

Lecture 6

Thurs: Seminar

Fri: HW by Spm

Tues → Read 2.12, 2.13  
HW by Spm

Heat capacities and energy

We can determine the energy equation of state via heat capacities: For a gas

Fixed volume

Heat capacity at constant volume

$$C_v = \frac{\delta Q}{dT}$$

Fixed pressure

Heat capacity at constant pressure

$$C_p = \frac{\delta Q}{dT}$$

First law:  $dE = \delta Q - PdV$

Calculus rule:  $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

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

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

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

Give  $\left(\frac{\partial E}{\partial T}\right)_V$  and  $\left(\frac{\partial E}{\partial V}\right)_T$

## Example: Ideal gas

Taking  $V$  and  $T$  as independent we have:

1) equation of state  $PV = NkT \Rightarrow P = \frac{NkT}{V}$

or  $V = \frac{NkT}{P}$

2) heat capacities:  $C_v, C_p$

Experiments indicate that:

For an ideal gas at moderate temperatures:

$$C_p = C_v + Nk$$

and

$$C_v = f Nk$$

where  $f = \frac{3}{2}$  (monatomic),  $\frac{5}{2}$  (diatomic) ...

Then

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v \Rightarrow \left(\frac{\partial E}{\partial T}\right)_v = f Nk$$

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

Now

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{\partial}{\partial T} \left( \frac{NkT}{P} \right) = \frac{Nk}{P}$$

gives

$$C_p = C_v + \frac{Nk}{P} \left(\frac{\partial E}{\partial v}\right)_T + Nk$$

and

$$C_p = C_v + Nk \text{ implies}$$

$$C_v + Nk = C_v + Nk + \frac{Nk}{P} \left(\frac{\partial E}{\partial v}\right)_T \Rightarrow \left(\frac{\partial E}{\partial v}\right)_T = 0$$

Then

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

$$\Rightarrow E = \int fNk dT$$

$$\Rightarrow E = fNkT + g(V)$$

Now

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \Rightarrow \frac{dg}{dV} = 0 \Rightarrow g = \text{constant} = C.$$

Thus

$$E = fNkT + C$$

We set the energy scale so that at  $T=0$ ,  $E=0$ . This gives

$$E = fNkT$$

### Enthalpy

If we regard  $T$  and  $V$  as the controllable independent variables then the above scheme works well. However, it is often easier to work with  $T$  and  $P$  as independent variables. We would then aim to construct the energy  $E = E(P, T)$  from

$$\left(\frac{\partial E}{\partial T}\right)_P \quad \text{and} \quad \left(\frac{\partial E}{\partial P}\right)_T$$

We would then need to relate these to  $C_p, C_v$ . But these relationships will not be simple. Starting with the first law

$$dE = \delta Q - PdV$$

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

We get

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

Thus:

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

which gives:

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

Then we also can use:

$$\begin{aligned} \delta Q &= dE + PdV \\ &= C_V dT + [ \dots ] dV \end{aligned}$$

to give

$$\begin{aligned} \left[ \left( \frac{\partial E}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P \right] dT + \left[ \left( \frac{\partial E}{\partial P} \right)_T + P \left( \frac{\partial V}{\partial P} \right)_T \right] dP &= C_V dT + [ \dots ] dV \\ &\downarrow \\ dP &= \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV \end{aligned}$$

and thus:

$$C_V = \left( \frac{\partial E}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P + \left( \frac{\partial E}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V + P \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V$$

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

$$C_V = \left( \frac{\partial E}{\partial T} \right)_P + \left( \frac{\partial E}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V \Rightarrow C_V = C_P - P \left( \frac{\partial V}{\partial T} \right)_P + \left( \frac{\partial E}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V$$

This would eventually give  $\left( \frac{\partial E}{\partial P} \right)_T$  and  $\left( \frac{\partial E}{\partial T} \right)_P$

We can avoid some mathematical complications by considering a new quantity.

