JIF 314
Thermodynamics

Sidang Video 2
22 OCT 2008
9.00 pm – 10.00 pm
By
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Chapters to discuss in the first sidang video

- Chapter 1: Temperature and the zeroth law of thermodynamics

- Chapter 2: Simple thermodynamics systems

- Chapter 3: Work

Chapter 1

- System is bounded by boundary
- Surroundings – everything outside the system
- System is said to be closed if no matter is allowed to pass through the boundary; its said to be open if otherwise
- A system can be described either macroscopically of microscopically

Example of a cylinder of a car engine

- Such a system can be described by specifying macroscopically measurable quantities – called macroscopic thermodynamic coordinates, such as the amount of gas, its temperature, volume, pressure.
- Description of such a system in terms of these macroscopic coordinates is an example of macroscopic description

Macroscopic description of a system

- Macroscopic coordinates – specification of fundamental measurable properties
- Example: hydrostatic system (or sometimes referred to as PVT system, of which the state is specified by three thermodynamics coordinates, P, V, T

Microscopic description

- Involving large degree of freedom, requiring huge amount of microscopic coordinates to specify the state of a system
- Take into account internal structures and various microscopic interactions among the particles in a system
- The probability of allowed energy states by the particles are determined by the microscopic interactions among the particles
- The purpose is to determine the density of states (populations of states) of particles in each of the microscopic energy states at equilibrium
- Statistically mechanics is the branch of physics that treats such microscopic description of a thermodynamical system

The aims of thermodynamics

- Thermodynamics aims to look for general rules for understanding macroscopic temperature-dependent phenomena
- To find among the thermodynamics coordinates, general relations that are consistent with the fundamental laws of thermodynamics

Definition of a thermodynamic system

- A thermodynamic system is a system that can be described by thermodynamic coordinates
- Different thermodynamic system has its own characteristic set of coordinates
- Example of thermodynamic systems: gas, steam, mixture of vapour in car cylinder engine, slab of dielectric, ferroelectric, soap films, etc.

Thermal Equilibrium (TE)

- Consider thermal equilibrium between two system in thermal contact (via a diathermic wall):
- Say (X,Y) and (X' ,Y') are two independent thermodynamics coordinates for the two system (system A and system B)
- In TE, (X, Y) for system A and (X' ,Y') for system B become constant – i.e. they are unchanged in time.

Example of TE

- A pot of containing water (system A)
- Boundary – the wall of the pot
- The surrounding (system B)– the atmosphere out side the pot at room temperature X',
- If initially the pot contains boiling water, the temperature (X) is not constant but will keep dropping. Hence during this period, both system A and B are not in TE
- Over the time, when X temperature drops to a value equal to X', both X and X' will change no more.
- We say that the water in the pot and the surrounding have achieved TE.

Zeroth law

- The zeroth law – two system in thermal equilibrium with a third one are in thermal equilibrium with each other.
- The operational definition of the zeroth law can be read from pg. 8 – 9, Zemaksky.
- At TE, both systems must have a common temperature.

Determining temperature experimentally

- In principle, the scale of temperature is arbitrary
- Hence, we have to define the scale of temperature through a standard procedure
- First, we choose to define (arbitrarily) the triple point of water as 273.16 K.
- Triple point of water is chosen since it's experimentally easy to be reproduced
- Then the empirical temperature of a system with thermometric property X is defined as

$$\theta\left(X\right)=273.16\mathrm{K}\frac{X}{X_{\mathrm{TP}}}$$

- X is the thermodynamic coordinate of thermometer with the other coordinates fixed
- The empirical temperature of a system can calculated once measurements on X and X_{TP} is performed, where X_{TP} is the experimentally measured value of X at the water's triple point.

Measuring ideal-gas temperature with constant-volume gas thermometer

- Consider a constant-volume gas thermometer: *X* → pressure; *Y* → volume (to be fixed). See figure 1-6, pg. 17, Zemansky.
- To measure the empirical temperature of a steam, θ, we carry out the following procedure:
- (1) Measure the pressure of the gas thermometer with the bulb in thermal contact with the steam until thermal equilibrium is achieved. Obtain *X* (steam). See figure 1-5, pg. 15, for triple-point cell
- (2) Repeat procedure (1) but this time putting the bulb in thermal contact with water at its triple point. *X* (TP) is then obtained.
- (3) Calculate
  - $\theta \text{ (steam)} = 273.16 \text{ K}$ [*X*(steam) / *X*(TP)]
- (4) Take out some gas from the thermometer, and repeat (1), (2), (3) to obtain a set of {θ (steam), *X* (TP)}
- (5) Plot θ (steam) vs *X* (TP).
- (6) The ideal-gas temperature of the steam is then given by

Figure 1-5

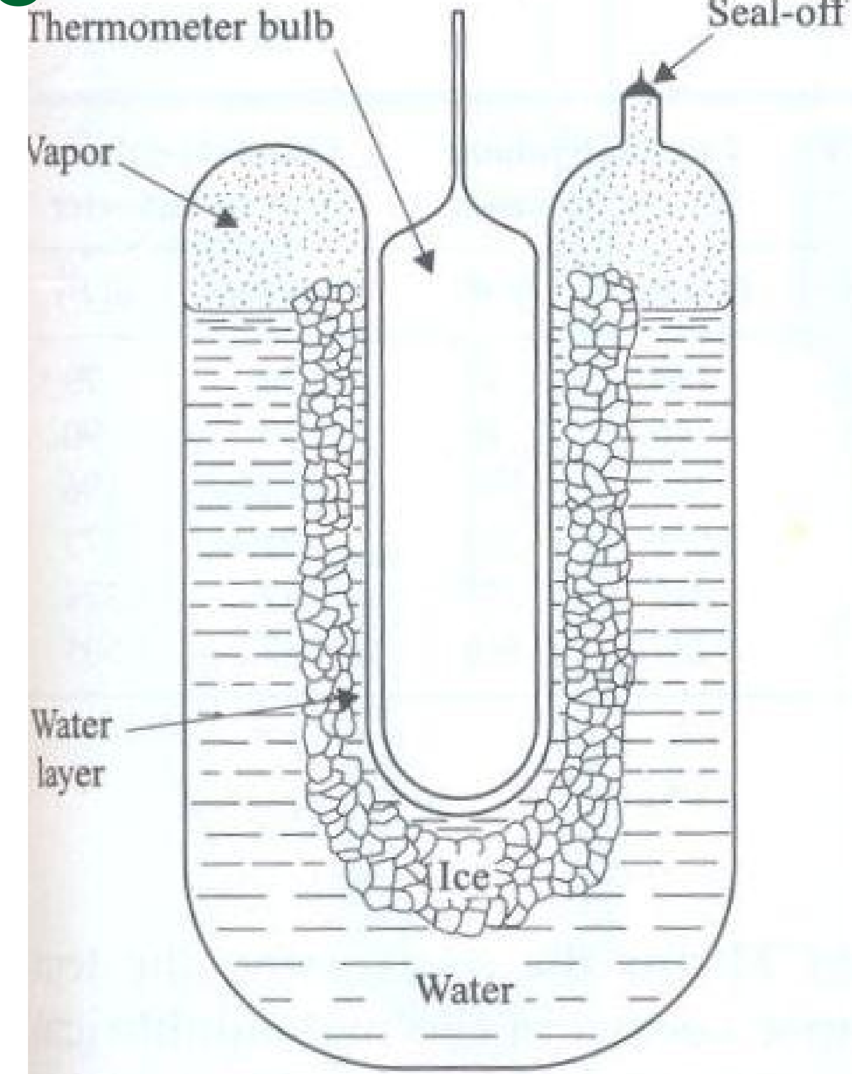


FIGURE 1-5
Triple-point cell.

Figure 1-6, Constant-volume gas thermometer

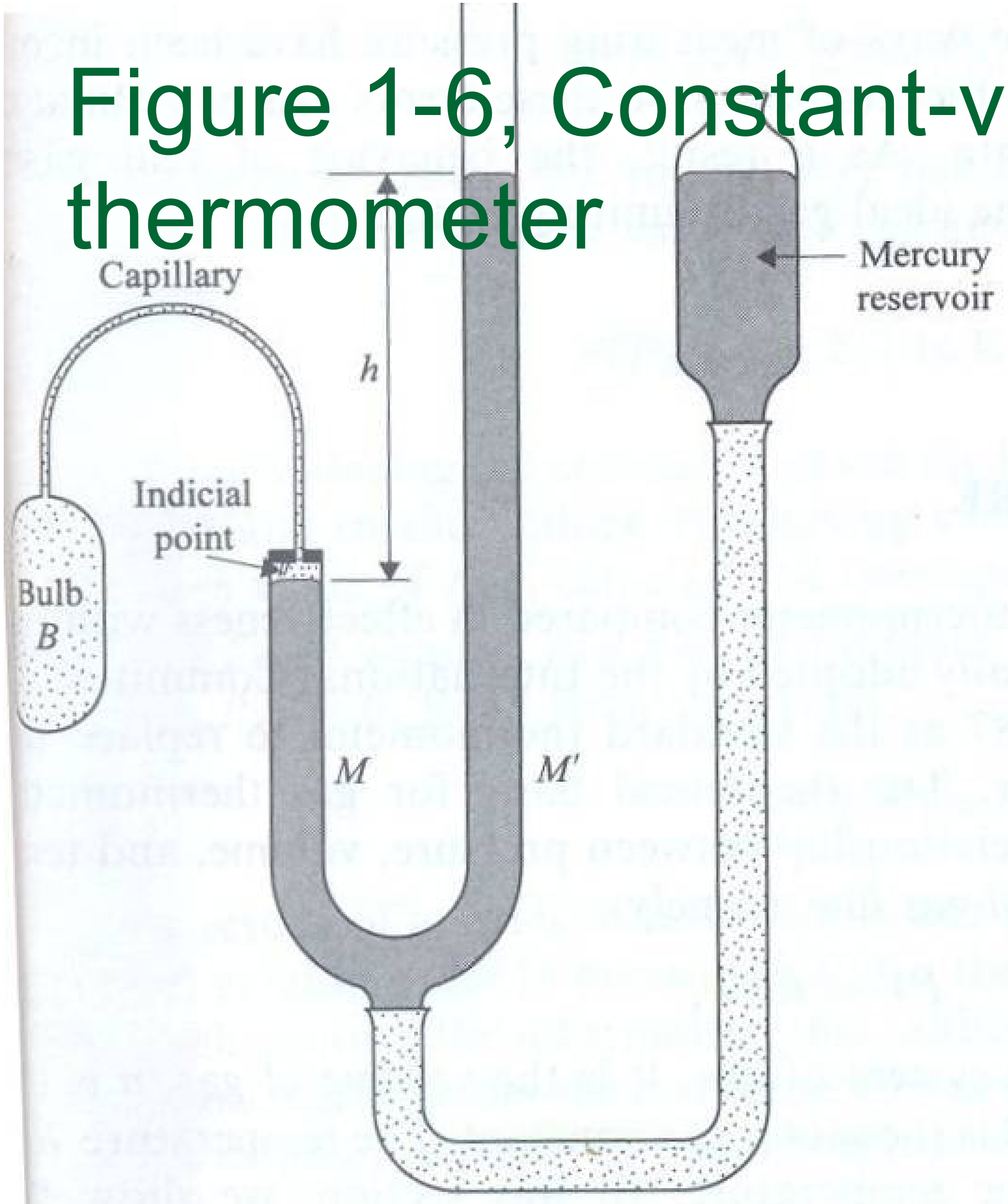


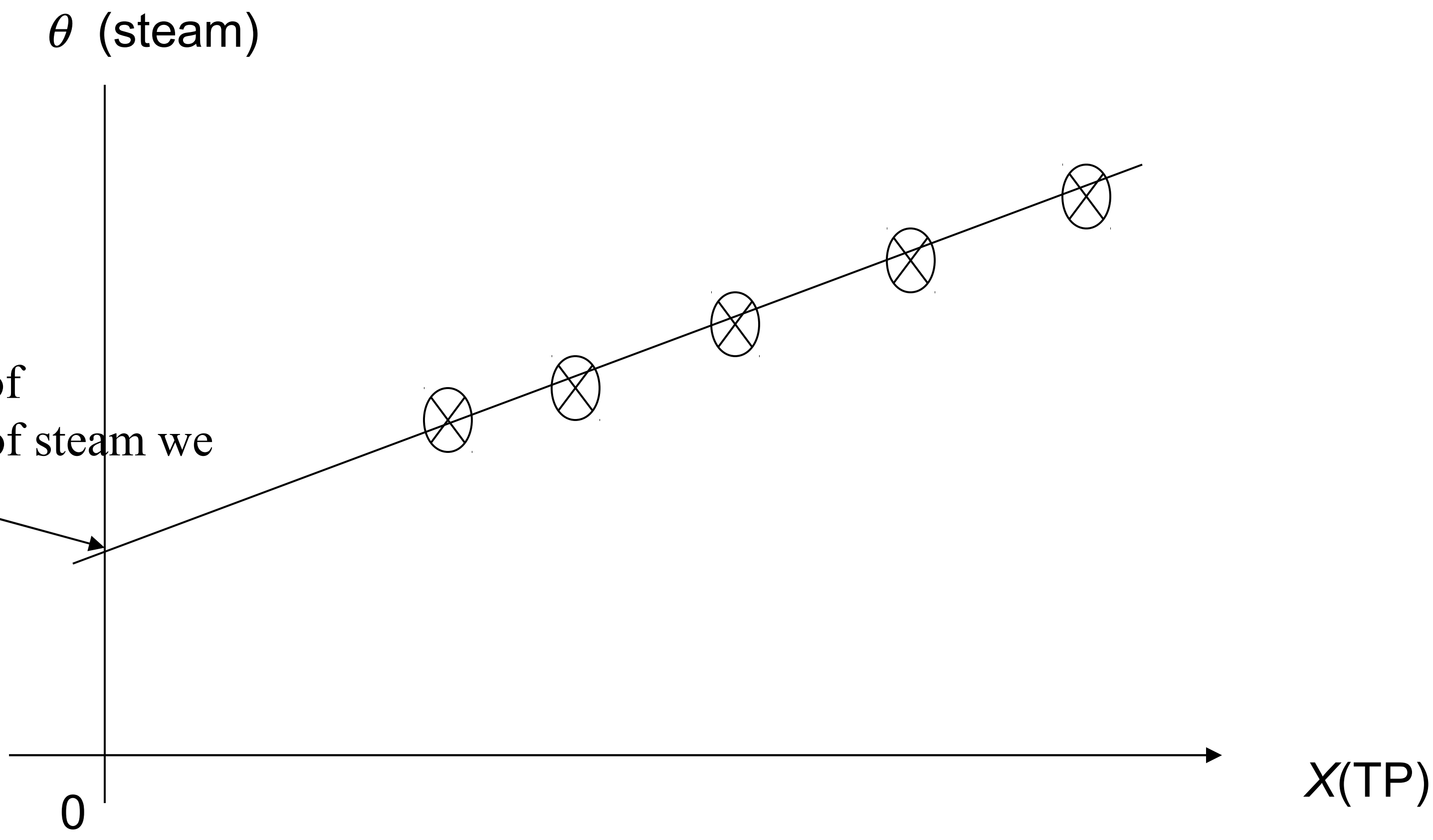
FIGURE 1-6
Simplified constant-volume gas thermometer. Mercury reservoir is raised or lowered so that the meniscus at the left always touches the indicial point. Bulb pressure equals *h* plus atmospheric pressure.

