

Kinetic Theory of Gases

Thermodynamics

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Zeroth law of thermodynamics

Reversible and Irreversible processes

First law of Thermodynamics

Second law of Thermodynamics

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Third Law of Thermodynamics

Phase diagram

- Thermodynamics is about MACROSCOPIC properties.
- The various properties that can be quantified without disturbing the system eg internal energy  $U$  and  $V$ ,  $P$ ,  $T$  are called state functions or state properties.
- Properties whose absolute values are easily measured eg.  $V, P, T$  are also called state variables.
- Relations between state functions for a particular system are called the equation of state of the system.
- Ideal gas:  $PV=NRT$

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- The State of a system is defined by its state variables, e.g.  $P$ ,  $T$ ,  $V$ .
- When a system is involved in a process, the values of its state functions (variables) change.
- A process typically involves quantities like Heat and Work which are not state variables.
- There are two kinds of processes - Reversible and Irreversible.
- Reversible Process: when every step for the system and its surroundings can be reversed.
- Irreversible Process - when the direction of the arrow of time is important. Brings in concept of time.

## Reversible Process

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- Consider a process between equilibrium endpoints (starting point and finishing point) e.g the compression of gas by a piston from state  $(P_1, V_1)$  to state  $(P_2, V_2)$ .
- For a reversible process, every (infinitesimal) step – for both the system and its surroundings – can be reversed.
- If you video record the process and you played it backwards, it would not look strange.
- The system goes through a sequence of equilibrium states, which implies that a reversible process is quasistatic.
- Reversible processes are quasistatic processes where no dissipative forces such as friction are present.

## Work done during a reversible change of volume of a fluid

- Consider the response of a system of gas particles to a gradual change in force on a piston [or to slow heating (a change in temperature)].
- The force on the piston = area  $A$  of the piston multiplied by the pressure  $P$  of the fluid.  $F = PA$ .
- The fluid expands or contracts quasistatically, with the piston moving infinitesimal distances  $dx$  much more slowly than the time the system take to reach equilibrium at the new volume.
- The infinitesimal amount of work done reversibly by the system on its surroundings is  $PAdx = PdV$  .
- For a finite quasistatic change in volume from  $V_1$  to  $V_2$ , the total work done on the surroundings  $= \int_{V_1}^{V_2} PdV$  .

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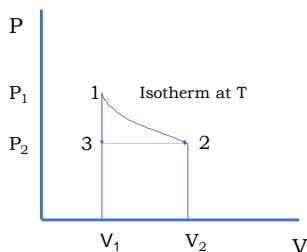
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## The total work done depends on the process even for reversible changes



- Work is the area under the graph on a PV diagram.
- For an ideal gas, work done moving from equilibrium state  $(P_1, V_1, T_1)$  to  $(P_2, V_2, T_2)$  depends on the process.
- Suppose  $T_2 = T_1 = T$ . For an isothermal expansion the work done is given by  $nRT \ln(V_2/V_1)$ ; path 1-2 (isothermal) in the sketch.
- path 1-3-2, a different amount of work is done given by:  
$$\int_{V_1}^{V_2} P dV = 0 + \int_{V_1}^{V_2} P_2 dV = P_2(V_2 - V_1)$$

# Sign Convention

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In physics we are generally interested in changes of the system and therefore consider work to be defined as the work done **ON** the system by its surroundings.

Hence for a reversible change of volume of a system consisting of a fluid,  $dW = - PdV$ .

If  $dV$  is negative, the gas is compressed and the work done on it,  $-PdV$ , is positive

The work done **on** the system is always equal and opposite to the work done **by** the system.

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Unlike for a reversible process where we can specify  $dW = -PdV$ , it is not possible to specify work done in terms of state variables of the system for dissipative processes, eg **stirring**.

Although the work done may be quantified, this requires knowledge of external forces. Reversing the process, via controlling the surroundings, does not reverse the sign of the work done eg reversing the direction of stirring does not extract energy from the system.

Therefore dissipative processes implies irreversible.

Irreversible processes where there is no direct dissipation (conversion of work into random motion) can also occur eg the irreversible flow of heat between bodies at different temperatures.