The enthalpy of a system is

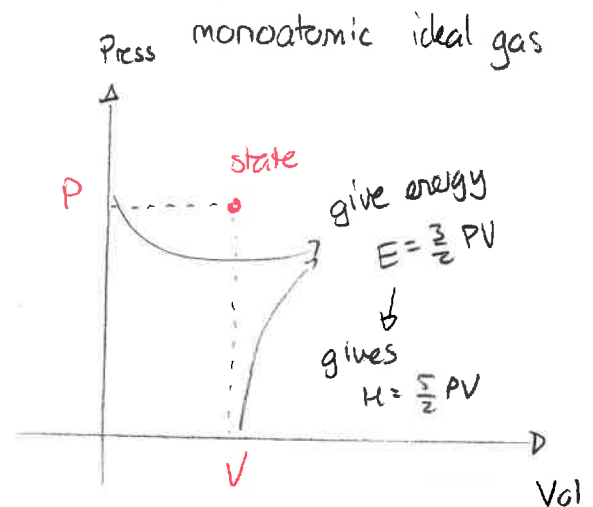
$$H = E + PV$$

This has the following features:

- 1) the enthalpy only depends on the state of the system since  $E, P, V$  only depend on the state of the system.

e.g. mono ideal gas

$$E = \frac{3}{2} PV \Rightarrow H = \frac{5}{2} PV$$



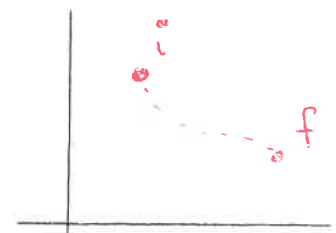
Thus

Enthalpy is a function of the state of the system:

$$H = H(N, P, T) \text{ or } H = H(N, V, T)$$

- 2) the units of enthalpy are Joules
- 3) changes in enthalpy can be computed for any process

$$\Delta H = \Delta E + \Delta PV = E_f - E_i + P_f V_f - P_i V_i$$



- 4) enthalpy is well suited to describe processes where pressure is constant.

## 1 Enthalpy

- a) Consider a process at constant volume in which the heat added is  $\delta Q$ . Determine an expression for the change in energy,  $dE$  in terms of the heat added.
- b) Consider a process at constant pressure in which the heat added is  $\delta Q$ . Determine an expression for the change in energy,  $dE$  in terms of the heat added. Is energy more suitable, for describing heat added, for processes at constant pressure or constant volume?
- c) Use the definition of enthalpy to determine an expression for  $dH$  and use the result to rewrite the infinitesimal version of the first law in terms of enthalpy.
- d) Consider a process at constant volume in which the heat added is  $\delta Q$ . Determine an expression for the change in enthalpy,  $dH$  in terms of the heat added.
- e) Consider a process at constant pressure in which the heat added is  $\delta Q$ . Determine an expression for the change in enthalpy,  $dH$  in terms of the heat added. Is enthalpy more suitable, for describing heat added, for processes at constant pressure or constant volume?
- f) Determine an expression for  $c_P$  in terms of a suitable derivative of enthalpy.
- g) Determine an expression for  $c_V$  in terms of a suitable derivative of enthalpy.
- h) Determine an expression for the enthalpy of a monoatomic ideal gas. Repeat this for a diatomic gas.

Answer:

a)  $dE = \delta Q - PdV$

$$\delta Q = dE + PdV$$

$\Rightarrow$

$$\delta Q = dE \quad \text{const volume}$$

b) Here

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

$$\Rightarrow \delta Q = dE + \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

If  $P$  is constant

$$\delta Q = dE + \left(\frac{\partial V}{\partial T}\right)_P dT \quad \text{constant pressure}$$

Energy is more suitable at constant volume processes.

