Chapter 3:: Mathematical properties of state functions

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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 interchangably. 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 $T \equiv const$,

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

When we assume $V \equiv const$,

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

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::

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

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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 $10.0°C$? $\alpha_{glass} = 2E - 5(°C)^{-1}$, $\alpha_{ethanol} = 11.2E - 4(°C)^{-1}$, $\kappa_{T,ethanol} = 11.0E - 5(bar)^{-1}$. Will the thermometer survive the experiment?

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

So ΔP becomes::

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

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::

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

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

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::

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

$$\int_i^f dq_V = \int_i^f \frac{\partial U}{\partial T}\bigg|_V dT \, or \, q_V = \Delta U$$

Internal pressure

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

$$\frac{\partial U}{\partial V}\bigg|_T = T \frac{\partial P}{\partial T}\bigg|_V - P$$

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

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

For $T \equiv const$

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

For $V \equiv const$

$$dU = dU_V = C_V dT$$

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

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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 $P \equiv const.$

After some work, we have that

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

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

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Phase chages

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

Derivation

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

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

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

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

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

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

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:

$$C_P = \lim_{dT \to 0} \frac{dq}{dT}\bigg|_P$$

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

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

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

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 $\Delta H = 30.8kJ$