Friction - Work done becomes heat - irreversible

Dissipation - Work done becomes heat - irreversible

## Some Mathematics of State Variables and Exact Differentials

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- Let  $\phi$  be a function of  $x$  and  $y$  such that whatever the values of  $x$  and  $y$ ,  $\phi = \phi(x,y)$  has a unique value.
- An infinitesimal change  $d\phi = \left(\frac{\partial\phi}{\partial x}\right)_y dx + \left(\frac{\partial\phi}{\partial y}\right)_x dy$  is then, by definition, an exact differential since it is the complete differential of an exactly defined function.
- Let  $x$  change from  $x_1$  to  $x_2$ , and  $y$  change from  $y_1$  to  $y_2$ . The finite change in  $\phi$  is then  $\Delta\phi = \phi(x_2, y_2) - \phi(x_1, y_1) = \int_{x_1, y_1}^{x_2, y_2} d\phi$ .
- So  $\Delta\phi$  is known exactly from the unique values of  $\phi$  at the points  $(x_1, y_1)$  and  $(x_2, y_2)$ , whatever the values of  $x$  and  $y$  along the integration path. The integral is **path-independent**. The value of  $\phi$ , depends only on the final state.



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- The defining mathematical property of such a state variable is that the second derivative is independent of the order of differentiation
- $$\frac{\partial^2 \phi}{\partial x \partial y} = \frac{\partial^2 \phi}{\partial y \partial x}$$
- **State variables in thermodynamics have path-independent integrals.**
- This is an incredibly useful result. If we want to know the change in a state variable due to some process, we can find it by considering any other process between the same start and end point. So we can choose a process which gives us an easy integral to solve.

## Work is not a state function

- Consider work, defined by  $dW = -PdV$ .
- If work were an exact derivative, there must be a function  $W(P,V)$  such that:  $dw = \left(\frac{\partial W}{\partial P}\right)_V dP + \left(\frac{\partial W}{\partial V}\right)_P dV$
- $\left(\frac{\partial W}{\partial P}\right)_V = 0$  and  $\left(\frac{\partial W}{\partial V}\right)_P = -P$ .
- Again differentiating:  $\frac{\partial}{\partial V} \left(\left(\frac{\partial W}{\partial P}\right)_V\right)_P = 0$  and  $\frac{\partial}{\partial P} \left(\left(\frac{\partial W}{\partial V}\right)_P\right)_V = -1$ .
- Clearly  $dW$  is not an exact differential, and no state function with total derivative  $dW$  can exist.
- To find the finite work done going between two states, we must specify the path, i.e. the trajectory of  $(P,V)$  on the indicator diagram.

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## Reciprocal & Cyclic rules

- Suppose we have a function  $z(x, y)$ .
- We can write  $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$
- Similarly,  $dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$
- Substituting one into the other gives.  $[1 - \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y] dz = \left[\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x\right] dy$ .
- As  $dy$  and  $dz$  are independent and arbitrary, both the coefficients must be zero.
- Reciprocal rule:  $\frac{1}{\left(\frac{\partial z}{\partial x}\right)_y} = \left(\frac{\partial x}{\partial z}\right)_y$
- Cyclic rule:  $\left(\frac{\partial z}{\partial y}\right)_x = - \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z$
- The cyclic rule warns us of the danger of dropping from the notation the symbols showing which variables are held constant. We might be tempted to 'cancel'  $\partial x$  from both numerator and denominator on the RHS of cyclic rule, but this is only allowed if the same variables are held constant in both functions, which is not the case.

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## Question

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- The state of a compressible fluid is changed reversibly and infinitesimally from  $(P, T)$  to  $(P + \Delta P; T + \Delta T)$ . How much does the volume change ?
- Write the problem as an integral in the form that gives the state function whose change we wish to find, as a differential in terms of the state variables whose changes are given
- $V = V(P, T) \implies dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$
- Identify the partial derivatives. e.g. the volume thermal expansivity  $\beta$  and isothermal bulk modulus  $K$  are defined in differential form as,  $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$  and  $K = -V \left(\frac{\partial P}{\partial V}\right)_T$
- Expressing the differentials in terms of standard definitions of properties,  $\Delta V = \int dV = - \int \frac{V}{K} dP + \int \beta V dT$ .
- $\beta$  and  $K$  depends on material, let us take it as constants.

## Question

- Because  $V = V(T,P)$  is a state variable, we can do the integral along any path.
- For simplicity, choose a reversible two-stage path which first goes isothermally from  $P$  to  $P + \Delta P$ , then isobarically from  $T$  to  $T + \Delta T$ .
- For stage 1,  $dT = 0$  and let  $V \rightarrow V_1$ .  $\int \frac{1}{V} dV = - \int \frac{1}{K} dP \implies \ln(V_1/V) = - \Delta P/K$ .
- For stage 2,  $dP = 0$  and let  $V_1 \rightarrow V + \Delta V$ .  $\int \frac{1}{V} dV = - \int \beta dT \implies \ln((V + \Delta V)/V_1) = - \beta/\Delta T$ .
- Cancelling the  $V_1$  for total change:  $V + \Delta V = V \text{Exp}(- \Delta P/K) \text{Exp}(\beta T)$
- Note that had we done the isobaric process before the isothermal one, the answer would have come out the same. If we had considered an irreversible path, the answer would still be the same even though the integral isn't defined for an irreversible process.

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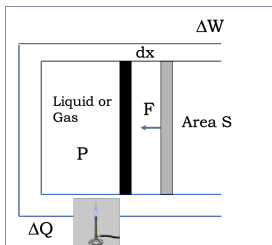
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# Internal energy, Heat and Work



- There are **two** ways to change the internal energy of a system keeping fixed mole number (constrained).
- 1. Work -  $\Delta W$  - Work done by external forces on the system, allows energy to be transferred via its macroscopic degrees of freedom. 2. Heat -  $\Delta Q$  - Transfer of energy by means of heat directly to the system by microscopic degrees of freedom.
- Example:  $F = \text{Force}$ ,  $S = \text{Area of the piston}$  and  $P = \text{Pressure}$ ;  
 $\Delta W = - Fdx = - PSdx = - PdV$

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- Conservation of energy :  $\Delta U = \Delta Q + \Delta W = \Delta Q - PdV$
- U - extensive thermodynamic variable. W & Q are not thermodynamic variables as a state of a system cannot be characterised by W & Q. W& Q depends on the history/process.
- $\Delta W = -PdV$  - the sign is chosen in such a way that the applied work is positive, energy of the system increases. Work performed by the system means a decrease of its internal energy and is therefore defined negative.

## First Law

The sum of the external heat  $\Delta Q$  applied to a thermodynamic system, and the supplied mechanical energy  $\Delta W$  is equal to the increase  $\Delta U$  in the internal energy:  $\Delta U = \Delta Q + \Delta W$

- Special case of conservation of energy.
- When a system performs work against an external force,  $\Delta W < 0$  and therefore  $\Delta U < 0$
- Many inventors have tried to develop machines that deliver more energy than they consume. Then they can consume a part of their delivered energy to run its operation. Then they could run **perpetually** - called Perpetuum mobile of the first kind (Why first kind as it contradicts first law of thermodynamics).
- Sometimes first law in a popular way is stated - **A perpetuum mobile of first kind is impossible**. This though cannot be mathematically proved, solely based on empirical knowledge.



## Ideal gas during expansion

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- Conservation of energy :  $dU = dQ + dW = dQ - PdV$
- $dV > 0$  : If the system expands (releases energy)  $\implies dU < dQ$  - that is the loss of internal energy cannot be compensated by the supplied heat.
- $dV < 0$  : If the system is compressed (gains energy)  $\implies dU > dQ$  - that is the gain of internal energy is larger than the supplied heat.
- This discussion shows that the state of the system does change with the supply of heat  $dQ$ . But one cannot unambiguously determine the final state of the system as either  $U$  or  $V$  or both variables can change. Hence  $Q$  is not a thermodynamic variable.  $dQ$  is not a complete differential.