

For an isochoric process, define the following::

$$dq_V = \frac{\partial U}{\partial T}_V dT$$

$$\frac{dq_V}{dT} = \frac{\partial U}{\partial T}_V = C_V$$

So now we can integrate for total change in internal energy.

$$\Delta U_V = \int_{T_1}^{T_2} C_V dT = n \int_{T_1}^{T_2} C_{V,m} dT$$

If $C_{V,m}$ is regarded as constant (small temperature range), we have that::

$$\Delta U_V = \int_{T_1}^{T_2} C_V dT = C_V \Delta T = nC_{V,m} \Delta T$$

$$\int_i^f dq_V = \int_i^f \frac{\partial U}{\partial T_V} dT \text{ or } q_V = \Delta U$$

Internal pressure

$\frac{\partial U}{\partial V_T}$ has units of $\frac{J}{m^3}$, which is internal pressure.

$$\frac{\partial U}{\partial V_T} = T \frac{\partial P}{\partial T_V} - P$$

Our total infinitesimal change in U can be expressed as the following::

$$dU = dU_V + dU_T = C_V dT + \left(T \frac{\partial P}{\partial T_V} - P \right) dV$$

For $T \equiv \text{const}$

$$dU = dU_T = \left(T \frac{\partial P}{\partial T_V} - P \right) dV$$

For $V \equiv \text{const}$

$$dU = dU_V = C_V dT$$

So this means that $\Sigma dU = dU_V + dU_T$ by virtue of common sense not so common.

Example 2

Evaluate $\frac{\partial U}{\partial V_T}$ for an ideal gas.

$$\frac{\partial U}{\partial V_T} = T \frac{\partial P}{\partial T_V} - P = T \left(\frac{\partial \left(\frac{nRT}{V} \right)}{\partial T} \right)_V - P = \frac{nRT}{V} - P = 0$$

This is unsurprising, since ideal gases' ΔU don't depend on ΔV . So we can conclude that U is only a function of T for ideal gases.

We can observe that

$$\Delta U_T = \int_{V_i}^{V_f} \frac{\partial U}{\partial V}_T dV \approx 0$$

to a good approximation for $g \in \mathbb{R}$ under most conditions.

So what is the magnitude of this for processes involving liquids and solids?

$$\Delta U_T^{solid,liquid} = \int_{V_1}^{V_2} \frac{\partial U}{\partial V}_T dV \approx \frac{\partial U}{\partial V}_T \Delta V \approx 0$$

Under most conditions encountered in lab, U can be regarded as a function of T alone \forall substances.

$$U(T_f, V_f) - U(T_i, V_i) = \Delta U = \int_{T_i}^{T_f} C_V dT = n \int_{T_i}^{T_f} C_{V,m} dT$$

Enthalpy as a state function

H is a function of P, V , and T .

$$H = f(P, V) = f(V, T) = f(T, P)$$

We can make $P \equiv \text{const.}$

After some work, we have that

$$\int_i^f dU = \int_i^f dq_P - \int_i^f PdV$$

$$U_f - U_i = q_P - P(V_f - V_i)$$

Phase changes

For both fusion and vaporization (solid \rightarrow liquid and liquid \rightarrow gas), $q > 0 \implies C_P \rightarrow \infty$

Derivation

Following our derivation of U and its differentials, we can do the same for H .

$$dH = \frac{\partial H}{\partial T}_P dT + \frac{\partial H}{\partial P}_T dP$$

Because $dP = 0$ at $P \equiv \text{const}$ and $dH = dq_P$, we have that

$$dq_P = \frac{\partial H}{\partial T}_P dT$$

and the heat capacity at $P \equiv \text{const}$ is defined as::

$$C_P = \frac{dq_P}{dT} = \frac{\partial H}{\partial T}_P$$

C_P is determined by measuring the heat flow dq at constant P with the resulting temperature change dT in the limit in which dT and dq approach zero:

$$C_P = \lim_{dT \rightarrow 0} \frac{dq}{dT}_P$$

For a process where $P \equiv \text{const}$ assuming no phase changes or reactions, we have that

$$\Delta H_P = \int_{T_i}^{T_f} C_P(T) dT = n \int_{T_i}^{T_f} C_{P,m}(T) dT$$

$$\Delta H_P = C_P \Delta T = n C_{P,m} \Delta T$$

Example 3 (full solution on slide 30)

