

Thurs: Seminar

Fri: HW by Spm

Tues: Read 3.1 → 3.3, 3.5
HW 12 due

Thurs: Exam 1 - all thermo Ch 1, 2
HW 1 → 12

Thermodynamic Identities

The mathematical structure of thermodynamics results in a variety of mathematical identities that connect various measurable quantities. Consider, as an example, heat capacities. These emanate from the infinitesimal version of the first law

$$dE = \delta Q - PdV \Rightarrow \delta Q = dE + PdV$$

Then we express the right hand side of this in terms of either i) T, V or ii) T, P and set the coefficient of dT equal to the associated heat capacity. So

$$\begin{aligned} \text{i)} \quad \delta Q &= \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV \Rightarrow \delta Q = \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV \\ &\Rightarrow C_V = \left(\frac{\partial E}{\partial T}\right)_V \end{aligned}$$

$$\begin{aligned} \text{ii)} \quad \delta Q &= \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right] \\ &= \underbrace{\left\{ \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] \right\}}_{C_P} dT + \{ \dots \} dP \end{aligned}$$

This gives:

$$C_p = \left(\frac{\partial E}{\partial V}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

$$\Rightarrow C_p = C_v + \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

This type of relationship is common in thermodynamics and in this case can be used to extract $\left(\frac{\partial E}{\partial T}\right)_V$ and $\left(\frac{\partial E}{\partial V}\right)_T$ and eventually construct the energy as a function of T, V : $E = E(T, V)$.

We suspect that it might be possible to determine $\left(\frac{\partial E}{\partial V}\right)_T$ if the equation of state of the gas is known and to thereby relate C_p to C_v and quantities derived from the equation of state. To do so we will use:

- 1) the fundamental thermodynamic identity
- 2) calculus of differentials involving multiple variables.

Calculus rule

Suppose that $f = f(x, y)$. Then suppose we are given

$$df = A dx + B dy$$

for some functions A, B . By calculus it follows that

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \quad \Rightarrow \quad A = \left(\frac{\partial f}{\partial x}\right)_y \quad B = \left(\frac{\partial f}{\partial y}\right)_x$$

and also

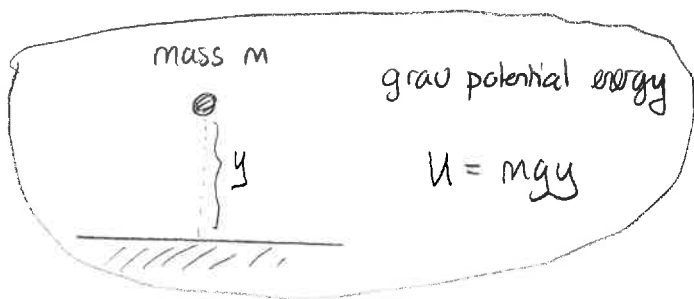
$$\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x}\right)_y = \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y}\right)_x \quad \Rightarrow \quad \left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y$$

Thus we have:

$$\begin{aligned} \text{If } f &= f(x,y) \text{ and} \\ df &= A dx + B dy \\ \text{then:} \\ 1) \quad A &= \left(\frac{\partial f}{\partial x}\right)_y \text{ and } B = \left(\frac{\partial f}{\partial y}\right)_x \\ 2) \quad \left(\frac{\partial A}{\partial y}\right)_x &= \left(\frac{\partial B}{\partial x}\right)_y \end{aligned}$$

Thermodynamic potentials

In general a potential is a function such that by suitable differentiation yields physically useful quantities. Recall that in classical physics a uniform gravitational field can be described via a potential and forces can be determined via differentiation:



Force components

$$F_x = -\frac{\partial U}{\partial x} = 0$$
$$F_y = -\frac{\partial U}{\partial y} = -mg$$

magnitude mg

A similar situation exists in thermodynamics although there are many different potentials. These include:

energy E

enthalpy $H = E + PV$

Gibbs free energy

entropy S

Helmholtz free energy $F = E - TS$

$G = E - TS + PV = H - TS$

The crucial connecting feature is the fundamental thermodynamic identity (ignoring particle number as a variable)

$$dE = TdS - PdV$$

or

$$dS = \frac{1}{T} dE + \frac{P}{T} dV$$

This means that if we obtain entropy as a function of E, V it can also serve as a potential since

$$\begin{aligned} \frac{1}{T} &= \left(\frac{\partial S}{\partial E} \right)_V && \text{potential} \\ \frac{P}{T} &= \left(\frac{\partial S}{\partial V} \right)_E && \text{derivatives} \end{aligned}$$

These potentials generate pressure + temperature expressions

Example: Suppose that

$$S(E, V) = \alpha E^{3/4} V^{1/4}$$

where α is constant. Determine T, P as functions of E, V

Answer: $\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_V = \frac{3}{4} \alpha E^{-1/4} V^{1/4}$

$$\Rightarrow T = \frac{4}{3} \frac{1}{\alpha} E^{1/4} V^{-1/4}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_E = \alpha E^{3/4} V^{-3/4} \frac{1}{4}$$

$$\begin{aligned}
 \text{Thus } P &= \alpha E^{3/4} V^{-3/4} \frac{1}{4} T \\
 &= \cancel{\alpha} E^{3/4} V^{-3/4} \frac{1}{4} \frac{4}{3} \frac{1}{\alpha} E^{1/4} V^{-1/4} \\
 &= \frac{1}{3} E V^{-1}
 \end{aligned}$$

$$\Rightarrow PV = \frac{1}{3} E \quad \Rightarrow \quad E = 3PV$$

$$\text{Also } T = \frac{4}{3} \frac{1}{\alpha} E^{1/4} V^{-1/4} \quad \Rightarrow \quad \frac{3\alpha}{4} T = E^{1/4} V^{-1/4}$$

$$\Rightarrow E^{1/4} = \frac{3\alpha}{4} T V^{1/4}$$

$$\Rightarrow E = \left(\frac{3\alpha}{4}\right)^4 V T^4$$

We could also regard $E = E(S, V)$ as a potential.

Then

$$dE = Tds - PdV$$

$$\Rightarrow \begin{cases} T = \left(\frac{\partial E}{\partial S} \right)_V \\ P = - \left(\frac{\partial E}{\partial V} \right)_S \end{cases}$$

Annotations:
 - Red arrows point from the text "potential" to the E in both equations.
 - Red arrows point from the text "deriv" to the S in the first equation and the V in the second equation.

Now consider the second derivatives:

$$\left(\frac{\partial T}{\partial V} \right)_S = \frac{\partial}{\partial V} \left(\frac{\partial E}{\partial S} \right)_V = \frac{\partial^2 E}{\partial V \partial S}$$

$$\left(\frac{\partial P}{\partial S} \right)_V = \frac{\partial}{\partial S} \left(- \frac{\partial E}{\partial V} \right)_S = - \frac{\partial^2 E}{\partial S \partial V}$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V}$$

This is an example of a Maxwell relation and there are many such relations that can be extracted from potentials.

1 Maxwell relations from energy

- a) Consider the infinitesimal version of the first law,

$$dE = TdS - PdV$$

This regards energy as a function of S and V . We aim to express $\left(\frac{\partial E}{\partial V}\right)_T$ in terms of entropy. To do this consider energy as a function of T and V and rewrite the right side of the first law in terms dT and dV . Then show that

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P.$$

- b) Now consider the Helmholtz free energy. Use the definition $F = E - TS$ and the infinitesimal version of the first law to show that

$$dF = -SdT - PdV.$$

- c) Use the second derivative rule to generate a Maxwell identity *relation*

$$\left(\frac{\partial S}{\partial V}\right)_T = ??$$

- d) Show that

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P.$$

- e) What does this rule imply for an ideal gas?

