

Tues HW by Spm

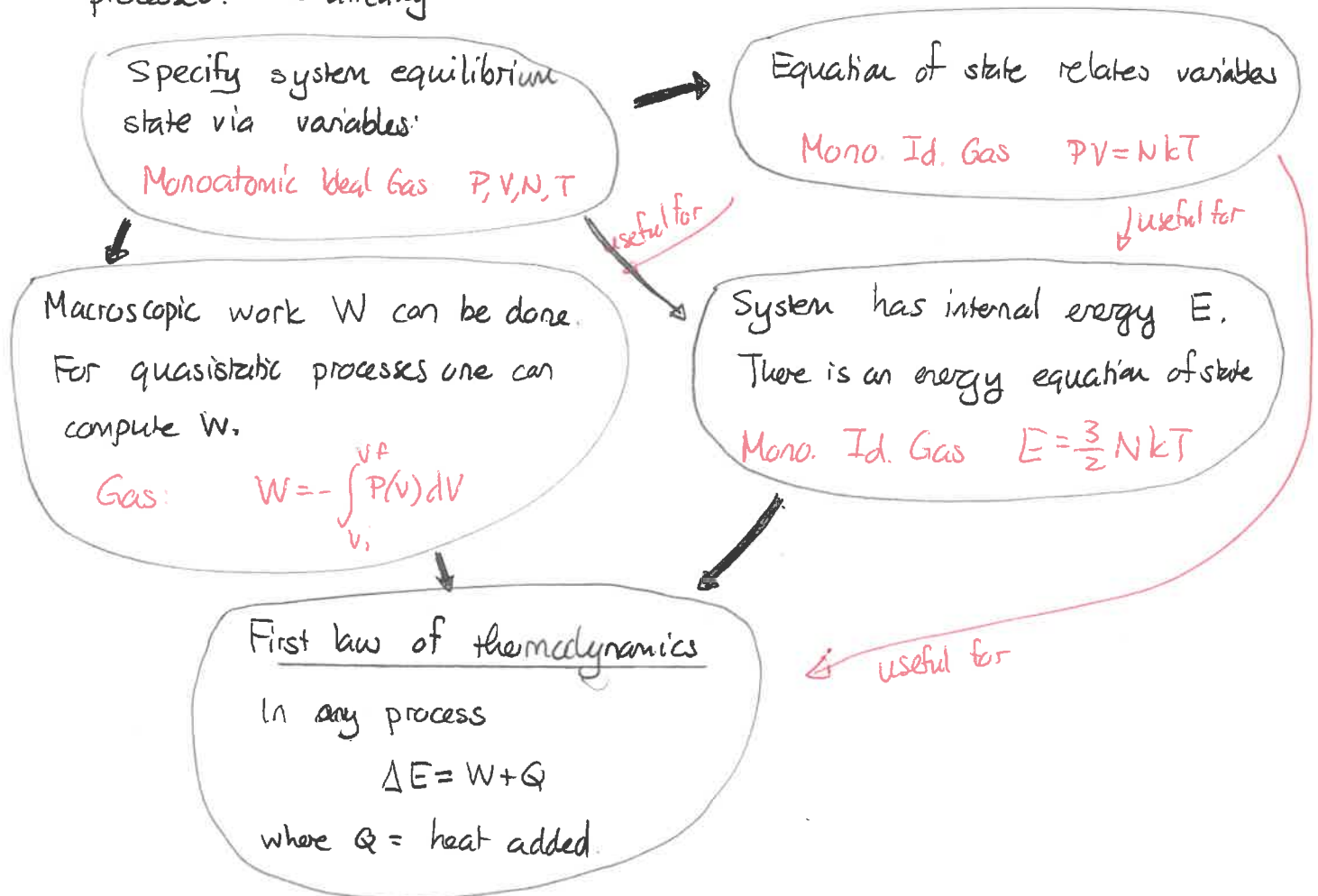
Thurs: Read

Fri: HW by Spm

Thurs: Seminar

First Law of Thermodynamics

The first law of thermodynamics accounts for energy in thermodynamic processes. Schematically