Ideal-gas temperature with constant-volume gas thermometer for steam

$$T = \lim_{X_{TP} \to 0} \theta(\text{steam})$$

$$= 273.16\ \text{K} \lim_{P_{TP} \to 0} \left(\frac{P}{P_{TP}} \right) \text{Constant } V$$

Reading of constant-volume gas thermometer of steam



θ, the value of temperature of steam we desired

Empirical temperature, Ideal gas temperature

- In the previous example, the thermodynamic ideal-gas temperature T of the steam is obtained by measuring the empirical temperature θ
- Empirical temperature, θ is a experimentally measured quantity, using gas thermometer
- The gas thermometer uses real gas that obeys ideal-gas law under low-pressure and high temperature region (that is generally coincide with daily-life temperature ranges)
- T, the ideal gas temperature, is an extrapolated quantity based on the graph of θ vs. P_{TP} .
- T is considered an theoretically defined quantity, in contrast to θ, which is an experimentally measured one.

Advantage of using the ideal-gas temperature

- The ideal gas temperature obtained in this was has the advantage of being independent of the type of gas used.
- Gas thermometer using different types of gas yields the same value for the ideal-gas temperature for the steam (which is good).
- Hence, the ideal-gas temperature scale provide us with a universal way to uniquely assign a value to the temperature of a given system.

JIF 314
Thermodynamics

Chapter 2
Simple thermodynamic systems

Thermodynamic equilibrium (TE)

- For a thermodynamic system, three types of equilibrium are possible: (a) Mechanical equilibrium, (b) Thermal equilibrium, (c) chemical equilibrium
- Thermodynamic Equilibrium (TE) – an equilibrium that has all three types of equilibrium (a) – (c).
- In a thermodynamic equilibrium, all thermo coordinates become constant in time.
- Only in a TE have the thermodynamic coordinates a valid meaning to represent the properties of the thermodynamic system.

Change of state is a result of ‘interactions’

- When a thermodynamic system suffers a change in any of the values of its thermodynamic coordinates, we say the system undergoes a change of state
- The change of state is a result caused by ‘interaction’ between the system with its surrounding
- These interaction may be in the form of e.g.
- external force acting on the system
- heat flowing in or out from the system, or
- Inflow or outflow of substances through the boundary
- work done by external agent on the system.
- etc…

Thermodynamic system in a non-equilibrium state

- In a Non-TE state, the thermo coordinates fails to account for the properties of the system of a whole since different parts of the system are thermodynamically inequivalent.
- A single value of e.g. temperature $T = 300$ K is insufficient to account for the temperature of the system as a whole since in different parts of a system in non-TE the temperature are different.

We will only study Equilibrium thermodynamics in this course

- In the thermodynamic course we shall learn here, we will deal exclusively with equilibrium thermodynamics only.
- That is, all formula that shall be mentioned in this course has a valid meaning only for system in TE.
- Non-equilibrium thermodynamics will not be discussed here. This is an advanced field of research that is beyond the scope of most undergraduate course.

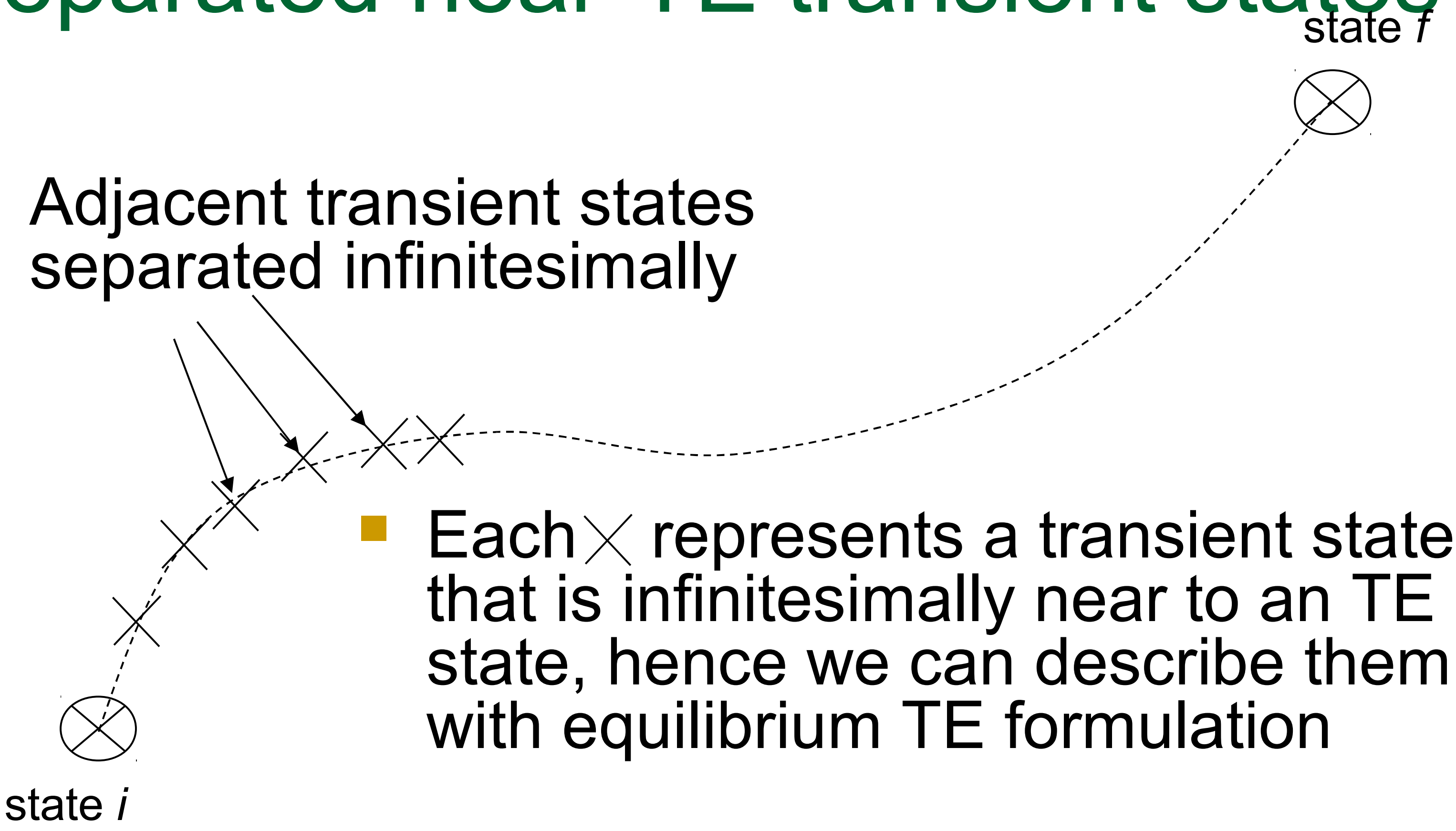
System is not in TE when state changes

- When a state of a thermo system changes during a transition of states, the system will not in an TE
- Hence, thermodynamic calculation/formulae that apply only on TE states may not apply in during the transient period of a change of states.
- So problem arises: How to calculate the thermo properties of a system undergoing a finite change of state from *i* to *f*, if the intermediate states are not in TE?
- SOLUTION: quasi-static assumption

Quasi-static process

- It is assumed that in a finite transitional process from state *i* to state *f*, the process happens in a series of intermediate transient states which are separated from one to another infinitesimally, and each of such transient states are at all times infinitesimally near a thermodynamic equilibrium.
- Such assumption is necessary so that we can treat each of the intermediate transient states as though they are in TE
- Hence this make it possible to calculate the thermo properties of the system from state *i* to state *f*, despite the thermo coordinates undergo changes.

A finite transition of state i→ f is made up of a series of infinitesimally separated near-TE transient states



- Adjacent transient states separated infinitesimally

- Each × represents a transient state that is infinitesimally near to an TE state, hence we can describe them with equilibrium TE formulation

A system with three thermo coordinates – the *xyz* system

- Consider a thermo system at TE that is described by three thermo coordinates {*x*, *y*, *z*}.
- At equilibrium, once any two of the coordinates, say {*x*, *y*} are fixed, the value of the other coordinate, here, *z* could not varied anymore.
- This means that there exists a relation that ties *z* to {*x*, *y*} such that *z* is not a free variable but is dependent on the values of {*x*, *y*}.
- This can be mathematically described as $z=z(x,y)$
- Despite having three coordinates, the system has only two degree of freedom.
- In this case, {*x*, *y*} is taken to be two free variable, whereas *z* is not.

Equation of state (EoS)

- In the previous example, the relation that ties z to $\{x,y\}$, a function of the form $z=z(x,y)$, is the so-called
- Equation of State (EoS)
- EoS relates the appropriate thermo coordinates of a system in equilibrium.

Example of EoS for a PVT system – Ideal gas system

- One specific *xyz*-system is the hydrostatic system
- It’s a system that exerts uniform hydrostatic pressure to the surrounding -sometimes is referred to as ‘fluid system’
- Example – gas, mixture of gases contained in a closed volume
- It can be described by three coordinates: P, V, T
- We refer such system as a PVT system
- A specific example of a PVT system is the ideal gas system
- EoS for ideal gas: $PV = nRT$
- This is the specific form of $z=z(x,y)$ taken by the idea gas system.
- Different system has different EoS.

Infinitesimal changes of hydrostatic system

- *V*, *T*, *P* are related by EoS.
- Hence, in general, we know how *V* is related to *P*, *T*, and we state $V = V(P,T)$
- If *V* change by a tiny amount d*V*, so will *T* change by an amount d*T*, and *P* by d*P*.
- Since $V = V(P,T)$, according to the calculus of differential variables, these changes are related via

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

- If EoS is known, we can then work out what $\left(\frac{\partial V}{\partial T}\right), \left(\frac{\partial V}{\partial P}\right)$ is

Definition of β

- Volume expansivity β is a measureable quantity, and from it we can determines via its relationship to the changes of thermodynamic coordinates *V* and *T*

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

- It is normally a positive number since most substance expand when its temperature rises

Definition of κ

- Isothermal compressibility κ is a measureable quantity, and from it we can determines via its relationship to the changes of thermodynamic coordinates *V* and *P*

$$B = -V\left(\frac{\partial P}{\partial V}\right)$$

Average bulk modulus

$$\kappa = 1/B = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)$$

- These are usually positive numbers

Relating partial derivatives with experimental measurements

- κ and β are experimental quantities
- The partial derivatives of the thermo coordinates are theoretical construct
- Measuring κ and β allows us to gain information on the equation of states in terms of the partial derivatives of the thermo coordinates.

Mathematical theorems in partial differential calculus

- Consider an EoS. This is in general an equation that relates the thermodynamical coordinates, say, x, y, z. (Think of P,V,T)
- The general form of an EoS is $f(x, y, z) = 0$.
- The EoS serves to constrain the relation of how x, y, z can vary
- Hence, in general, any one of the he thermodynamical coodrinates can be expressed as a function of each another, e.g. $x=x(y,z)$

Mathematical theorems in partial differential calculus

- Since *x*=*x*(*y*,*z*), the differential of *x*, according to calculus, is

$$\mathrm{d}x = \left(\frac{\partial x}{\partial y}\right)_z \mathrm{d}y + \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z$$

- So is

$$\mathrm{d}y = \left(\frac{\partial y}{\partial x}\right)_z \mathrm{d}x + \left(\frac{\partial y}{\partial z}\right)_x \mathrm{d}z$$

- Combining both equation, we have

$$\mathrm{d}x = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z \mathrm{d}x + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] \mathrm{d}z$$

Mathematical theorems in partial differential calculus

- If d*z* = 0 and d*x* ≠ 0, then

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial x}\right)_z=1 \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z=\frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

- d*x* and d*z* are two independent variables
- If d*x* = 0, and d*z* ≠ 0, then

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x+\left(\frac{\partial x}{\partial z}\right)_y=0$$

- Combining both,

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x=-\left(\frac{\partial x}{\partial z}\right)_y=-\frac{1}{\left(\frac{\partial z}{\partial x}\right)_y} \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y=-1$$

Apply the theorem to PVT system

- Identifying $x \rightarrow P$, $y \rightarrow V$, $z \rightarrow T$,

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \;\Rightarrow\; \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

- By definition, $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ $\quad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

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

d*P* in terms of β and κ

- Consider an infinitesimal change in *P*:

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

- Then, d*P* is expressed as

$$dP = \frac{\beta}{\kappa} dT - \frac{1}{\kappa V} dV$$

- Changes in pressure (d*P*), temperature (d*T*) and volume (d*V*) are related by β and κ

Calculation of compression in mercury when temperature rises at constant volume

$$\mathrm{d}P = \frac{\beta}{\kappa}\mathrm{d}T - \frac{1}{\kappa V}\mathrm{d}V$$

- Read the example in page 37 on compressing mercury at constant volume when it temperature rises from 15°C → 25°C. In this case, d*V* = 0

$$\mathrm{d}P = \frac{\beta}{\kappa}\mathrm{d}T - \frac{1}{\kappa V}\mathrm{d}V \quad ▪$$

$$\int_{P_\mathrm{i}}^{P_\mathrm{f}} \mathrm{d}P = \int_{T_\mathrm{i}}^{T_\mathrm{f}} \frac{\beta}{\kappa}\mathrm{d}T$$

$$P_\mathrm{f} - P_\mathrm{i} = \frac{\beta}{\kappa}\left(T_\mathrm{f} - T_\mathrm{i}\right) = \frac{\beta}{\kappa} 10^\circ\mathrm{C} = \ldots 4.51 \times 10^7\,\mathrm{Pa!!}$$

Extensive and intensive coordinates

- Intensive coordinates – coordinates that are independent of the mass.
- Example: temperature, pressure
- Extensive coordinates – coordinates that are dependent of the mass.
- Example: volume

Discussion of problem 2.1

- The equation of state of an ideal gas is $PV=nRT$, where n and R are constants.

a) Show that the volume expansivity β is equal to $1/T$

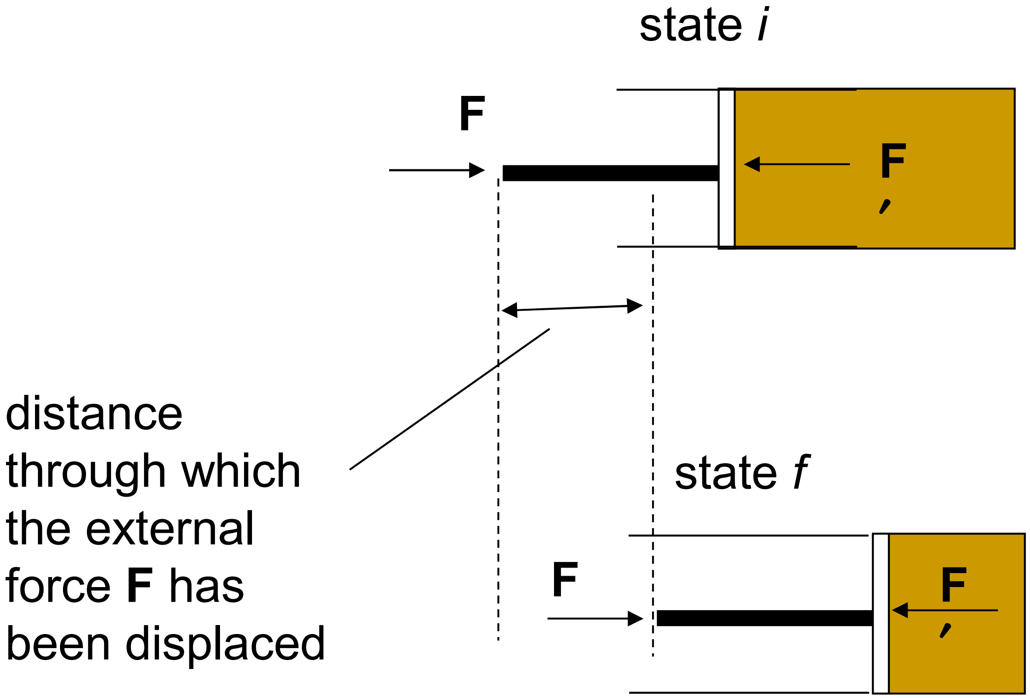
b) Show that the isothermal compressibility κ is equal to $1/P$.