Answer: a)
$$\begin{aligned} dE &= \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = TdS - PdV \\ &= T \left\{ \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \right\} - PdV \\ &= T \left(\frac{\partial S}{\partial T}\right)_V dT + \left[T \left(\frac{\partial S}{\partial V}\right)_T - P \right] dV \end{aligned}$$

Thus
$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial T}\right)_V - P$$

$$b) \quad F = E - TS$$

$$\Rightarrow E = F + TS$$

$$\Rightarrow dE = dF + TdS + SdT$$

The fundamental thermodynamic identity gives

$$dE = TdS - PdV$$

$$\Rightarrow TdS - PdV = dF + TdS + SdT$$

$$\Rightarrow dF = -SdT - PdV$$

$$c) \quad S = -\left(\frac{\partial F}{\partial T}\right)_V \quad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$\text{Thus } \left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 F}{\partial V \partial T} \quad \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V}$$

} equal

$$\text{So } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$d) \quad \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$e) \quad \text{Here } P = NkT/V \Rightarrow \frac{\partial P}{\partial T} = \frac{Nk}{V} = \frac{P}{T}$$

$$\Rightarrow \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{P}{T}\right) - P = 0$$

\Rightarrow For any ideal gas $\left(\frac{\partial E}{\partial V}\right)_T = 0$.

So $E = E(V, T)$ cannot depend on V for an ideal gas.

Relating heat capacities

The definition of the two heat capacities and mathematical rules from calculus give

$$C_p = C_v + \left(\frac{\partial v}{\partial T}\right)_P \left[\left(\frac{\partial E}{\partial v}\right)_T + P \right]$$

for any gas. We saw that a Maxwell identity from the fundamental identity gives that for an ideal gas

$$\left(\frac{\partial E}{\partial v}\right)_T = 0 \quad \Rightarrow \quad C_p = C_v + \left(\frac{\partial v}{\partial T}\right)_P P$$

Thus we only need the equation of state to relate the heat capacities. Is there a comparable rule for any gas?

We have seen that a Maxwell relation and the fundamental identity give

$$\left(\frac{\partial E}{\partial v}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_v - P$$

$$\Rightarrow \boxed{C_p = C_v + T \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P}$$

This is true for any gas. So now we have

Measure one of C_p or C_v by experiment

Determine equation of state by experiment $P = P(T, v)$

Obtain the other of C_p or C_v via

$$C_p = C_v + T \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P$$

2 Relating heat capacities

In general

$$c_P = c_V + T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V$$

- Use the general rule to relate the heat capacities for an ideal gas.
- Show that for any gas

$$c_P = c_V + TV \frac{\alpha^2}{\kappa}$$

where α is isobaric expansion coefficient and κ is the isothermal compressibility.

Answer: a) $P = \frac{NkT}{V} \Rightarrow \left(\frac{\partial P}{\partial T} \right)_V = \frac{Nk}{V}$

$$V = \frac{NkT}{P} \Rightarrow \left(\frac{\partial V}{\partial T} \right)_P = \frac{Nk}{P}$$

$$\Rightarrow T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V = N^2 k^2 \frac{T}{PV} = \frac{N^2 k^2 T}{NkT} = Nk$$

$$\Rightarrow c_P = c_V + Nk.$$

b) $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$

We need $\left(\frac{\partial P}{\partial T} \right)_V$ in terms of these.

$$\left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T = -1$$

$$\Rightarrow \left(\frac{\partial P}{\partial T} \right)_V = -1 / \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T$$

Then $\left(\frac{\partial T}{\partial V} \right)_P = 1 / \left(\frac{\partial V}{\partial T} \right)_P$ gives

$$\left(\frac{\partial P}{\partial T} \right)_V = - \left(\frac{\partial V}{\partial T} \right)_P / \left(\frac{\partial V}{\partial P} \right)_T$$

Thus:

$$\left(\frac{\partial p}{\partial T}\right)_V = -V\alpha / -V\kappa = \alpha / \kappa$$

So

$$T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V = T\frac{\alpha}{\kappa}V\alpha$$

$$\Rightarrow \boxed{C_p = C_v + T\frac{\alpha^2}{\kappa}}$$

This tells us that for cases where α^2/κ is very small $C_p \approx C_v$.

Note also that in order to recreate the energy function $E = E(V, T)$ we need:

