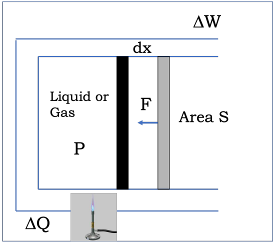
Question

- The state of a compressible fluid is changed reversibly and infinitesimally from (P, T) to (P + ΔP; T + ΔT). 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) $\Longrightarrow \mathrm{d}V = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$
- Identify the partial derivatives. e.g. the volume thermal expansivity β and isothermal bulk modulus K are defined in differential form as, $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and $K = -\mathrm{V}\left(\frac{\partial P}{\partial V}\right)_T$
- Expressing the differentials in terms of standard definitions of properties, $\Delta V = \int dV = -\int \frac{V}{K} dP + \int \beta V dT$.
- β 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 + ΔP, then isobarically from T to T + ΔT.
- For stage 1, dT = 0 and let V → V_1. $\int \frac{1}{V} dV$ = - $\int \frac{1}{K} dP \Longrightarrow$ ln(V_1/V) = - ΔP/K.
- For stage 2, dP = 0 and let $V_1 \rightarrow V + \Delta V$. $\int \frac{1}{V} dV = \int \beta dT \Longrightarrow \ln((V + \Delta V)/V_1) = \beta \Delta T$.
- Cancelling the V_1 for total change: $V + \Delta V$ = V Exp(- ΔP/K) Exp(β Δ 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.

Internal energy, Heat and Work



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

Internal energy, Heat and Work

- 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 of Thermodynamics

First Law

The sum of the external heat ΔQ applied to a thermodynamic system, and the supplied mechanical energy ΔW is equal to the increase ΔU 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 Perpetumm 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 perpetumm mobile of first kind is impossible.** This though cannot be mathematically proved, solely based on empirical knowledge.

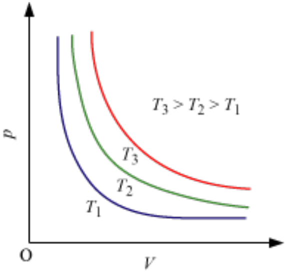
Ideal gas during expansion

- Conservation of energy : $dU = dQ + dW = dQ$ - PdV
- $dV > 0$: If the system expands (releases energy) $\Longrightarrow dU < dQ$ - that is the loss of internal energy cannot be compensated by the supplied heat.
- $dV < 0$: If the system is compressed (gains energy) $\Longrightarrow$ $dU > dQ$ - 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.

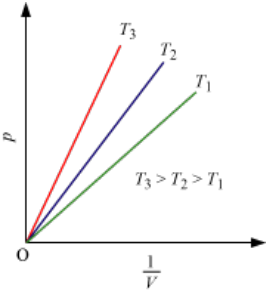
First Law Examples

- Isochoric process (V = constant) : $dV = 0$.
- $dQ = dU = C_V dT$
- Heat supplied to the system is solely used for the increase in the internal energy.
- Therefore Specific Heat : $C_V = \left(\frac{\partial U}{\partial T}\right)_V$
- Isobaric process (P = constant)
- $dQ = dU + \mathrm{P}\ dV = C_p dT$
- Define a new quantity - Enthalpy : $\mathrm{H} = \mathrm{U} + \mathrm{PV} \Longrightarrow dH = dU + \mathrm{P}dV + \mathrm{V}dP = dQ + \mathrm{V}dP$.
- First law of thermodynamics for an isobaric process ($dP = 0$) can be written as $dH = dU + \mathrm{P}dV = dQ$. Enthalpy is equal to supplied Heat. H is often used for phase changes, chemical reactions or process where P is constant and V changes.
- Therefore Specific Heat at constant pressure : $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

Isotherms



p vs V graph

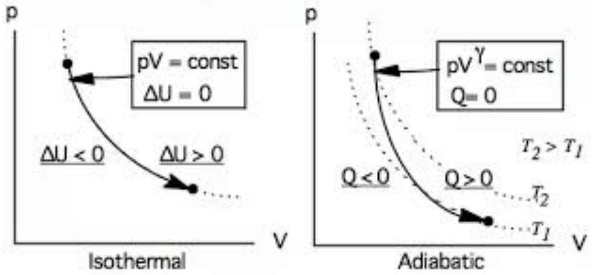


p vs $\frac{1}{V}$ graph

First Law Examples contd

- Isothermal process (T = constant)
- As internal energy per mole of a gas depends on T and not on P or V, for isothermal process U = constant, i.e $dU = 0$.
- $dQ = PdV$.
- External heat energy dQ supplied to the system is completely transferred to the work done PdV that the system releases to outside.
- The systems internal energy does not change.
- Boyle-Marrioty Law : P V = RT. Isothermal : PV = Contant $\implies P = \frac{Constant}{V}$
- How large is the work that a system has to perform for an isothermal expansion of volume V_1 to $V_2 > V_1$.
- $W = - \int_{V_1}^{V_2} PdV = - R\ T \int_{V_1}^{V_2} \frac{dV}{V} = - R\ T\ Ln\ \frac{V_2}{V_1} = R\ T\ Ln\ \frac{V_1}{V_2}$

P vs. V


p
pV = const
ΔU = 0
ΔU < 0
ΔU > 0
V
Isothermal
p
pV^γ = const
Q = 0
T_2 > T_1
Q < 0
Q > 0
T_2
T_1
V
Adiabatic

First Law Examples contd

- Adiabatic process ($dQ = 0$)
- dU = -PdV = $C_V\ dT$.
- P = $\frac{RT}{V} \implies C_V\ \frac{dT}{T}$ = - R $\frac{dV}{V}$
- Integrate: C_V ln T = - R ln V + Constant (We know that R = C_P - C_V).
- $\implies$ ln $(T^{C_V} V^R)$ = Constant = ln $(T^{C_V} V^{C_P - C_V}) \implies T^{C_V} V^{C_P - C_V}$ = Constant
- If κ = adiabatic index = $\frac{C_P}{C_V}$, then $TV^{\kappa-1}$ = constant $\implies PV^{\kappa}$ = Constant as T = $\frac{PV}{R}$
- $\kappa = \frac{f+2}{f}$; f = degrees of freedom. Ideal gas f = 3, N_2 f = 5.... so on.
- Example: In a pneumatic cigarette lighter, the volume V filled with an air-benzene mixture is suddenly compressed to 0.1 V. T rises from room temperature 293 K (T_1) to $T_2 = T_1$ $(V_1/V_2)^{\kappa-1}$. For Air - $\kappa = 7/5$. So T_2 = 736 K ≈ 463 degree Celsius - greater than ignition temperature of the air-benzene mixture.

Second Law

- The first law dealt with the energy conservation and how thermal energy is converted to mechanical energy.
- The second law gives the maximum fraction of the thermal energy that can be really transferred into mechanical energy.

Second Law of thermodynamics

Based on experimental experience: Heat flows by its own only from the warmer body to the colder one, never into the opposite direction.

A quantitative formulation requires understanding of transformation of heat into mechanical work. Hence requires understanding of **thermodynamic cyclic process**.