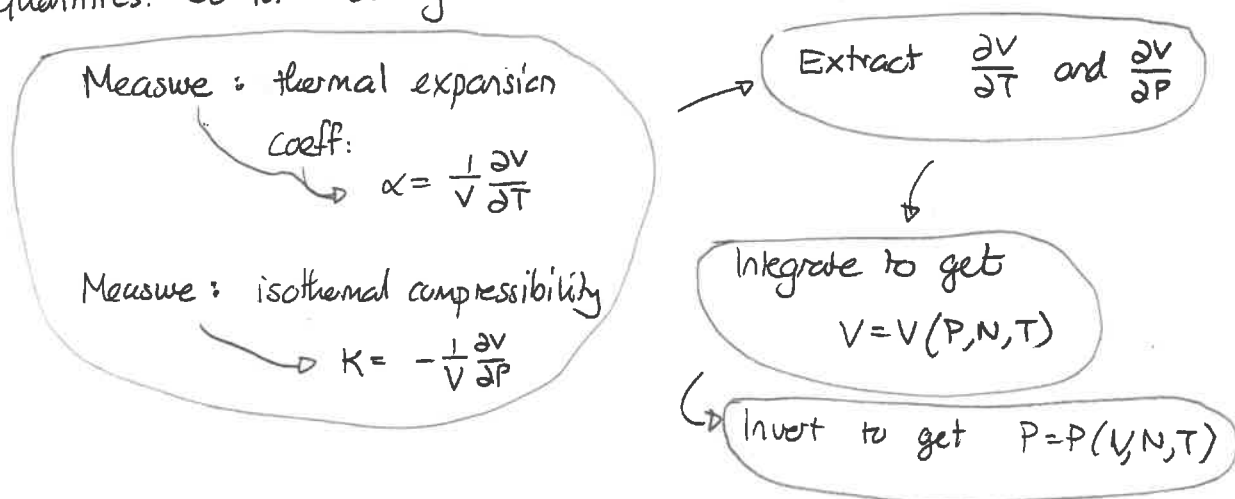
Using the first law can be facilitated via:

- 1) the energy equation of state
- 2) methods for computing heat

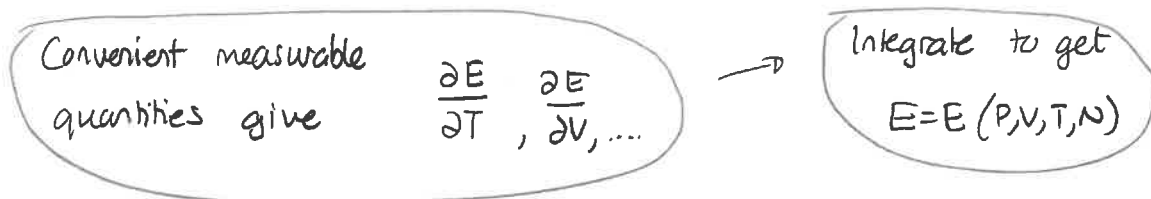
We aim to determine expressions for these

Determining equations of state

We saw that for gases the pressure equation of state can be determined via appropriate derivatives that are closely connected to measurable quantities. So for a gas



We will determine the energy equation of state via a similar procedure:



However, there is a mathematical issue to do with the number of variables available. Consider a monoatomic ideal gas. Eventually we get

$$E = \frac{3}{2} NkT \quad \text{OR} \quad E = \frac{3}{2} PV$$

Thus the result of differentiating will depend on the variables that we use to express E .

In general we have.

In the mathematics of thermodynamics, any derivative of a function will depend on the particular choice of independent variables used to express the function.