Discussion of problems 2.2

- Given the equation of state of a van der Waals gas, calculate
- (a) $\left(\frac{\partial P}{\partial v}\right)_T$
- (b) $\left(\frac{\partial P}{\partial T}\right)_v$

Chapter 3: Work

- When system undergoes a displacement under the action of a force, work is said to be done.



External force **F** compresses the gas-in-the-cylinder system quasi-statically, making it to go from state *i* to state *f*. External work is said to be done ON the system by the external force **F**.

Internal vs. external work

- Two kinds of work done on a system can be distinguished: work done due to external forces, and work done due to internal forces
- Unless specified, when the word work is referred, it shall refer to external work
- Internal work is due to forces acting among the particles within a system
- As the internal net force is always summed to zero, there shall be no net change to the internal energy of the system due to the work done by these forces.

Work in changing the volume of a hydrostatic system quasi-statistically

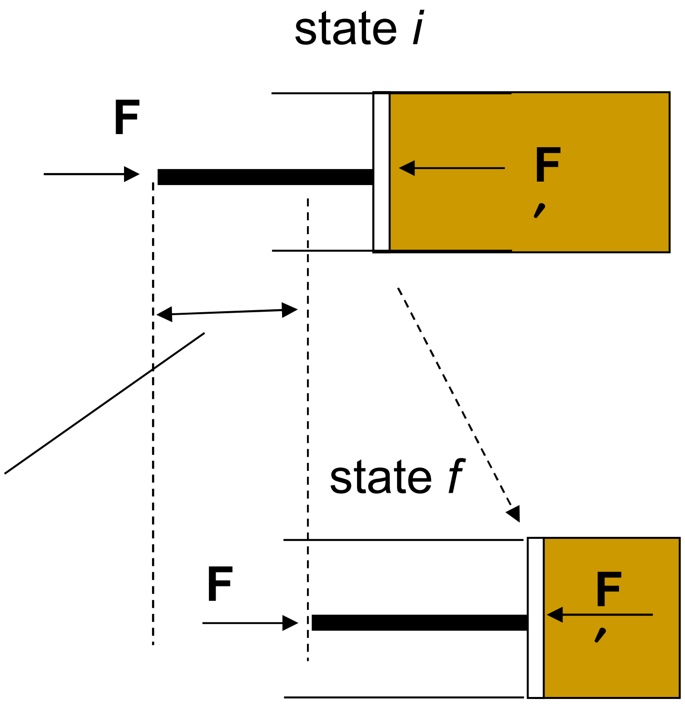
$$dW = -PdV$$

$$W_{\mathrm{i} \to \mathrm{f}} = W_{\mathrm{if}} = -\int_{V_\mathrm{i}}^{V_\mathrm{f}} PdV \longleftarrow$$

Definition: Work done BY the system from i to f

- Compression: $V_\mathrm{f} < V_\mathrm{i}$, or equivalently, $\mathrm{d}V < 0$
- Expansion: $V_\mathrm{f} > V_\mathrm{i}$, or equivalently, $\mathrm{d}V > 0$

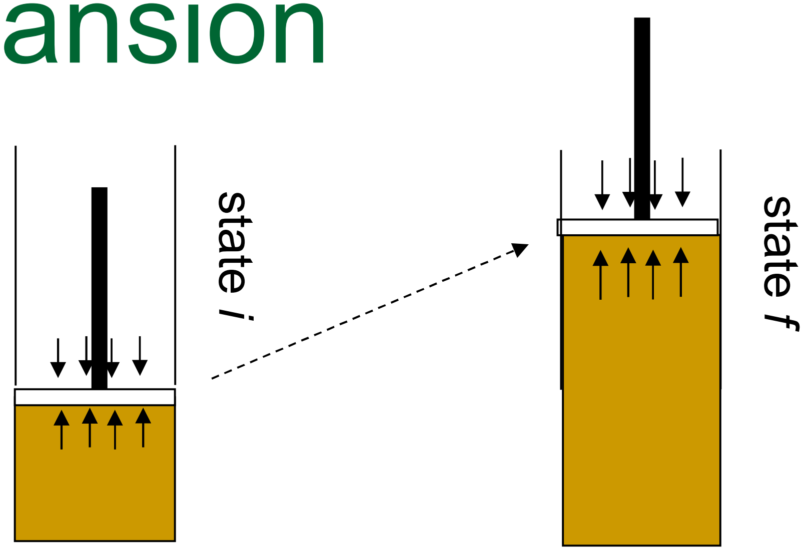
External work done during compression



distance through which the external force **F** has been displaced

- During compression, the work done BY the system, $W_{i \to f} = -\int_{V_i}^{V_f} P dV$ is positive
- As a result, the energy of the gas-in-the-cylinder system increases.
- "work is done on the system"

External work done during expansion



A gas-in-the-cylinder system expands against the pressure from atmosphere, making it going from state *i* to state *f*.

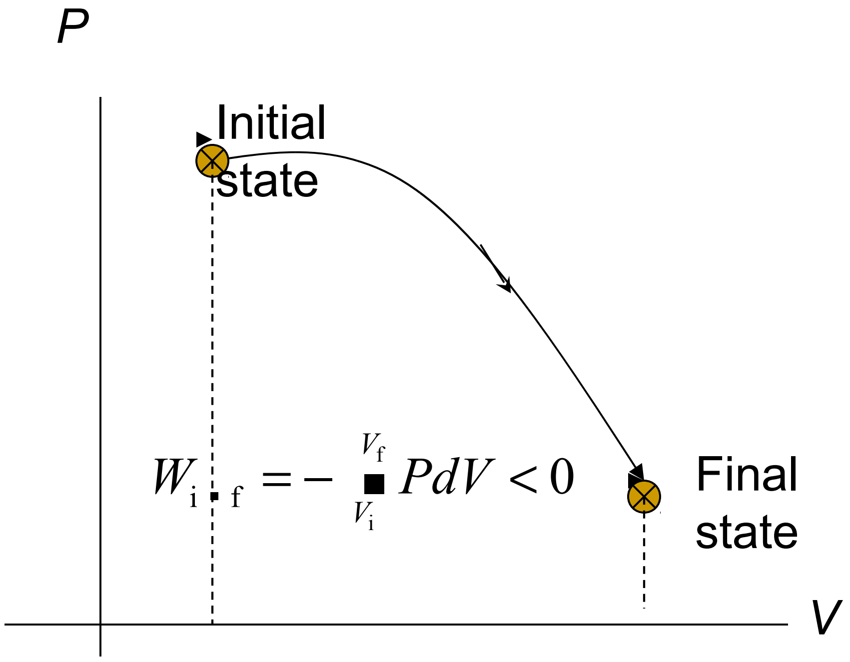
The work done BY the system, $W_{i \rightarrow f} = -\int_{V_i}^{V_f} P\,dV$ is –ve.

As a result the total energy of the gas-in-the-cylinder system decreases.

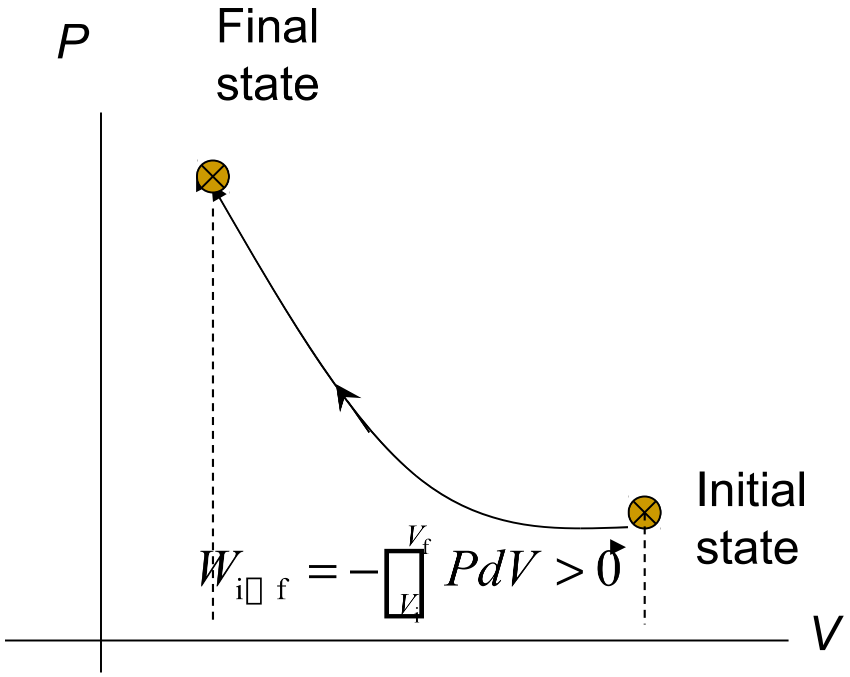
“Work is done BY the system”.

PV diagram

- The area under the PV curve represent work done on or by the gas



Expansion of gas – work is done by system, $W_{i\to f} < 0$



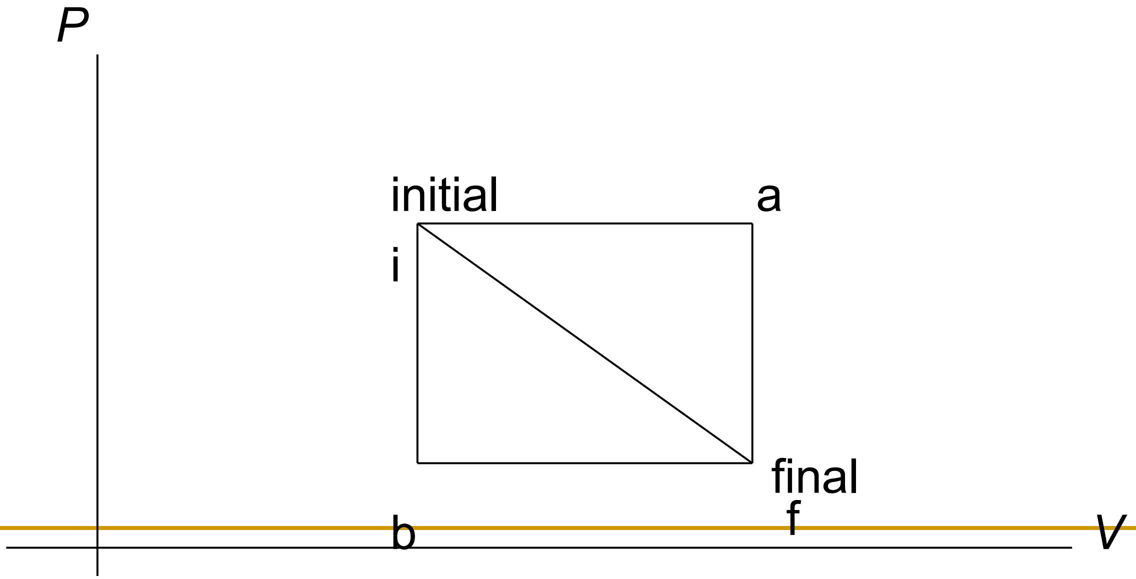
Compression of gas – work is done on the system, $W_{i\to f} > 0$

3 types of thermodynamic processes

- Isochoric – volume kept constant
- Isobaric – pressure kept constant
- Isothermal – temperature kept constant

Hydrostatic work depends on the path

- Path ibf, iaf, if, has different area – work done are different if different path are followed
- Hence, work is not a state function of the system
- If it were, the work done will only depends on the initial and final state, but not on the path chosen



Work done by ideal gas when compressed

- Page 57 example on how to calculate the work done by the gas when it is compressed is calculated isothermally at $T=T_0=293\text{K}$
- In the calculation, we want to evaluate, with V_i and V_f known, the integral of

$$-\int_{V_i}^{V_f} P\,dV$$

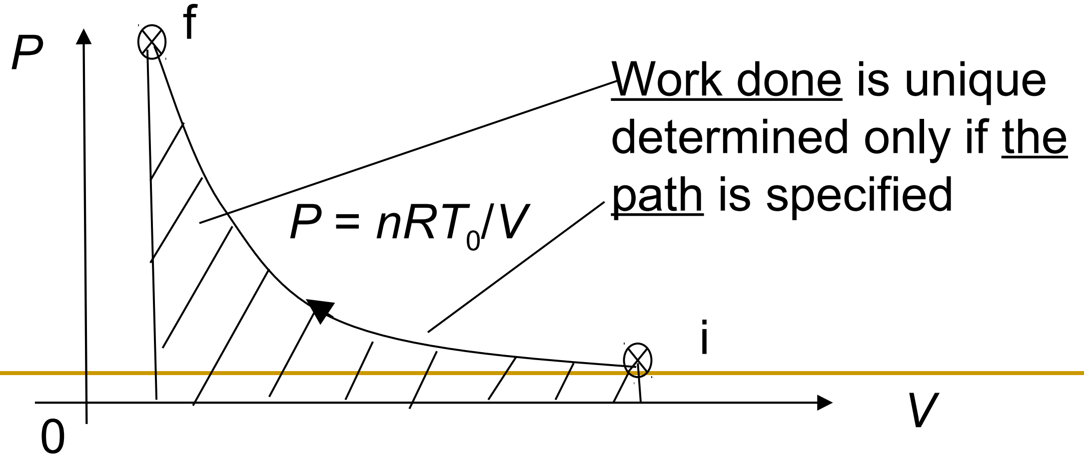
- To do so, we need the equation of state for the ideal gas – which is simply $PV = nRT$, from which the V-dependence of P is deduced, that is,

$$P = P(V) = nRT/V$$

with T kept constant at T_0

Work done is only uniquely determined if the path on a PV diagram is fixed

- Should the behaviour of *P* as a function of *V* is not specified, we could not evaluate the work done uniquely since different path followed by the process when making transition from i to f on a PV diagram will result in different values for the integration