c)  $dH = dE + d(PV)$

$$= dE + PdV + VdP$$

$$\Rightarrow dE = dH - PdV - VdP$$

The first law is  $dE = \delta Q - PdV$

$$\Rightarrow dH - PdV - VdP = \delta Q - PdV$$

$$\Rightarrow dH = \delta Q + VdP$$

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

$$= dH - V \left(\frac{\partial P}{\partial T}\right)_V dT - V \left(\frac{\partial P}{\partial V}\right)_T dV$$

When volume is constant,  $dV = 0 \Rightarrow$

$$\delta Q = dH - V \left(\frac{\partial P}{\partial T}\right)_V dT \quad \text{constant volume}$$

$$e) \quad \delta Q = dH - VdP$$

If pressure is constant  $dP = 0 \Rightarrow \delta Q = dH$  constant pressure

Enthalpy is more suitable when pressure is constant.

$$f) \quad dH = \delta Q + VdP$$

$$\Rightarrow \delta Q = dH - VdP$$

$$= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP - VdP$$

$$= \left(\frac{\partial H}{\partial T}\right)_P dT + [ \dots ] dP$$

$$\Rightarrow \boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

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

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

coefficient of  $dT$  when  $T, V$  are independent

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

$$h) \quad E = fNkT \quad f = 3/2 \text{ (monoatomic)}, f = 5/2 \text{ (diatomic)}$$

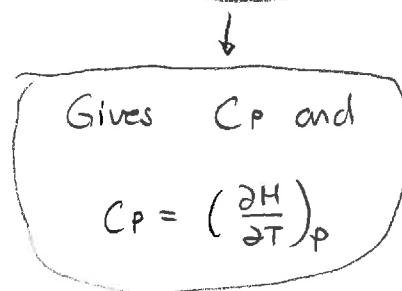
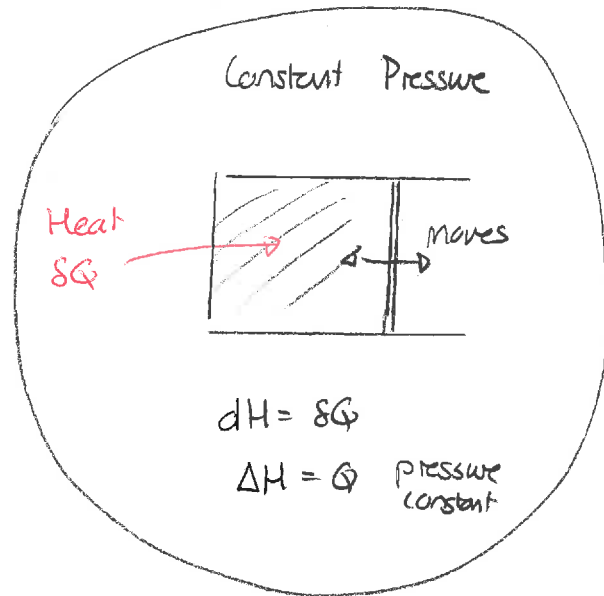
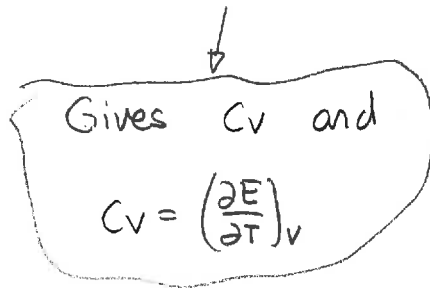
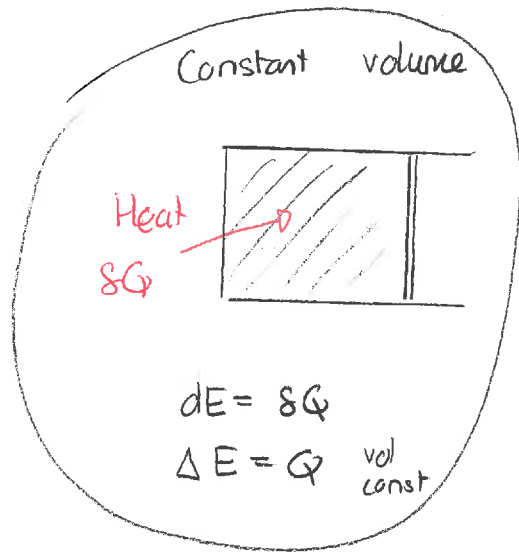
$$H = E + PV = fNkT + PV \\ = fNkT + NkT$$