Functions of multiple variables

Consider an ideal gas and suppose that a particular function of the state of the gas is.

$$f = \alpha \frac{V^2}{T} = f(V, T)$$

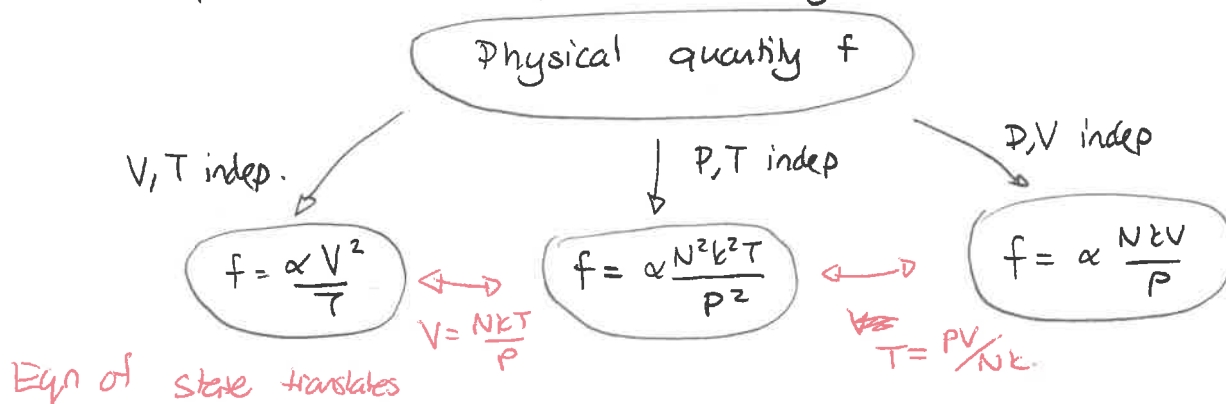
where α is a constant. It appears that f is independent of pressure.

But $PV = NkT$ gives two alternatives:

$$f = \alpha \frac{N^2 k^2 T}{P^2} = f(P, T)$$

$$f = \alpha \frac{NkV}{P} = f(P, V)$$

So there are many possible different representations of the function. They all depend on which quantities we regard as independent.



We will see that

When we differentiate any function of the state, the result will depend on which variables are regarded as independent

1 Differentiating functions of multiple variables.

Consider an ideal gas and suppose that a quantity is described by

$$F = F(T, P) := \frac{T}{P}.$$

- Using the expression above, determine $\frac{\partial F}{\partial T}$.
- Express F in terms of T and V , i.e. $F = F(T, V)$ and use this new expression to determine $\frac{\partial F}{\partial T}$.
- Are these expressions the same or different?

Answer

a) $\frac{\partial F}{\partial T} = \frac{1}{P}$

b) $F = \frac{T}{NkT/V} = \frac{V}{Nk} \Rightarrow \frac{\partial F}{\partial T} = 0$

c) No

We see that when differentiating we need to state the independent variables used to describe the function. So we could have have

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

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

We would then modify the notation for derivatives according to:

Consider P, T independent \rightsquigarrow express f in terms of P, T \rightsquigarrow differentiate w.r.t T $\rightarrow \left(\frac{\partial f}{\partial T}\right)_P$

Consider V, T independent \rightsquigarrow express f in terms of V, T \rightsquigarrow differentiate w.r.t T $\rightarrow \left(\frac{\partial f}{\partial T}\right)_V$

Mathematically the procedure is:

Decide which variables are independent:

x, y, z, \dots

→

Express f in terms of the independent variables

$$f = f(x, y, z, \dots)$$

Compute derivative and label as.

$$\left(\frac{\partial f}{\partial x} \right)_{y, z, \dots}$$

↑ ↑ ↑

lists all independent variables

In the previous exercise we computed

$$\left(\frac{\partial f}{\partial T} \right)_P \quad \text{and} \quad \left(\frac{\partial f}{\partial T} \right)_V$$

↓ ↓
~~P, T indep~~
P, T indep

↓ ↓
V, T indep.

The two results were different but as long as we label them, there will be no ambiguity. We then also need to ensure that we use them appropriately

Energy equation of state

One approach to determine the energy equation of state is:

Consider N fixed
Assume V, T independent

→

Find $\left(\frac{\partial E}{\partial T} \right)_V$ AND $\left(\frac{\partial E}{\partial V} \right)_T$

and integrate to get $E = E(T, V)$

2 Determining an energy equation of state from its partial derivatives

Suppose that

$$\left(\frac{\partial E}{\partial T}\right)_V = aNkV \quad \text{and} \quad \left(\frac{\partial E}{\partial V}\right)_T = aNkT + bV$$

where a and b are constants.