Work done is unique determined only if the path is specified

Isothermal work done by ideal gas (pg. 57, Zemansky)

$$W = -\int_{V_i}^{V_f} P\,dV = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV = -nRT\int_{V_i}^{V_f} \frac{1}{V}\,dV = nRT\ln\left(\frac{V_i}{V_f}\right)$$

- Work done by gas is positive if $V_f < V_i$ (compression)
- Work done by gas is negative if $V_f > V_i$ (expansion)

Example of work done by other thermodynamic system

- Chapter 3.8: Work in changing the area of a surface film
- Chapter 3.9: Work in moving charge with an electrochemical cell
- Chapter 3.10: Work in changing the total polarisation of a dielectric solid
- Chapter 3.11: Work in changing the total magnetisation of a paramagnetic solid

Solution to assignment questions on Chapter 1 – Chapter 3 can be found in assignment1_sol.pdf

JIF 314 Thermodynamics

Intensive Course

Dec 2008

Contact hours

- Thursday, 4 Dec 2008, 8.00 – 9.00 pm
- Saturday, 6 Dec 2008, 9.00 – 10.00 pm
- Sunday, 7 Dec 2008, 12.00 – 1.00 pm

Lecture Plan during intensive course

- To discuss briefly chapter 1,2,3 (1/2 hour).
- To discuss tutorial questions of chapter 1,2,3 (1/2 hour).
- Test on 6 Saturday Dec 2008, 8.00 – 9.00 pm (1 hour).
- To discuss chapters 3, 4, 5 on (1 -2 hours)

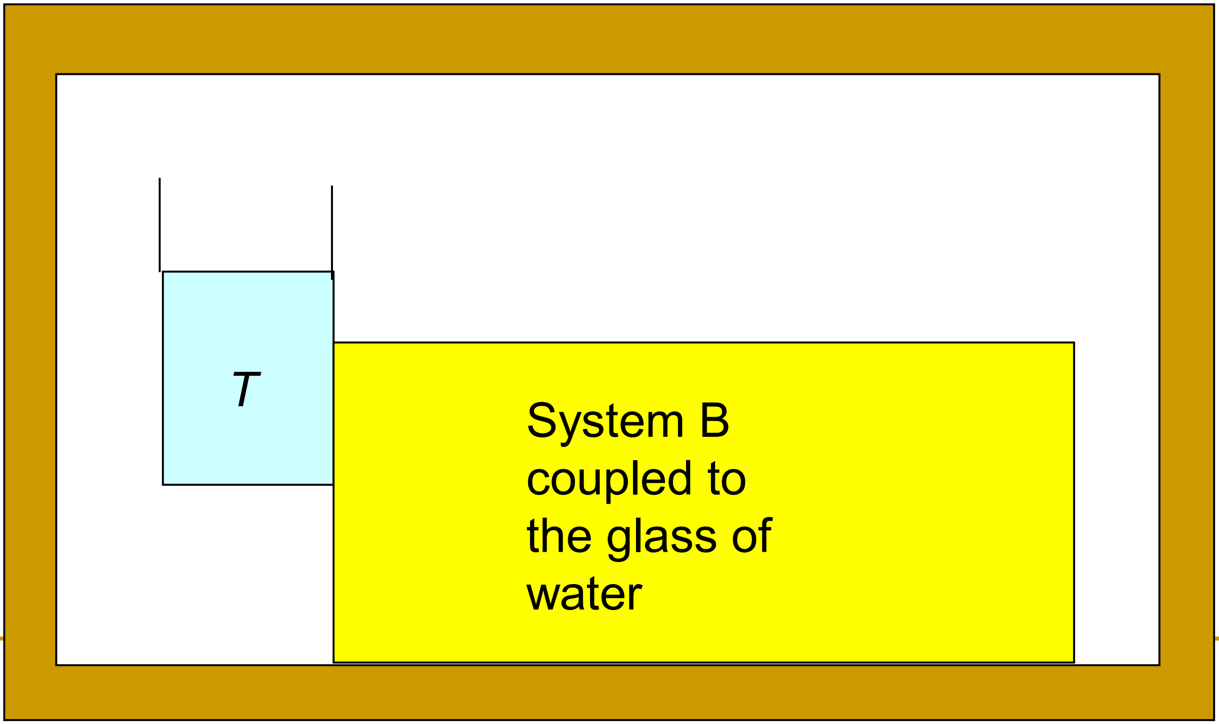
JIF 314 Thermodynamics

Chapter 4

Heat and the first law of thermodynamics

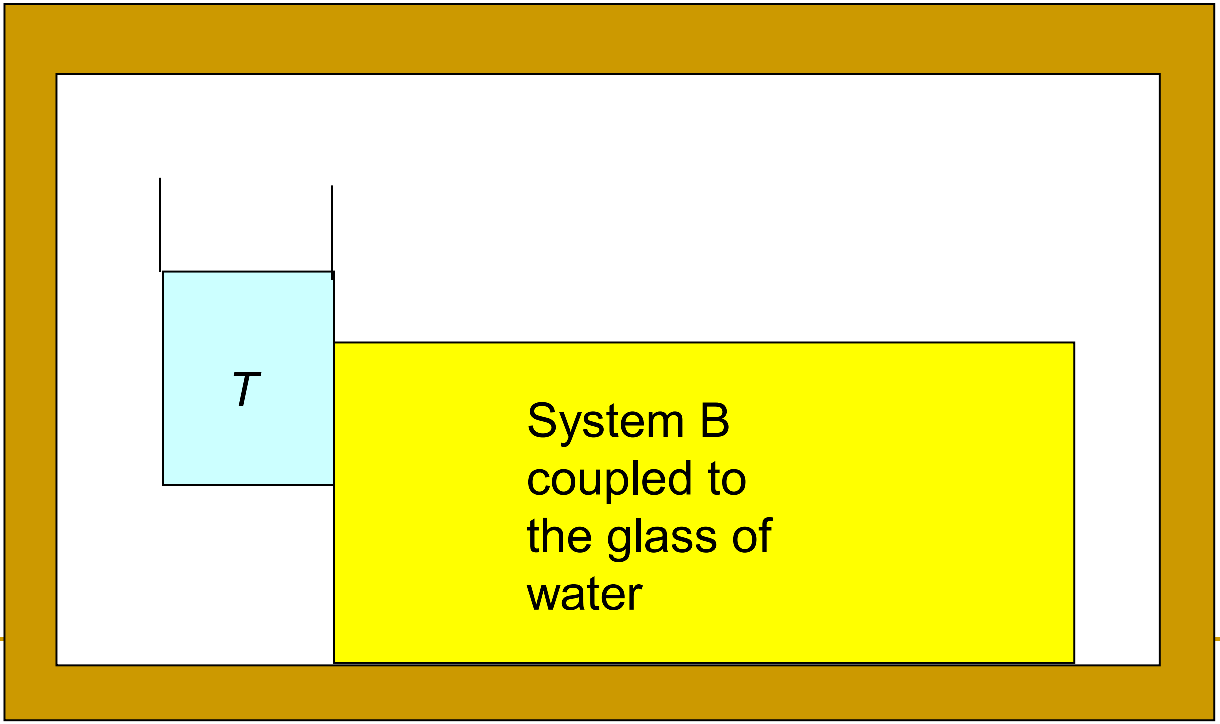
Distinction between heat and work

- Consider a system consist of a glass of water at temperature *T*, coupled to a generic system B, and both are contained within adiabatic walls.



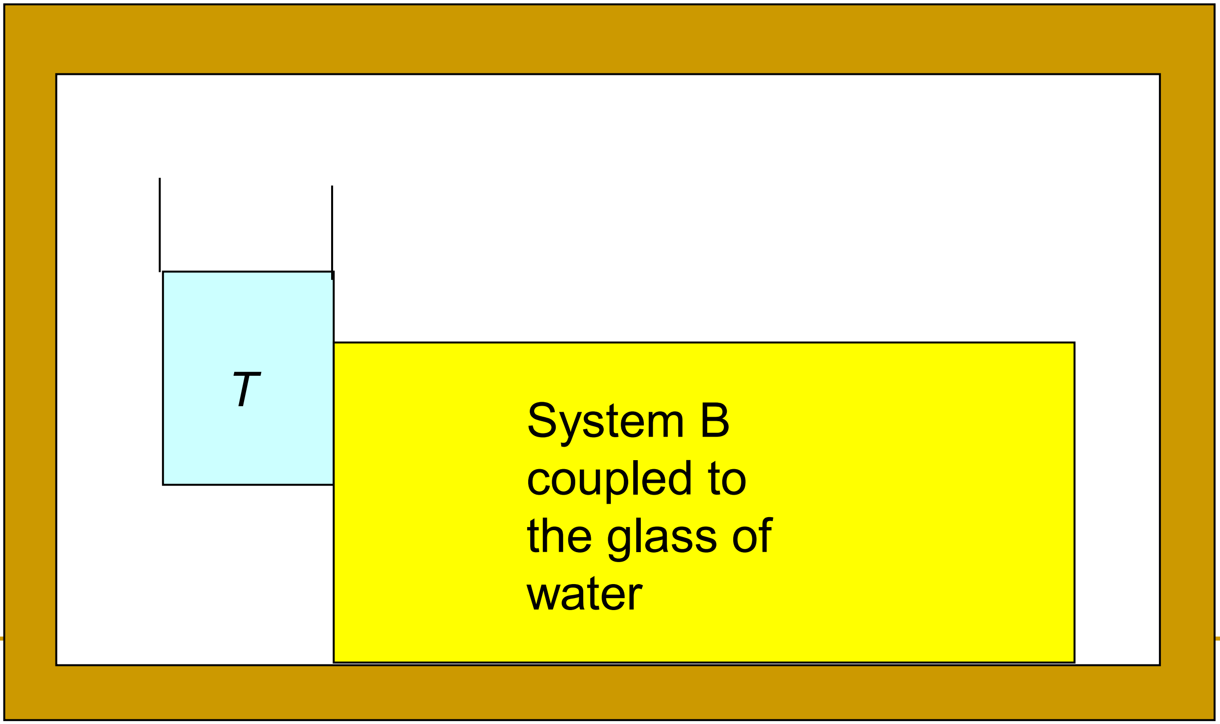
Distinction between heat and work (cont.)

- The temperature of water can be raised if (i) system B perform external work on it (e.g. via mechanical or electrical means), or (ii) system B can raise the temperature of the glass of water through “*non-work*” means, such as heating with fire or radiation.



Distinction between heat and work (cont.)

- Conclusion: the total energy of water can be changed either via work done on it, or via means that is otherwise. This ‘otherwise’ means is ‘heat’.



Adiabatic process

- Consider a system confined within an adiabatic boundary allowing no heat to penetrate
- Refer to figure 4.2, page 75, Zemansky.
- Adiabatic process – a process in which no heat is allowed to flow through the boundary when changes of states are taking place
- Example: compressing a gas contained in a adiabatic cylinder, or a gas undergo free expansion (with external pressure zero) in a adiabatic container.
- A good question to ask: What is the work done by the system when it undergoes an adiabatic process from an state U_i to state U_f?
- Here: *U* measure the total energy contained in the system. It is called internal energy of the system, which is to be defined later.
- Furthermore, if the initial and final states U_i, U_f are fixed, but the process follow a different adiabatic path, will the work done be the same?

Figure 4-2

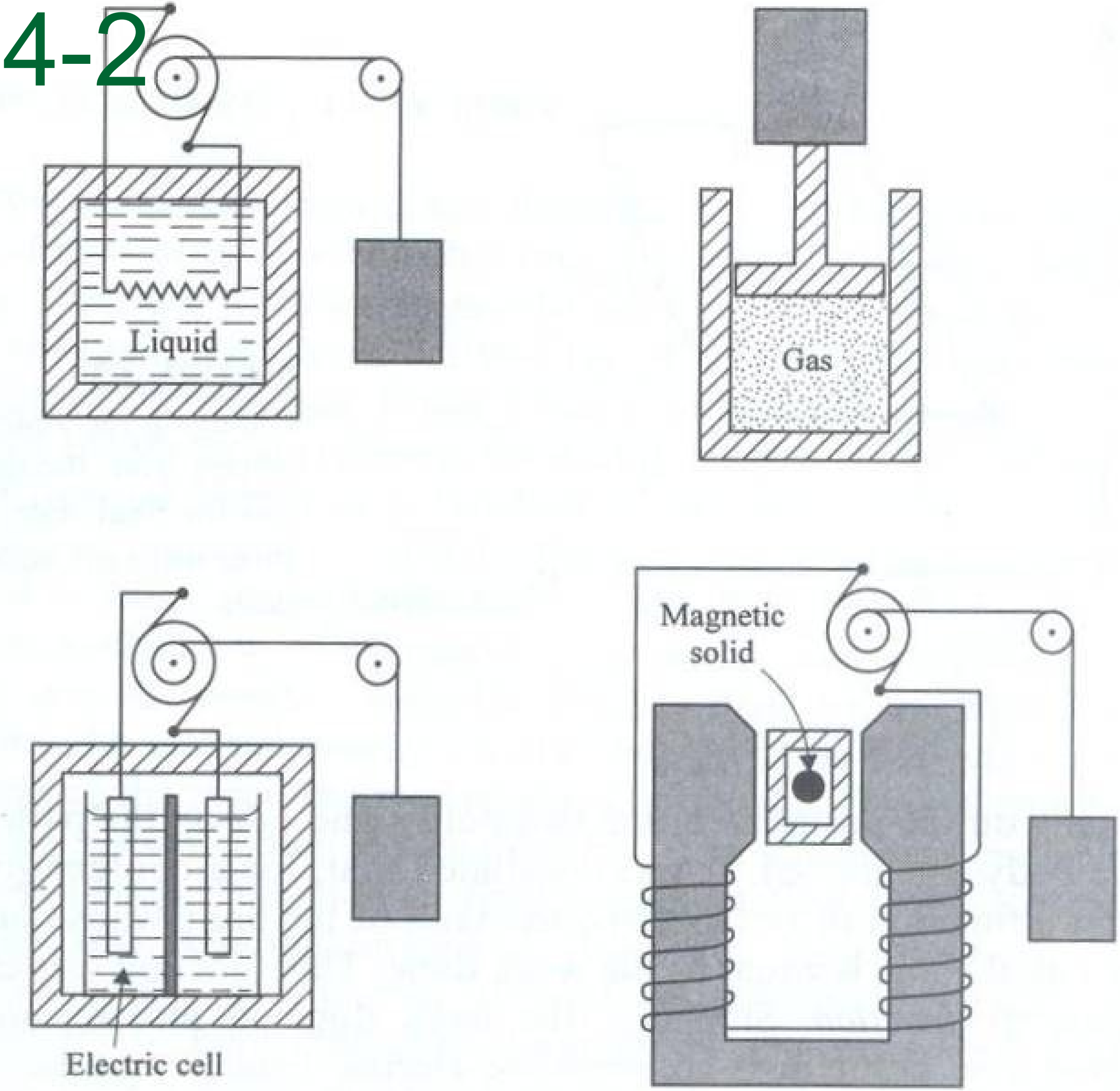


FIGURE 4-2
Adiabatic work for different types of systems.