$$\Rightarrow H = (f+1)NkT \quad \Rightarrow \quad H = \frac{5}{2}NkT \text{ monoatomic}$$

$$H = \frac{7}{2}NkT \text{ diatomic}$$



We could replicate the procedure using  $C_p, C_v$  to determine  $H = H(P, T)$ . We could combine processes:



Then to reconstruct say the energy function  $E = E(T, v)$  we only need

1)  $H = E + PV$

2)  $C_v = \left( \frac{\partial E}{\partial T} \right)_v$

3)  $C_p = \left( \frac{\partial H}{\partial T} \right)_p$

and we can translate from  $\left( \frac{\partial H}{\partial T} \right)_p$  to eventually get  $\left( \frac{\partial E}{\partial v} \right)_T$ .

## Enthalpy change for any process

In general

$$dH = \delta Q + VdP$$

Then for a non-infinitesimal process the total heat added is

$$Q = \int \delta Q$$

and for a quasistatic process.

$$\int dH = \int \delta Q + \int VdP$$

$$\Rightarrow \boxed{\Delta H = Q + \int VdP}$$

## Adiabatic process

An adiabatic process is one in which no heat enters or leaves the system. Two possible ways in which this occurs are:

- 1) the system is isolated from its surroundings
- 2) the process occurs too rapidly for heat to enter or leave.

We first consider a quasistatic adiabatic process and compare it to an isothermal process for a gas.

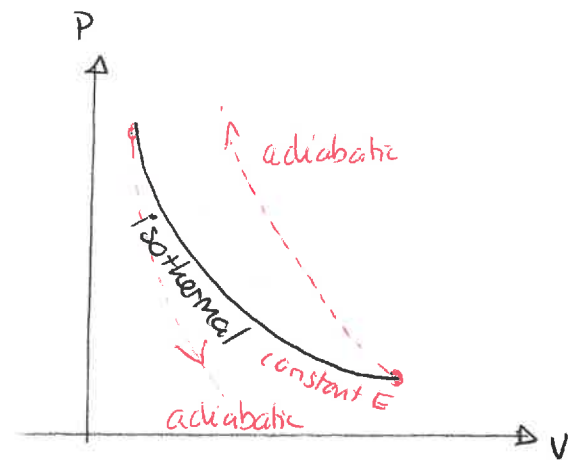
### 1) isothermal process

Here  $T$  is constant and

$$P = \frac{NkT}{V} \Rightarrow P = \underbrace{NkT}_{\text{constant}} \frac{1}{V}$$

This gives a hyperbola

Note that the energy is constant along this curve.



### 2) adiabatic process

The first law gives  $\Delta E = \overset{0}{Q} + W$   
 $\Rightarrow \Delta E = W$

For a compression  $W > 0 \Rightarrow \Delta E > 0 \Rightarrow \Delta T > 0$

For an expansion  $W < 0 \Rightarrow \Delta E < 0 \Rightarrow \Delta T < 0$

We can see that the curves for an adiabatic process are steeper than isothermal curves.

We can also have non-quasistatic adiabatic processes such as a free expansion of a gas.

Demo: Fire syringe video

## 2 Adiabatic processes for an ideal gas

Consider an ideal gas. The aim of this exercise is to determine an expression for the  $PV$  curve for an adiabatic process. There are several general facts that we need:

$$\begin{aligned}1 &= \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial T}\right)_P \\ \left(\frac{\partial T}{\partial P}\right)_V &= - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T \\ c_V &= \left(\frac{\partial E}{\partial T}\right)_V, \\ c_P &= c_V + \left(\frac{\partial V}{\partial T}\right)_P \left[ \left(\frac{\partial E}{\partial V}\right)_T + P \right] \quad \text{and}\end{aligned}$$

the internal energy as a function of  $V$  and  $T$  only depends on  $T$ .

- a) Consider an infinitesimal step in the process. Using the first law and regarding  $T$  and  $V$  as independent, show that

$$c_V dT = -PdV.$$

- b) Rewrite the left hand side in terms of  $dP$  and  $dV$  and manipulate the expression to give

$$\left[ c_V \left(\frac{\partial T}{\partial V}\right)_P + P \right] dV = -c_V \left(\frac{\partial T}{\partial P}\right)_V dP.$$

- c) Use this to show that

$$\gamma PdV = -VdP$$

where  $\gamma := c_P/c_V$ . Integrate to find the  $PV$  relationship for an adiabatic process.

Answer:

$$a) \quad dE = \delta Q - PdV$$

$$\text{But } \delta Q = 0$$

$$\Rightarrow dE = -PdV$$

Then

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

$$\Rightarrow C_V dT = -PdV$$

b) Here

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

$$\Rightarrow C_V \left(\frac{\partial T}{\partial V}\right)_P dV + C_V \left(\frac{\partial T}{\partial P}\right)_V dP = -PdV$$

$$\Rightarrow \left[ C_V \left(\frac{\partial T}{\partial V}\right)_P + P \right] dV = -C_V \left(\frac{\partial T}{\partial P}\right)_V dP$$

c) Note that  $\left(\frac{\partial T}{\partial V}\right)_P = 1/\left(\frac{\partial V}{\partial T}\right)_P$

$$\Rightarrow \left[ C_V \frac{1}{\left(\frac{\partial V}{\partial T}\right)_P} + P \right] dV = -C_V \left(\frac{\partial T}{\partial P}\right)_V dP$$

$$\Rightarrow \left[ C_V + \left(\frac{\partial V}{\partial T}\right)_P P \right] dV = -C_V \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial V}{\partial T}\right)_P dP$$

Then in general

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

Thus

$$\left[ C_V + \left( \frac{\partial V}{\partial T} \right)_P P \right] dV = C_V \left( \frac{\partial V}{\partial P} \right)_T dP$$

We could now insert the equation of state and integrate. To involve the heat capacity at constant pressure:

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

We consider an ideal gas, for which

$$\left( \frac{\partial E}{\partial V} \right)_T = 0$$

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

Thus:

$$\left[ C_V + \frac{C_P - C_V}{P} P \right] dV = C_V \left( \frac{\partial V}{\partial P} \right)_T dP$$

$$\Rightarrow C_P dV = C_V \left( \frac{\partial V}{\partial P} \right)_T dP$$

For an ideal case  $V = \frac{NkT}{P} \Rightarrow \left( \frac{\partial V}{\partial P} \right)_T = -\frac{NkT}{P^2} = -\frac{V}{P}$

$$\text{Thus } C_P dV = -C_V \frac{V}{P} dP$$

$$\Rightarrow \frac{C_P}{C_V} P dV = -V dP$$

$$\Rightarrow \gamma P dV = -V dP$$

To integrate:

$$\gamma \frac{dV}{V} = -\frac{dP}{P}$$

$$\text{Thus } \gamma \ln V = -\ln P + \text{const}$$

$$\Rightarrow e^{\gamma \ln V} = e^{-\ln P} e^{\text{const}}$$

$$\Rightarrow (e^{\ln V})^\gamma = \frac{1}{P} e^{\text{const}}$$

$$\Rightarrow V^\gamma P = \text{const}$$

So for any ideal gas:

An adiabatic process follows the curve given by

$$PV^\gamma = \text{const}$$

where  $\gamma = C_P/C_V$