- Using the derivative with respect to T , determine a (partial) expression for $E(T, V)$.
- Now use the derivative with respect to V to determine a (nearly complete) expression for $E(T, V)$.

Answer:

$$a) \quad \left(\frac{\partial E}{\partial T}\right)_V = aNkV$$

$$\int dE = \int aNkV dT \quad \Rightarrow \quad E = aNkVT + g(V)$$

where g is any function of V

$$b) \quad \left(\frac{\partial E}{\partial V}\right)_T = aNkT + \frac{dg}{dV} = aNkT + bV$$

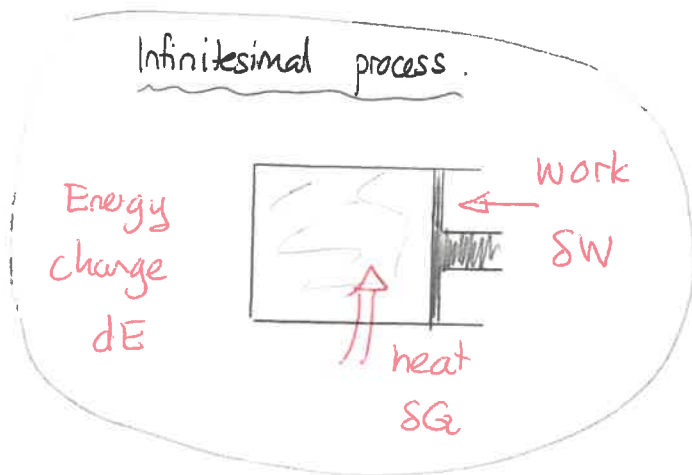
$$\Rightarrow \quad \frac{dg}{dV} = bV \quad \Rightarrow \quad g = \frac{1}{2}bV^2 + c \quad \text{constant}$$

So

$$E(V, T) = aNkTV + \frac{1}{2}bV^2 + c$$

Heat Capacities

We need a method that connects various partial derivatives of energy to physically measurable quantities. These will all involve physical processes in which the state of the gas can be made to change. We will consider infinitesimal quasistatic processes



First Law (infinitesimal version)

$$dE = \delta W + \delta Q$$

Here "d" denotes a small change in some function of state variables and "δ" denotes a small change in a quantity that depends on the process. Then this gives:

$$\begin{aligned} dV &= \text{change in volume} \\ dT &= \text{" " temp} \\ dP &= \text{" " pressure} \\ dE &= \text{" " energy} \end{aligned}$$

$$\delta Q = \text{heat added}$$

$$\delta W = \text{work done}$$

Not differentials. Depend on state and process.

All differentials of a function only depend on change in state

In all cases, for any gas,

$$\delta W = -PdV$$

⇒

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

Infinitesimal First Law for any gas

Now suppose we regard V, T as fixed. Then we can vary these independently:

$$V \rightarrow V + dV \quad \leftarrow \text{can be varied}$$

$$T \rightarrow T + dT \quad \leftarrow \text{independently}$$

These will produce a change in energy

$$E \rightarrow E + dE$$

By calculus:

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

\swarrow lists indep variables \uparrow independent


Combining with the first law:

$$\left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV = -PdV + \delta Q$$

\Rightarrow If V, T independent then

$$\delta Q = \left(\frac{\partial E}{\partial T} \right)_V dT + \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] dV$$

So we could find $\left(\frac{\partial E}{\partial T} \right)_V$ via:

Keep volume fixed
 Add heat δQ \rightarrow 
 Measure temp change dT \leftarrow thermometer

$$dV = 0$$

$$\delta Q = \left(\frac{\partial E}{\partial T} \right)_V dT$$

$$\left(\frac{\partial E}{\partial T} \right)_V = \frac{\delta Q}{dT}$$

We can then define the heat capacity of the system at constant volume via:

Suppose T, V are independent. Then in any infinitesimal process the heat added is

$$\delta Q = C_V dT + [\text{expression}] dV$$

where $C_V =$ heat capacity at constant volume.

Then the experiment indicates how to measure the coefficient in front of dT . The mathematics yields:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

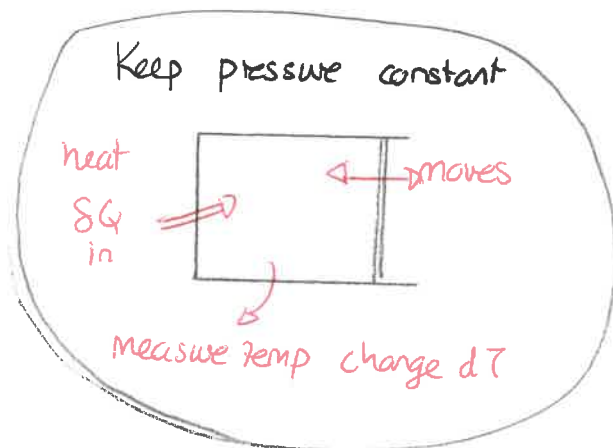
We can define a heat capacity at constant pressure via a similar procedure.

Suppose T and P are independent. Then in any infinitesimal process the heat added is

$$\delta Q = C_P dT + [\text{expression}] dP$$

and the coefficient of dT is called the heat capacity at constant pressure.

We can evaluate C_P experimentally via:



Since $dP = 0$

$$\delta Q = C_P dT$$
$$\Rightarrow C_P = \frac{\delta Q}{dT}$$

We need to relate C_P to derivatives of energy using mathematics. We aim to connect this to $\left(\frac{\partial E}{\partial T} \right)_P$??

The mathematical process involves changing variables and identifying terms in differentials. The key result is

Suppose that f is a function of two independent variables, x, y , and we have

$$df = a dx + b dy$$

Then

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

ImPLY

$$\left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = a dx + b dy$$

If x and y are independent then we can separately set $dx \neq 0$ and $dy = 0$. Then:

$$\left(\frac{\partial f}{\partial x}\right)_y = a \quad \text{and} \quad \left(\frac{\partial f}{\partial y}\right)_x = b.$$

We will see how this relates C_p to $\left(\frac{\partial E}{\partial V}\right)_T$.

3 Heat capacities

Consider any gas and note that, when using T, V as independent variables,

$$\delta Q = c_V dT + [\text{expression ...}] dV$$

serves to define c_V . Similarly when using T, P as independent variables,

$$\delta Q = c_P dT + [\text{expression ...}] dP$$

serves to define c_P .

a) Starting with

$$\delta Q = c_P dT + [\text{expression ...}] dP,$$

use the infinitesimal version of the first law to substitute for δQ . This will produce an expression on the right that involves dE and dV .

b) The resulting expressions for dE and dV must be re-expressed in terms of the two independent variables on the right side, i.e. dT and dP . To do this for dV , use a standard rule from calculus to write dV in terms of dT and dP . Repeat this for dE and substitute into the result from the previous part.

c) Since T and P are independent, the resulting expression can only be true if the coefficients of dT on both sides are equal. Use this to determine an expression for c_P .

This does not produce a result for $(\frac{\partial E}{\partial V})_T$. Doing that requires a similar strategy.

d) Equate

$$\delta Q = c_V dT + \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] dV$$

and

$$\delta Q = c_P dT + [\text{expression ...}] dP$$

Again re-express everything in terms of dT and dP . Use the result to relate c_P, c_V and $(\frac{\partial E}{\partial V})_T$.

e) Use the result from the last part to determine an expression for $(\frac{\partial E}{\partial V})_T$ in terms of heat capacities.

f) If the equation of state of the gas and the two heat capacities are known, is it possible to determine $(\frac{\partial E}{\partial V})_T$?

Answer: a) $dE = -PdV + \delta Q$

$$\delta Q = dE + PdV$$

$$\Rightarrow dE + PdV = C_p dT + [\dots] dP$$

b) $dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$

$$dE = \left(\frac{\partial E}{\partial T}\right)_P dT + \left(\frac{\partial E}{\partial P}\right)_T dP$$

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

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

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

d) $C_v dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + P \right] dV = C_p dT + [\dots] dP$

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

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

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

e) $(C_p - C_v) / \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial E}{\partial V}\right)_T + P$

f) Yes

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

← use eqn state