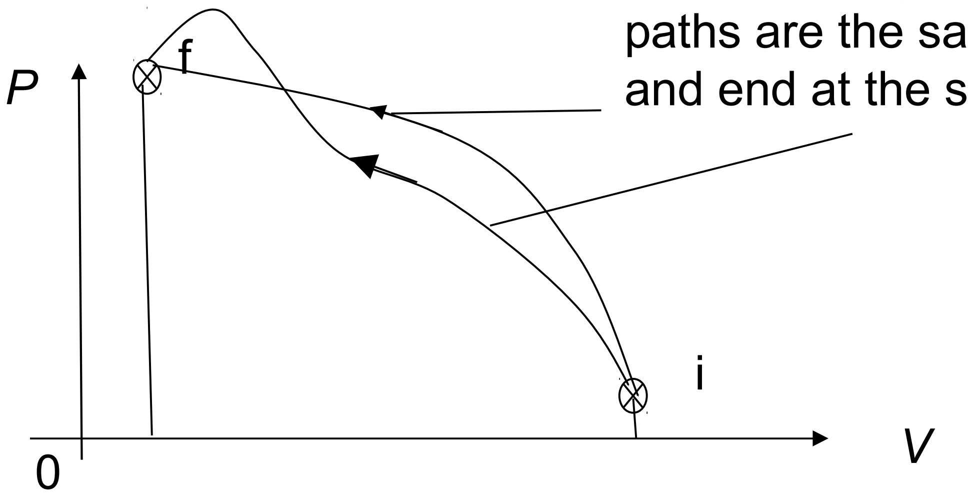
Restricted statement of the first law of thermodynamics

- If a closed system is caused to change from an initial state to a final state by adiabatic means only, then the work done on the system is the same for all adiabatic paths connecting the two states.

Work done adiabatically is path independence

- According to the restricted statement of the first law, the answers to the questions asked earlier are:
- $W_{i \to f}$ (adiabatic) is simply the difference between U_f and U_i, and is independent of the path as long as the process is adiabatic.
- In other words, $W_{i \to f}$ (adiabatic) is uniquely fixed as long as the *f* and *i* states are known.

Work done by two adiabatic processes with common *i* and *f* are the same



Work done by two adiabatic paths are the same, if both begin and end at the same states

Internal energy function

- There exists a function of the coordinates of a thermo system whose value at the final state minus the value at the initial state is equal to the adiabatic work done in going from one state to the other.
- This function is called: the Internal energy function, *U*
- It is a state function of the system.
- In fact, the difference in the values of internal energy function at two different states = energy change in the system.

Internal energy function

- By definition, $U_f > U_i$ when work is done on the system.
- Interpretation of $\Delta U = U_f - U_i$:
- When work is done on the system, the internal energy increases, $U_f > U_i$, hence, $\Delta U > 0$
- When work is done by the system, the internal energy decreases, $U_f < U_i$, hence, $\Delta U < 0$

Internal energy function for PVT system

- For a PVT system, *U* in general is a function of any two thermodynamic coordinates, e.g. $\{P,T\}$, $\{P,V\}$,$\{V,T\}$
- *U* is a function of only two thermo coordinates but not three because the third coordinate is a dependent variable that is already fixed by the equation of state.

Internal energy function for PVT system (cont.)

- As an example, consider a special PVT system, the ideal gas system, with equation of state $PV = RT$
- If we choose $\{V, T\}$ as two independent variables, P is then the dependent variable that is fixed by the equation of state via

$$P = RT/V.$$

- Alternatively, we can also choose $\{P, T\}$ instead as the two independent variables. V is then the dependent variable via the equation of state,

$$V = RT/P.$$

- Essentially, to specify the state of U, we need only a pair of independent thermodynamic coordinates.

Since *U* is path-independent, d*U* is an exact differential

- Say $U\,(X, Y)$, $U\,(X+\mathrm{d}X, Y+\mathrm{d}Y)$, with X, Y any two thermodynamic coordinates, with dY and dX infinitesimally small*
- Two such states are said to be differ from each other infinitesimally, with the difference described by

$$\mathrm{d}U = U\,(X+\mathrm{d}X,\ Y+\mathrm{d}Y) - U(X,Y)$$

- *A number *N* that is infinitesimally small means it is extremely small, smaller than any possible finite number, but *N* is never be exactly zero.

Exact differential of *U*, d*U*

$$\mathrm{d}U = U(X+\mathrm{d}X,\ Y+\mathrm{d}Y) - U(X,Y)$$

$$\mathrm{d}U = \left.\frac{\partial U}{\partial X}\right|_{Y\ \text{fixed}} \mathrm{d}X + \left.\frac{\partial U}{\partial Y}\right|_{\text{X fixed}} \mathrm{d}Y$$

- {*X*, *Y*} can be e.g. {*T*, *V* } or {*T*, *P* } or {*V*, *P* }.
- In each case, the third variable, *Z*, are *P*, *V* and *T* respectively.

Example of choosing $U=U(T,V)$

For example, if we choose $U = U(X = T,\, Y = V)$,

with P fixed by EoS via $P = P(T,V)$,

Then the exact differential dU is given by

$$\mathrm{d}U = \left.\frac{\partial U}{\partial T}\right|_V \mathrm{d}T + \left.\frac{\partial U}{\partial V}\right|_T \mathrm{d}V$$

$\left.\frac{\partial U}{\partial X}\right|_{Y\text{ fixed}}, \left.\frac{\partial U}{\partial X}\right|_{Z\text{ fixed}}$ are two different functions

$$\left.\frac{\partial U}{\partial X}\right|_{Y\text{ fixed}} \neq \left.\frac{\partial U}{\partial X}\right|_{Z\text{ fixed}}$$

- $U = U(X, Y)$
- $U = U(X, Z)$

Definition of diathemic wall

- Diathermic wall – a heat conductor wall that permits heat to flow through (in contrast to diabatic wall)

Non-adiabatical process

- Consider work done by a system bounded by not a diabatic wall but a diathermal one.
- See figure 4-4, page 78, Zemansky.
- Such are examples of non-adiabatic processes.
- Unlike the case of adiabatic process, in non-adiabatic process, heat is allowed to flow through the wall of the system
- What is the work done by such a diathermalprocess $W_{i\rightarrow f}$(diathermal)?
- The answer is answered experimentally,

$$W_{i\rightarrow f}(\text{diathermal}) \neq U_f - U_i$$

Figure 4-4

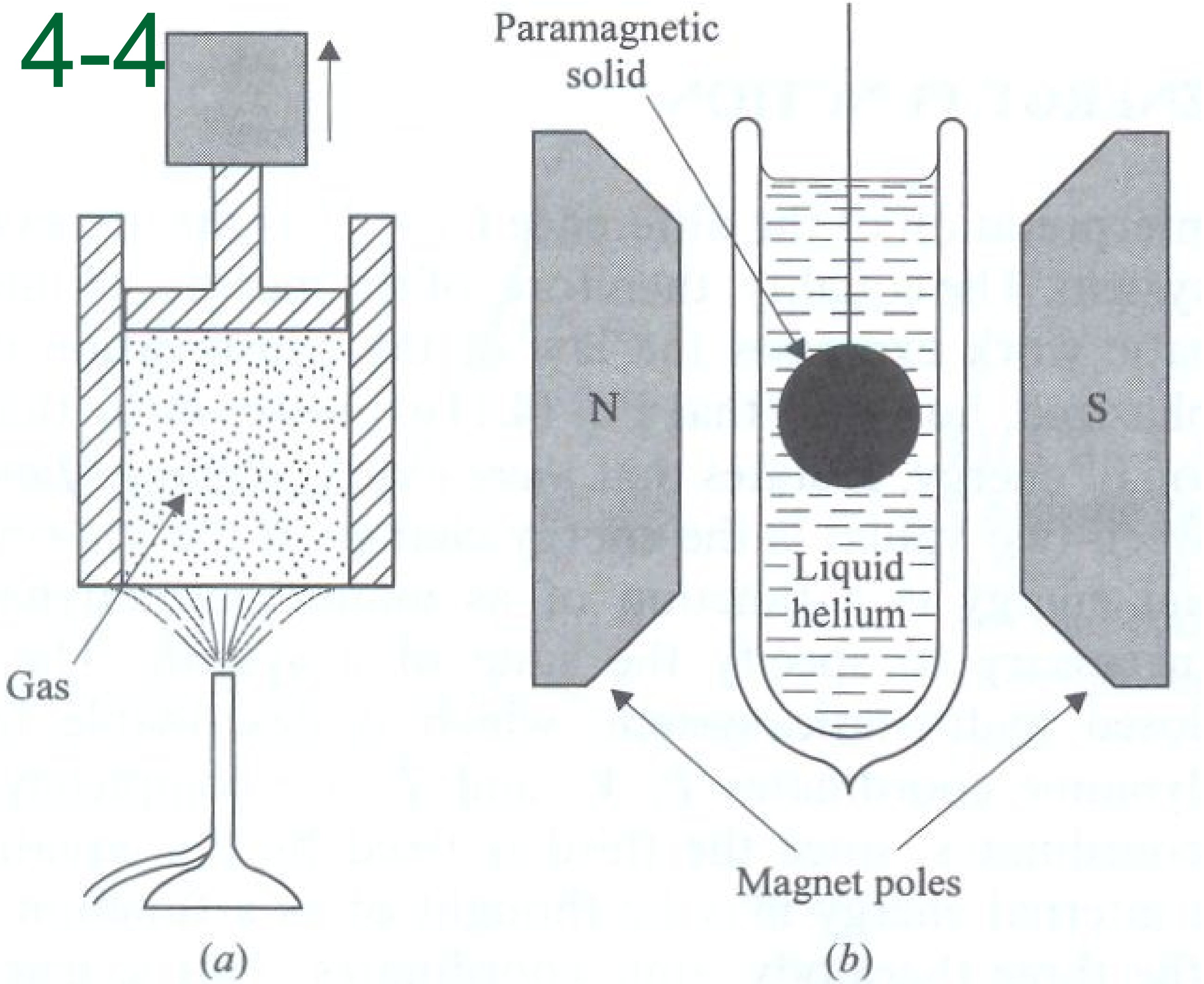


FIGURE 4-4
Nonadiabatic processes.

Thermodynamic definition of heat

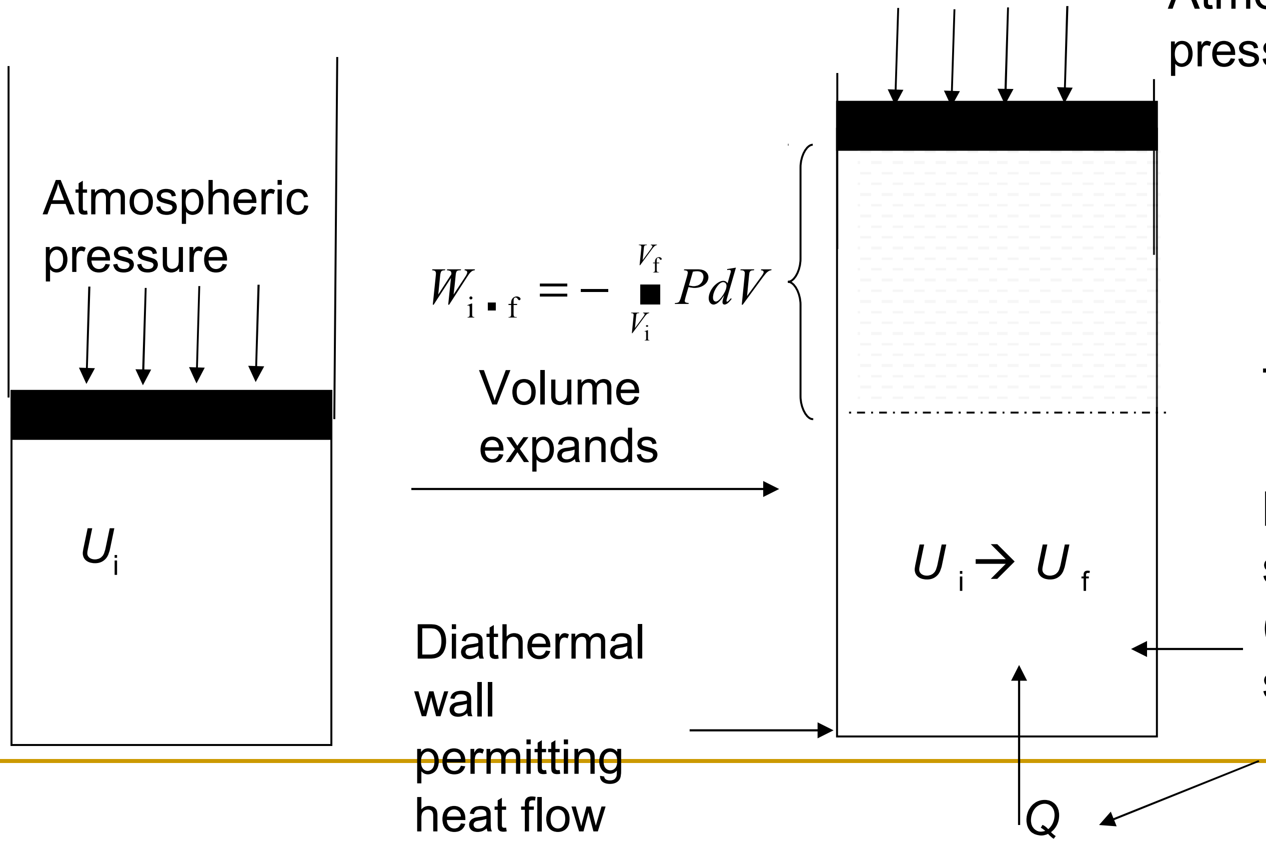
- The difference between $W_{i \rightarrow f}$ (diathermal) and $(U_f – U_i)$ is called heat,

$$Q = (U_f – U_i) - W_{i \rightarrow f}(\text{diathermal})$$

- Convention: Q is positive if heat enters a system, negative when if leave the system.
- Transit of heat is a result of a temperature difference
- Heat, being a difference in terms of work and internal energy, is itself a form of energy.