A 143.0g sample of $C(s)$ in the form of graphite is heated from $300K \rightarrow 600K$ at a constant pressure. Over this temperature range, $C_{P,m}$ has been determined to be

$$\frac{C_{P,m}}{JK^{-1}mol^{-1}} = -12.19 + 0.1126 \frac{T}{K} - (1.947E - 4) \frac{T^2}{K^2} + (1.19E - 7) \frac{T^3}{K^3} - (7.800E - 11) \frac{T^4}{K^4}$$

$$\Delta H = \frac{m}{M} \int_{T_i}^{T_f} C_{P,m}(T) dT$$

If $C_{P,m}$ at 300K is used instead, after some work, we have that $\Delta H = 30.8kJ$

Variations of enthalpy with pressure at $T \equiv \text{const}$

$$\Delta H = \int_{T_i}^{T_f} C_P(T) dT = n \int_{T_i}^{T_f} C_{P,m}(T) dT$$

Because H is only a function of T , the equation above holds $\forall g \in \mathbb{C}$ even if $\neg P \equiv \text{const}$. For an ideal gas, we know that

$$\left(\frac{\partial H}{\partial P} \right)_T = 0$$

$$\left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P \approx V(1 - T_\alpha)$$

For systems that consist of liquids and solids, $T_\alpha \ll 1 \forall T < 1000K$ and $\left(\frac{\partial H}{\partial P} \right)_T \approx V$ and $dH \approx C_P dt + V dp$.

Joule-Thomson experiment (slide 34)

$$dU = dU_V + dU_T = C_V dt + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

Assume N_2 is used in the expansion process ($P_1 > P_2$), it is found that $T_2 < T_1$; the gas is cooled as it expands. Why does this happen?

$$w = w_{\text{left}} + w_{\text{right}} = - \int_{V_1}^0 P_1 dV - \int_0^{V_2} P_2 dV = P_1 V_1 - P_2 V_2$$

Because the pipe is insulating, $q = 0$ and

$$\Delta U = w = P_1 V_1 - P_2 V_2 \implies U_2 + P_2 V_2 = U_1 + P_1 V_1 \implies U_2 + P_2 V_2 = U_1 + P_1 V_1 \implies H_2 = H_1$$

So this means that the system is **isenthalpic** (no enthalpy change)

The Joule-Thomson coefficient

The constant can be expressed in the formula

$$\mu_{J-T} = \lim_{\Delta P \rightarrow 0} \left(\frac{\Delta T}{\Delta P} \right)_H = \left(\frac{\partial T}{\partial P} \right)_H$$

$$dH = C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \implies C_P \left(\frac{\partial T}{\partial P} \right)_H + \left(\frac{\partial H}{\partial P} \right)_T = 0$$

So then,

$$\left(\frac{\partial H}{\partial P} \right)_T = -C_P \mu_{J-T}$$

Example

Using the equation::

$$\left(\frac{\partial H}{\partial P} \right)_T = \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial P} \right)_T + V$$

show that $\mu_{J-T} = 0 \forall g \in \mathbb{C}$

Pf.

$$\begin{aligned} \mu_{J-T} &= \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T = -\frac{1}{C_P} \left[\left(\frac{\partial V}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T + V \right] \\ &= -\frac{1}{C_P} \left(0 + \left(\frac{\partial V}{\partial P} \right)_T + V \right) \\ &= -\frac{1}{C_P} \left[P \left(\frac{\partial \left[\frac{nRT}{P} \right]}{\partial P} \right) + V \right] = -\frac{1}{C_P} \left[-\frac{nRT}{P} + V \right] = 0 \blacksquare \end{aligned}$$

Example 2 (slide 40)

If the Joule-Thomson coefficient for carbon dioxide, CO₂, is $0.6375 \frac{K}{atm}$, estimate the final temperature of carbon dioxide at 20 atm and 100°C that is forced through a barrier to a final pressure of 1 atm.

How are C_P and C_V related?

We can start with the differential form of the first law of thermodynamics.

$$dq = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV + P_{ext} dV$$

Assume that $P \equiv \text{const}$, so

$$dq_P = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV + P dV$$

$$\begin{aligned} C_P &= C_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P = C_V + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P \\ &= C_V + T \left(\frac{\partial P}{\partial V} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \end{aligned}$$

Applying the cyclic rule along with the isobaric volumetric thermal expansion coefficient and isothermal compressibility, we have that

$$C_P = C_V - T \frac{\left(\frac{\partial V}{\partial T} \right)_P^2}{\left(\frac{\partial V}{\partial P} \right)_T}$$

Applying our α and κ rules, we can conclude

$$C_P = C_V + TV \frac{\alpha^2}{\kappa_T} \text{ or } C_{P,m} = C_{V,m} + TV_m \frac{\alpha^2}{\kappa_T}$$

What can we conclude from this? Well, $\forall g \in \mathbb{C} \wedge g \in \mathbb{R}$, we can say

$$\alpha > 0, \kappa_T > 0 \implies C_P - C_V = nR$$

For solids and liquids, $C_P \approx C_V$.