Pictorial illustration of $Q = (U_f – U_i) - W$

Positive *Q* flows in, causing volume to expand from V_i to V_f against atmospheric pressure. Internal energy changes from U_i to U_f. Work is done by the system, $W_{i \to f}$



Atmospheric pressure

U_i

$$W_{i \to f} = -\int_{V_i}^{V_f} P\,dV$$

Volume expands

Atmospheric pressure

$U_i \to U_f$

Diathermal wall permitting heat flow

Temperature $T_{su} > T_{sy}$ so that heat flows from surrounding (su) to the system (sy)

Q

The sign of ΔU

The change in internal energy, $\Delta U = U_f - U_i$, could be positive of negative

If ΔU negative, it means internal energy decreases after the expansion,

If ΔU positive, it means internal energy increases after the expansion

The sign of ΔU depends on the balance between the “input” Q, and the “output”, W.

Q and *W* have meaning only if a state undergoes transitional process

- Heating and working are transient processes that causes a system to change from one state to another.
- Heat and work are involved only in the process of making transition from a state to another.
- Once the transition of states ceases and equilibrium achieved, heat or work does not endure anymore.
- Once the transition of state ceases, what endures finally is the new state, and the final internal energy.
- Hence, it is meaningless to talk of “the heat of a state” or “work of a state”

Infinitesimal amount of *Q*, *W* are not exact differentials

- Since *U* is a state function of the coordinates of the system, and hence path-independent, the difference in *U* between two infinitesimally different states is an exact differential, d*U*, and we can write it as, e.g.

$$dU = \left.\frac{\partial U}{\partial T}\right|_P dT + \left.\frac{\partial U}{\partial P}\right|_T dP$$

Infinitesimal amount of *Q*, *W* are not exact differentials (cont.)

- In contrast, *Q* and *W* are not state functions, and they are path-dependent.
- The difference in *Q* and *W* between two infinitesimally different states are not exact differential,
- that is, e.g., we CANNOT write

$$dQ \neq \left.\frac{\partial Q}{\partial T}\right|_P dT + \left.\frac{\partial Q}{\partial P}\right|_T dP$$

Inexact differential form of Q and *W*

- Hence, we use $\bar{d}Q$ to denote an infinitesimal amount of heat, but not the differential form, d*Q*.
- The same notation goes to *W*.

Calculations of *W* and *Q* are path-dependence

- What all these meant: the calculation involving heat and work is path-dependent, and normally we have to carry out integration, which is path-dependent, to determine *W* and *Q* between two states, and the results are path-dependent.
- (In contrast, calculation of ΔU is much easier since ΔU is simply a difference of two numbers, = $U_i - U_f$, a value which can be easily evaluated without the need to carry out path-dependent integration.)

Path-independence and path-dependence

- As an example, when we calculate the difference in internal energy between two states, we only need to calculate the difference, $\Delta U = U_f - U_i$. This difference is always the same for two fixed states of U_f and U_i, since U is a state function. This infers path-independence.

Path-independence and path-dependence (cont.)

- However, in calculating the work done, $W_{i \to f}$ when a system change from state i to state f, we cannot simply calculate $W_{i \to f}$ as $W_f - W_i$ but have to perform the integration $\int_{\text{path}} \bar{d}W$,

  which will result in different value for process carried out via different path (e.g. adiabatical path result in a value of work done that is different from that of a non-adibatical one)

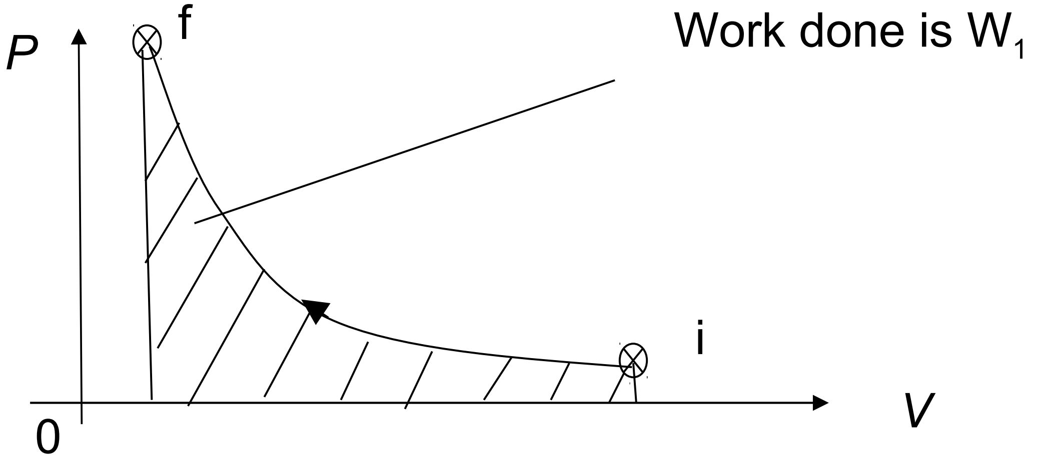
$$\int_{\text{path 1}} \bar{d}W \neq \int_{\text{path 2}} \bar{d}W$$

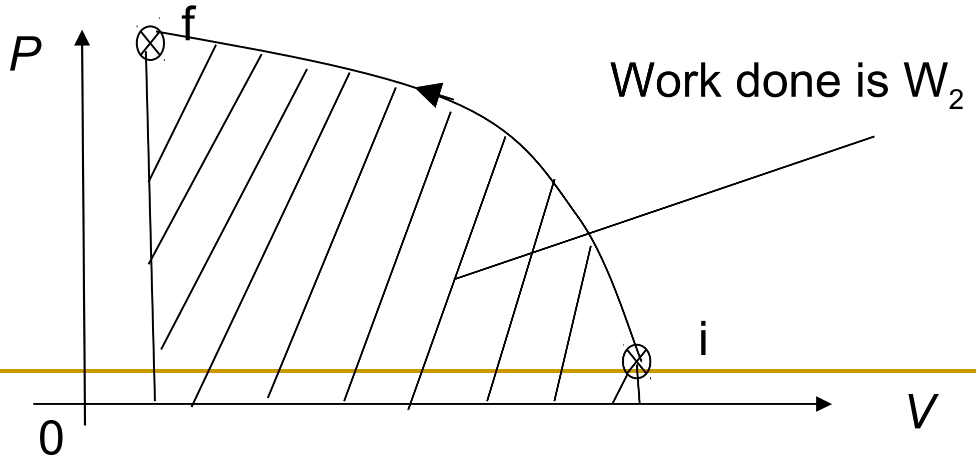
Path-independence and path-dependence (cont.)

- So does the argument for work done applies to the heat flow as well

$$\int_{\text{path 1}} \bar{d}Q \neq \int_{\text{path 2}} \bar{d}Q$$

Different paths , common {i, f} states, resulted in different work done, and different heat flow





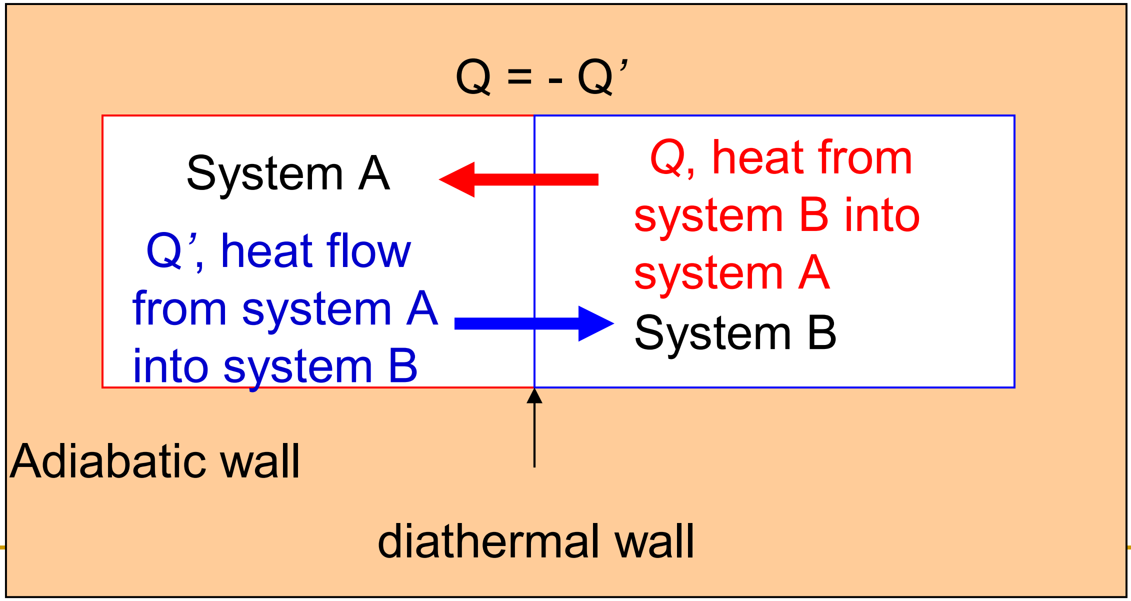
$\Delta U = U_f - U_i$ are the same in both cases

$W_{i\rightarrow f}$ are different in both cases

$Q_{i\rightarrow f}$ are different in both cases

Net heat flow within a compartmentalised adiabatic system is zero

- Within an adiabatic boundary, the heat lost (or gained) by system A is equal to the heat gained (or lost) by system B, $\Delta Q = Q + Q' = 0$



$Q = - Q'$

System A

Q, heat from system B into system A

Q', heat flow from system A into system B

System B

Adiabatic wall

diathermal wall

Differential form of the first law

$$dU = \bar{d}Q + \bar{d}W$$

- Two inexact differentials on the right hand side (RHS) make one exact differential on the left hand side (LHS).
- For hydrostatic system (fluid),

$$\bar{d}W \quad \blacksquare -P\mathrm{d}V$$

- and the first law reduces to

Work done is path dependent

Heat transfer is path dependent

$$\bar{d}Q = dU + \boxed{PdV}$$

Heat Capacity

$$C = \lim_{T_i \blacksquare T_f} \frac{Q}{T_f - T_i} \blacksquare \frac{\bar{d}Q}{dT}\Bigg|$$

- In unit of joules per kelvin (J/K)
- It is an extensive quantity (i.e. the larger the mass the larger is the value of *C* since a larger amount of heat is require to heat up the material for 1 degree.)

Specific heat Capacity

$$c = C / m$$

- In unit of joules per kelvin per kg (J/kg·K)
- Intensive quantity, i.e. it’s value remains the same for different amount of mass of the same material.

Molar heat capacity

$$c = C / n$$

- *n* is the amount of material measured in unit of mole.
- In unit of joules per kelvin per mole (J/mol·K)
- Intensive quantity, i.e. it’s value remains the same for different amount of mass of the same material.

Amount of substance in terms of mole

- 1 mole of substance is defined to contain N_A atom
- N_A = Avogardo number, 6.023 ▪ 10^{23}
- If an atom has a mass of m, N atoms will have a total mass of $M' = mN$
- Number of atoms of a substance with a total mass M' is $N = M'/m$.
- The ratio of the two numbers, N/N_A defines the amount of atom of that material in term of mole:

$$n = N/N_A$$

Heat capacity at constant pressure

$$C_\mathrm{P} = \left(\frac{\bar{\mathrm{d}}Q}{\mathrm{d}T}\right)_P = C_\mathrm{P}\left(P, T\right)$$

$\bar{\mathrm{d}}Q$ amount of heat required to heat up the temeperature of the system by $\mathrm{d}T$

Heat capacity at constant volume

$$C_\mathrm{V} = \left(\frac{\text{đ}Q}{\mathrm{d}T}\right)_V = C_\mathrm{V}\left(V,T\right)$$

Deriving heat capacities for hydrostatic system from the first law

$$dU = \bar{d}Q - PdV$$

- Choose *U*=*U*(*T*,*V*)

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

$$\bar{d}Q + PdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

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

$$\div dT$$

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

Special case, d*V* = 0 (for the case of C_V)

- If the temperature is raised by d*T* by heating the substance without changing the volume, (i.e. set d*V* =0)

$$\frac{\bar{d}Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\cancel{\frac{dV}{dT}} \Rightarrow \left.\frac{\bar{d}Q}{dT}\right|_V \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

- Specific heat at constant volume of a substances C_V can be calculated from theory if the internal energy function of that substance, *U*, is known, via $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

Special case, d*P* = 0 (for the case of C_P)

- If the temperature is raised by d*T* by heating the substance without changing the pressure
- $\Rightarrow V = V(T)$ only $\Rightarrow$ $\dfrac{dV}{dT} = \left(\dfrac{\partial V}{\partial T}\right)_P = V\beta$

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

$$\left.\frac{\bar{d}Q}{dT}\right|_P \equiv C_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

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

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V - PV\beta}{\beta V}$$

- Specific heat at constant pressure of a substances C_P can be calculated from theory if the internal energy function *U*, *β* and the equation of state of that substance are known.

Heat reservior

- A body of such a large mass that it may absorbed or reject an unlimited quantity of heat without experiencing an appreciable change in temperature or in any other thermodynamic coordinate.

Calculating quasi-static isobaric heat transfer process via a temperature difference

$$Q_P = \int_{T_i}^{T_f} C_P dT$$

- If C_p is constant in temperature in the range of T_i to T_f,

$$Q_P = C_P\left(T_f - T_i\right)$$

Calculating quasi-static isochoric heat transfer process via a temperature difference

$$Q_V = \int_{T_i}^{T_f} C_V \, dT$$

- If C_V is constant in temperature in the range of T_i to T_f,

$$Q_V = C_V \left(T_f - T_i \right)$$

Three mechanism of heat conduction

- Conduction
- Convection
- Radiation

Heat conduction

Heat flow from high temperature to low temperature

Thermal conductivity

$$\frac{\bar{d}Q}{dt} = -KA\frac{dT}{dx}$$

Cross section perpendicular to direction of heat flow

Temperature gradient

Heat convection

Convection coefficient

$$\frac{\bar{d}Q}{dt} = hA\Delta T$$

Temperature difference

Thermal radiation

- Emission of heat as electromagnetic radiation
- Absorbitivity
- Radiant exitance, *R*
- Emissivity, ε
- Black body
- Kirchhoff's law
- Radiated heat

$$\frac{\bar{d}Q}{dt} = A\varepsilon\left(T\right)\left[R_{bb}\left(T_W\right) - R_{bb}\left(T\right)\right]$$

Stefan-Boltzmann law

$$R_{bb}\left(T\right)=\sigma T^{4}$$

Stefan-Boltzmann constant, = 5.67051 ▪ 10^{-8} W/m^{2}·K^{4}

$$\frac{\bar{d}Q}{dt}=A\varepsilon\sigma\left(T_{W}^{4}-T^{4}\right)$$

Experimental determination of σ

- Nonequilibrium method
- Equilibrium method

Problem 4.10

- Regarding the internal energy of a hydrostatic system to be a function of *T* and *P*, derive the following equations:
- a) $dQ = \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right]dT + \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]dP$
- b) $\left(\frac{\partial U}{\partial T}\right)_P = C_P - PV\beta$
- c) $\left(\frac{\partial U}{\partial P}\right)_T = PV\kappa - (C_P - C_V)\frac{\kappa}{\beta}$

Solution for 4.10(a)

$$U = U(T, P) \longrightarrow dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

- First law of Thermodynamics => $dU = dQ - PdV$
- Combining both

$$dQ = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP + PdV$$

Eq. (1)

Solution for 4.10(a) (cont.)

- For a PVT system, we can write *V* as a function of *T* and *P*.

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

- By substituting the expression of d*V* into equation Eq. (1), we get

- $$dQ = \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right]dT + \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]dP$$

Eq. (2)

Solution for 4.10 (b)

- At constant pressure, d*P*=0. Setting d*P*=0, and dividing Eq. (2) by d*T*, we get

$$\left.\frac{dQ}{dT}\right|_P \quad C_P = \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right]$$

- Since $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$
- Therefore, $C_p = \left(\frac{\partial U}{\partial T}\right)_P + PV\beta$

Solution for 4.10(c)

- At constant volume, d*V*=0. Setting d*V*=0, and dividing Eq. (1) by d*T*, we get

$$dQ = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP + PdV$$

$$\boxed{\left.\frac{dQ}{dT}\right|_V \equiv C_V = \left(\frac{\partial U}{\partial T}\right)_P + \left(\frac{\partial U}{\partial P}\right)_T \left.\frac{dP}{dT}\right|_V = \left(\frac{\partial U}{\partial T}\right)_P + \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V;} \qquad \left.\frac{dP}{dT}\right|_V = \left(\frac{\partial P}{\partial T}\right)_V$$

Eq. (3)

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

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow V = \frac{1}{\beta}\left(\frac{\partial T}{\partial V}\right)_P \Rightarrow \left(\frac{\partial T}{\partial V}\right)_P = \beta V$$

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

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}$$

Eq. (4)

Solution for 4.10 (c)

- Combining Eq. (3), (4), and $C_p = \left(\frac{\partial U}{\partial T}\right)_P + PV\beta$

$$C_V = \left(C_P - \beta PV\right) + \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial \beta}{\partial \kappa}\right)_T \Rightarrow \frac{C_V - C_P + \beta PV}{\left(\frac{\partial \beta}{\partial \kappa}\right)_T} = \left(\frac{\partial U}{\partial P}\right)_T$$

Problem 4.14

- One mole of a gas obeys the van der Waals equation of state: $\left(P+\frac{a}{v^2}\right)(v-b)=RT$

  and its molar internal energy is given by $u=cT-\frac{a}{v}$ where *a*,*b*,*c* and *R* are constants. Calculate the molar heat capacities c_v and c_P.

Solution

- We write *u* = *u*(*T*,*v*)

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$ Eq. (1)

$$dq = du + Pdv$$ Eq. (2)

Eq. (1) combined with Eq. (2)

$$dq = \left(\frac{\partial u}{\partial T}\right)_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] dv \xrightarrow{\blacksquare\ dT} \frac{dq}{dT} = \left(\frac{\partial u}{\partial T}\right)_v + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]\frac{dv}{dT}$$

Eq. (5)

$$c_V = \left(\frac{\partial u}{\partial T}\right)_v$$

Solution

- At constant volume, Eq. (5) becomes

$$\left.\frac{dq}{dT}\right|_v \equiv c_V = \left(\frac{\partial u}{\partial T}\right)_v = c, \text{since } u = cT - a/v$$

Solution

- At constant pressure, Eq. (5) becomes

$$\left.\frac{dq}{dT}\right|_P \Rightarrow c_P = \left(\frac{\partial u}{\partial T}\right)_P + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]\left.\frac{dv}{dT}\right|_P$$

$$c_P = c_V + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]\left(\frac{\partial v}{\partial T}\right)_P = c_V + \left[\frac{a}{v^2} + P\right]\left(\frac{\partial v}{\partial T}\right)_P \text{ since } u = cT - a/v$$

At constant pressure, there is no difference between $\left(\frac{\partial v}{\partial T}\right)_P$ and $\left.\frac{dv}{dT}\right|_P$ since $v = v(T)$ only when pressure is kept constant.

- From $\left(P + \frac{a}{v^2}\right)(v - b) = RT$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P + \frac{a}{v^2} - \frac{2a(v-b)}{v^3}}$$

$$C_P - C_V = \left[\frac{a}{V^2} + P\right]\left(\frac{\partial V}{\partial T}\right)_P = \left[\frac{\frac{a}{V^2} + P}{P + \frac{a}{v^2} - \frac{2a(v-b)}{v^3}}\right]R$$

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Chapter 5

Ideal gas

Internal every of real gas

- In adiabatic free expansion (Joule expansion), the internal energy of a system of gas molecules remains unchanged
- dU = dQ + dW = 0 since dQ = 0 (adiabatic) and dW = 0 (since it’s a free expansion)
- Will the temperature change in such a adiabatic free expansion?
- This effect is described by the Joule coefficient

$$\left(\frac{\partial T}{\partial V}\right)_U$$

If $U=U(T)$ only

- In that case, there will be no temperature change in a joule expansion
- In other words, if U is not only dependent on T but also on P (or V) then temperature change will take place in a Joule expansion
- Follow the argument in Zemansky, page 109 – 110, beginning with

$$\mathrm{d}U = \left.\frac{\partial U}{\partial T}\right|_V \mathrm{d}T + \left.\frac{\partial U}{\partial V}\right|_\mathrm{T} \mathrm{d}V$$

Real gas vs. ideal gas

- For real gas, $U=U(T,P)$ or $U=U(T,V)$
- For ideal gas, $U=U(T)$ only
- For real gas with van der Waals force acting among the molecules, the equation of state is relatively complicated, $\left(P+\frac{a}{v^2}\right)(v-b)=RT$
- In low pressure limit, real gas behaves like ideal gas, where the molecular forces becomes weak due to the increase in the average separation between the molecules.

Some thermodynamical properties of Ideal gas

$PV = nRT; U = U(T)$ for ideal gas

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

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

Derived from $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T ; \left(\frac{\partial P}{\partial V}\right)_T = \frac{-nRT}{V^2} \neq 0$

$U = U(T)$ only

$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\mathrm{d}U}{\mathrm{d}T}$, because $U = U(T)$ only, hence there is

no difference between $\left(\frac{\partial U}{\partial T}\right)_V$ and $\frac{\mathrm{d}U}{\mathrm{d}T}$

Some thermodynamical properties of Ideal gas (cont.)

$$C_P = C_V + nR; C_P = C_P(T) \text{ alone}$$

$$\bar{d}Q = C_P dT - V dP$$

- All of these properties can derived based on the first law of thermodynamics, definitions of the quantities concerned, and the equation of state of idea gas, and the calculus of infinitesimal changes.
- Refer to page 112-114 in Zemansky for details.

The ratio $\gamma = c_P/c_V$

- For idea gas, the ratio of molar heat capacities, γ is predicted to be

  $$\gamma = c_P/c_V = (c_V + nR)/c_V = 1 + nR/c_V > 1$$

Experimental measurement of molar heat capacities of real gas at low pressure

- (a) c_V is a function of *T* only
- (b) c_p is a function of *T* only, and is greater than c_V
- (c) c_p - c_V is NOT a function of *T* but equals to *R*
- (d) the ratio $\gamma = c_p/c_V$ is a function of *T* only, and is greater than 1

For monoatomic gasses

- c_V is almost constant for most T, and nearly equal to $3R/2$
- c_p is almost constant for most T, and nearly equal to $5R/2$
- The ratio γ is nearly a constant for most T, and is nearly equal to 5/3.

For permanent diatomic gasses

- c_V is almost constant for some lower range of T, nearly equal to $5R/2$, and increases as T increases.
- c_P is almost constant for some lower range of T, nearly equal to $7R/2$, and increases as T increases.
- The ratio γ is nearly a constant for some lower range of T, nearly equal to 7/5, and decreases as T increases.
- We often write $c_P/R = 7/2 + f(T)$
- where $f(T)$ is an empirical equation used to fit the experimental behavior of the gases.
- It is theoretically difficult to derive $f(T)$

Quasi-static adiabatic process of ideal gas

$$dQ = C_v dT + P dV ; C_P = C_V + nR ; dQ = C_P dT - V dP$$

- Combining the first law with the definition of C_V, C_P, in adiabatic process, where dQ = 0, and assuming γ stays constant, one arrives at

$$\frac{dP}{P} = -\gamma \frac{dV}{V} \blacksquare \ln P = -\gamma \ln V + \text{constant} \blacksquare PV^{\gamma} = \text{constant}$$

Taking ∂ /∂V leads to

Slope of PV diagrame

$$\left(\frac{\partial P}{\partial V}\right)_{\text{adiabatic}} = -\gamma \frac{P}{V} = -\text{constant} \blacksquare \gamma V^{-\gamma-1}$$

Quasi-static isothermal process of ideal gas

- Using *PV* = *nRT*, the slope of PV curve for isothermal process is

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

- The slope of PV curve for adiabatic process is steeper than that of corresponding isothermal process (with a common initial temperature) due to the fact that $\gamma > 1$.

$$\left(\frac{\partial P}{\partial V}\right)_{\text{adiabatic}} = \gamma\left(\frac{\partial P}{\partial V}\right)_T$$

PVT surface for ideal gas

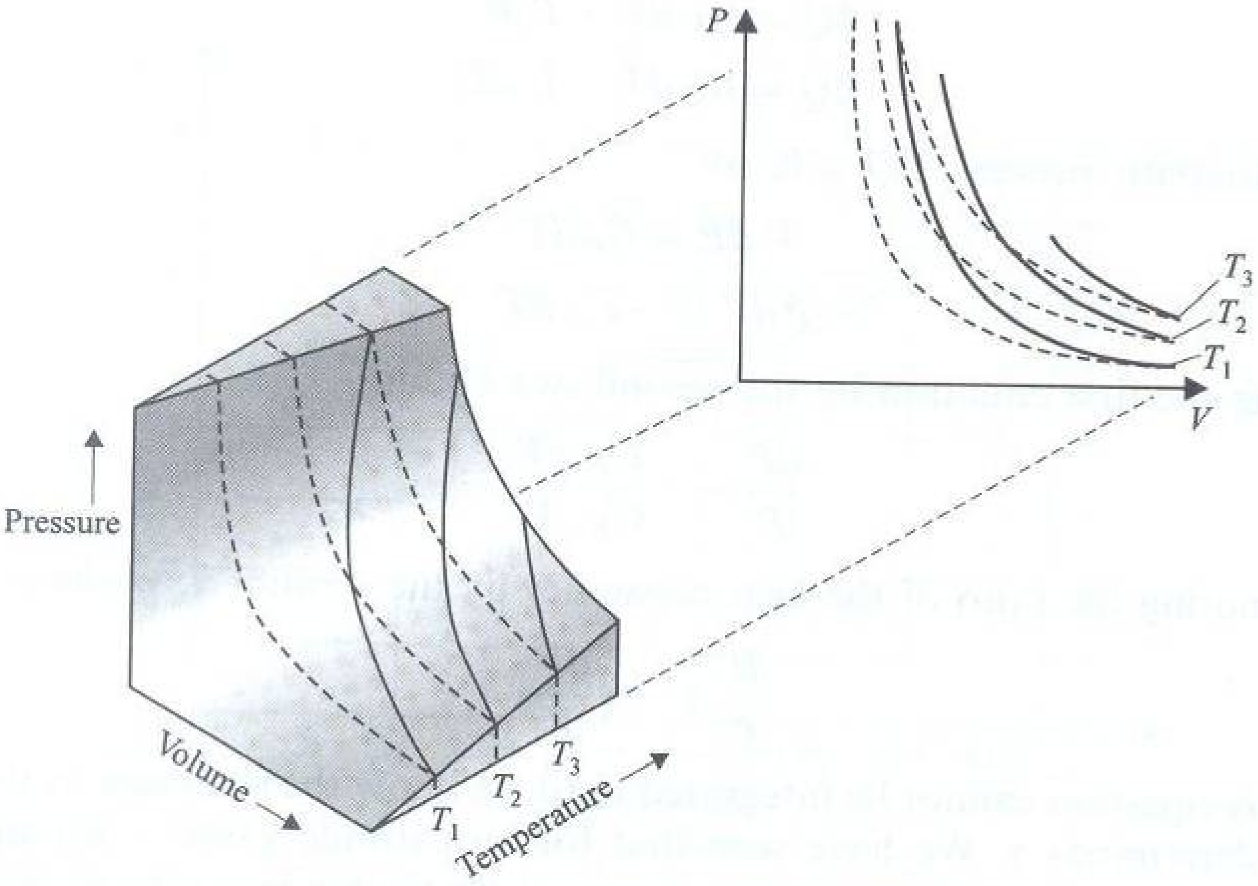

FIGURE 5-5
The *PVT* surface for the ideal gas and its projection onto a *PV* diagram. (Isotherm
shown as dashed curves, and adiabatics as full curves.)

The microscopic point of view

- Given a system, to know its thermodynamic behaviour, we need to know

(i) its internal energy function, *U*

(ii) its equation of state

- These information can sometimes be obtained by performing experimental measurement on a case-by-case basis.
- In addition, it is sometimes difficult if not impossible to do so.
- It will be much more satisfying if we can obtain these thermodynamical information theoretically rather than experimentally

The microscopic point of view (cont.)

- To obtain theoretically *U* and the equation of state, we need to model the system microscopically based on the collective behaviour of the particles of the system.
- First approach: kinetic theory of gas
- Second approach: statistical mechanics

Kinetic theory of ideal gas

Assumptions:

- Number of particles, N, is enormous
- Particles are identical hard sphere (no internal degree of freedom such as vibration nor rotation), and chemically inert
- If m particle mass, the total mass of gas = Nm
- M denotes molar mass in kg/mol (e.g. M=1 g/mol for hydrogen atom, water molecule has M = 18 g/mol).
- The number of moles $n = Nm/M$
- Avogadro’a number $N_A = N/n = M/m = 6.023 \times 10^{23}$
- At standard pressure and temperature (STP), $P = 1$ atm, $T = 273$K (water’s freezing point), 1 mole of ideal gas occupy a volume of 22.4 litre = 22.4×10^3 cm^3.

Assumptions of kinetic theory of ideal gas (cont.)

- The particles of ideal gas resemble hard sphere with negligible diameter compared to the average distance between these particle
- Particles are in perpetual random motion
- Particles exert no force among themselvea except when the collide among themselves or against the wall
- Collision is perfectly elastic
- Between collision particles move with uniform rectilinear motion
- Upon bouncing against the wall, a particle suffers change of a velocity by $-2w_{\perp}$($w_{\perp}$ is the initial velocity before bouncing)

Assumptions of kinetic theory of ideal gas (cont.)

- Particle density N/V is assumed uniform and constant (V volume of the ideal gas)
- In an infinitesimal volume dV, number of particle is $dN = (N/V)\mathrm{d}V$
- Motion of particles is anisotropic
- The speed of particle is distributed non-uniformly in the range from zero to speed of light.
- $\mathrm{d}N_w$ is a function of w.

System of ideal particles moving in 3–D spherical coordinate system

- Differential solid angle, $d\Omega$ (in unit of steradians), see Figure 5-9, pg. 129.
- Solid angle covering the whole solid sphere is 4π
- dN_w denotes number of particle having speed $[w, w+dw]$
- $d^3N_{w,\theta,\phi} = dN_w \, d\Omega/4\pi$ denotes number of particle with speed $[w, w+dw]$ in the solid angle at spherical coordinate interval $[\theta, \theta+d\theta]$, $[\phi, \phi+d\phi]$
- Note that $d^3N_{w,\theta,\phi}$ is independent of ϕ, θ, hence 'particle speed distribution is anisotropic'

Figure 5-9

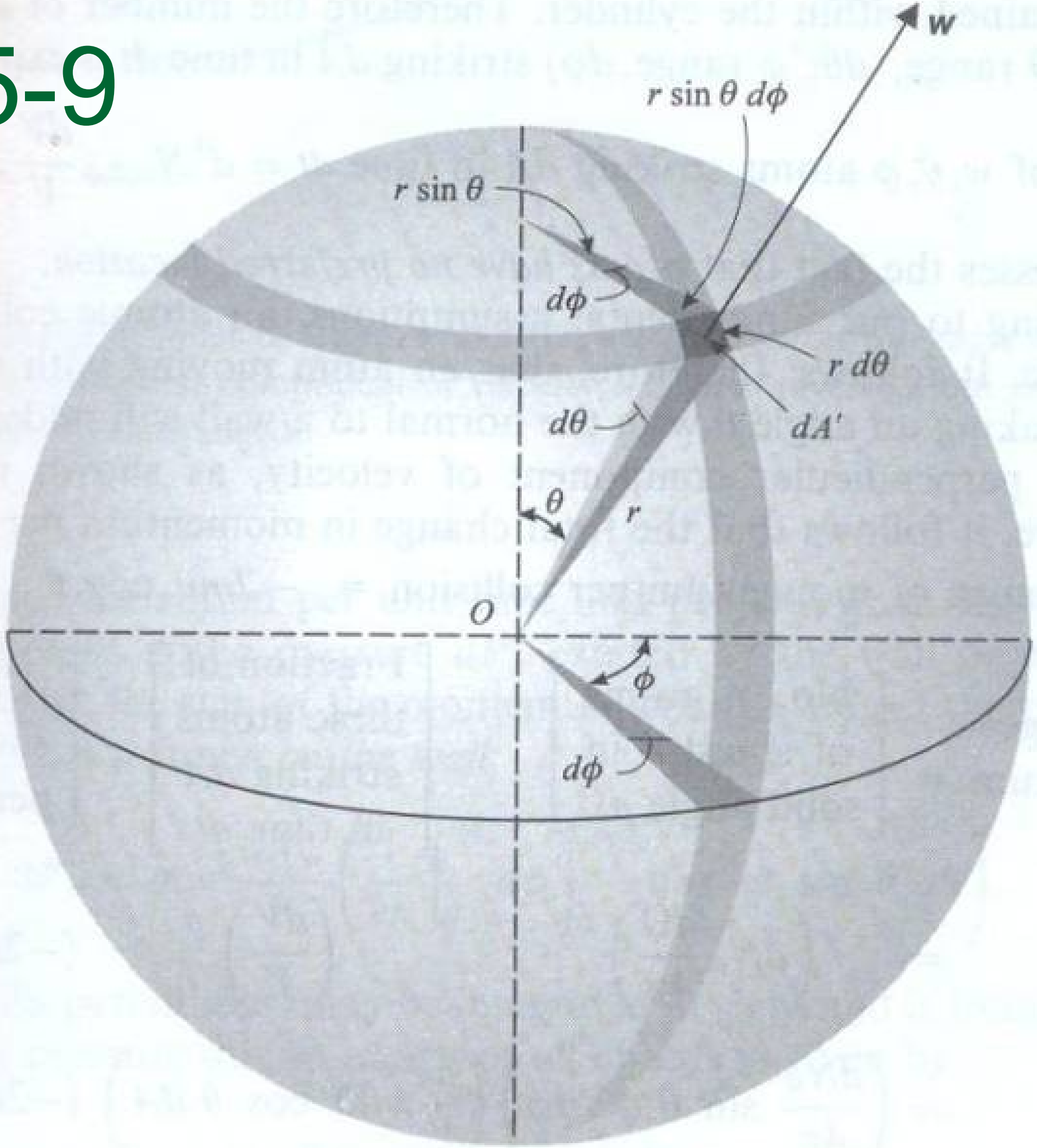

FIGURE 5-9
The solid angle $d\Omega = \sin\theta \, d\theta \, d\phi$.

System of ideal particles moving in 3–D spherical coordinate system (cont.)

- Number of particles striking dA in time dt is $d^3N_{w,\theta,\phi} = dN_w \, d\Omega/4\pi \; dV/V$
- where dV is the infinitesimal volume subtended by solid angle dΩ
- $dV = w \, dt \cos\theta \, dA$

Figure 5-10

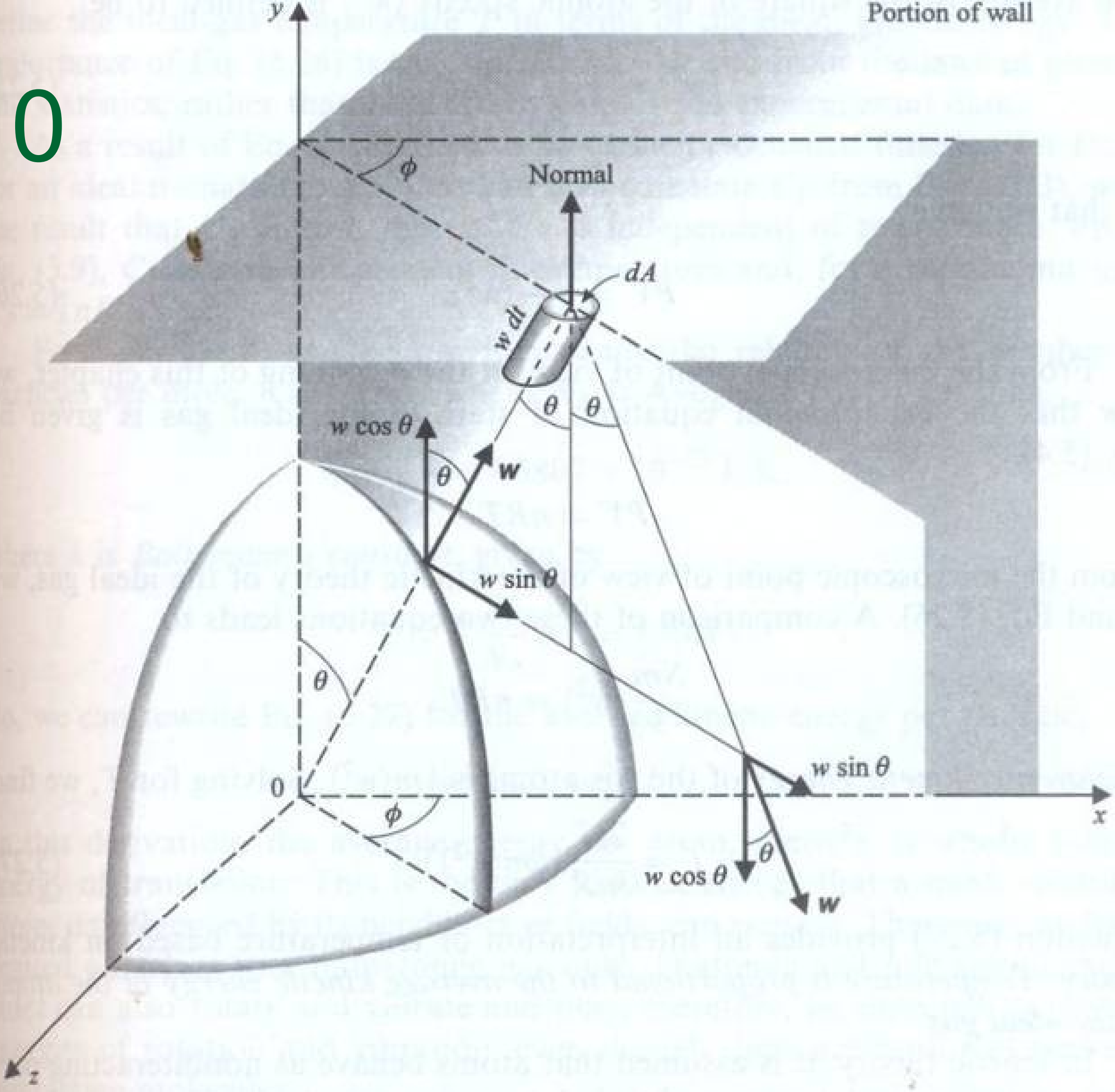

FIGURE 5-10
All the atoms in the cylinder of length $w\,dt$ strike the area dA at the angle θ to the normal. The perpendicular component of velocity $w \cos\theta$ is reversed, but the parallel component $w \sin\theta$ is unchanged.

Derivation of *PV* in term of microscopic quantities

- Change of momentum per collision at this surface is $-2mw\cos\theta$
- Total change of momentum = (no of atoms of speed *w* in solid angle, dΩ) x (fraction of these atoms striking d*A* in time d*t*) x (change in momentum per collision)
- Total pressure = total change of momentum / d*t*
- The pressure exerted on the wall, dP_w, by the dN_w gas atoms is the total change of momentum per unit time per unit area:

$$dP_w = mw^2 \frac{dN_w}{V}\left(\frac{1}{2\pi}\int_0^{2\pi} d\phi \int_0^{2\pi} \cos^2\theta \sin\theta \, d\phi\right) = mw^2 \frac{dN_w}{V}\left(\frac{1}{3}\right)$$

Derivation of *PV* in term of microscopic quantities (cont.)

- Integrating over θ and ϕ, and making used of the definition of root mean square of the speed, $\langle w^2 \rangle = \frac{1}{N}\int_0^c w^2 \, dN_w$

$$P = \int_0^P dP = \frac{m}{3V}\int_0^c w^2 \, dN_w = \frac{m}{3V}\left(\int_0^c w^2 \, dN_w\right) = \frac{m}{3V}\left(N\langle w^2 \rangle\right)$$

$$PV = \frac{mN}{3}\langle w^2 \rangle$$

ŷ

- LHS is a a macroscopic description, RHS is microscopic description
- Since *PV* =*nRT*
- Hence, we can equate $PV = \frac{mN}{3}\langle w^2 \rangle = nRT$

Internal energy of ideal gas is temperature dependent only

- Average kinetic energy per particle $\frac{m}{2}\left\langle w^2 \right\rangle$ (a microscopic quantity), can then be related to the macroscopic quantity *T*, via $\frac{m}{2}\left\langle w^2 \right\rangle = \frac{3}{2}\frac{R}{N}nT = \frac{3}{2}\frac{R}{N}\frac{N}{N_A}T = \frac{3}{2}\frac{R}{N_A}T = \frac{3}{2}kT;\ \ k = \frac{R}{N_A}$
- Total kinetic energy of the ideal gas is $K = N\frac{m\left\langle w^2 \right\rangle}{2} = \frac{3}{2}nRT$
- Since ideal gas assumes no interaction among the particle, hence total internal energy of the system = total kinetic energy of the system, where no internal energy is stored in the form of potential energy

$$K = U = \frac{3}{2}nRT = \frac{3}{2}NkT$$

Generalisation of idean gas to non-ideal gas interacted via van der Waals force

$$PV = nRT \quad \blacksquare \quad \left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT$$

- *a* accounts for cohesive forces between atoms
- *b* accounts for volume occupied by atoms inside the system volume *V*
- *a, b* varies from gas to gas, and have to be measured experimentally.

Problem 5.1

- By defination, the ideal gas satisfies the equations *PV=nRT*. Find the relationships between C_p and C_V for an ideal gas
- **Solution**
- For ideal gas, the internal energy function is a function of temperature only, *U=f*(*T*).

$$\text{Hence } C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} = \frac{d}{dT}\left(\frac{3}{2}NkT\right) = \frac{3}{2}Nk$$

$$c_V = C_V/n = \frac{3N}{2}\frac{1}{n}k = \frac{3N}{2}\frac{1}{\left(N/N_A\right)}\frac{R}{N_A} = \frac{3}{2}R$$

Solution 5.1 (cont.)

- When temperature is raised by d*T*, the increase in *U* is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \cancel{\left(\frac{\partial U}{\partial T}\right)_T} \mathrm{d}V = \left(\frac{\mathrm{d}U}{\mathrm{d}T}\right)_V \mathrm{d}T = C_V \mathrm{d}T$$

- For an infinitesimal quasi-static process of a hydrostatic system, the first law is
- $\mathrm{d}Q = \mathrm{d}U - \mathrm{d}W = C_V\mathrm{d}T + P\mathrm{d}V$
- or, $\mathrm{d}Q = C_V\mathrm{d}T + P\mathrm{d}V$
- For an infinitesimal quasi-static process at constant volume
- $\mathrm{d}(PV = nRT) \rightarrow P\mathrm{d}V + V\mathrm{d}P = nR\mathrm{d}T$
- Eliminating $P\mathrm{d}V$, by combining both equation, we get $\mathrm{d}Q = (C_V + nR)\mathrm{d}T - V\mathrm{d}P$.
- Divide by d*T*, yields $\mathrm{d}Q/\mathrm{d}T = (C_V + nR) - V\,(\mathrm{d}P/\mathrm{d}T)$

$$\frac{dQ}{dT} = C_V + nR - V\frac{dP}{dT}$$

- At constant pressure, dP=0, the LHS becomes C_p and, dP/dT = 0
- Hence the equation reduce to

$(C_p = C_V + nR)/n$

→ $c_p = c_V + R = 3R/2 + R = 5R/2$

JIF 314 Thermodynamics

Chapter 6

The second law of thermodynamics

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Chapter 7

The Carnot cycle and the thermodynamic temperature scale

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Chapter 8
Entropy