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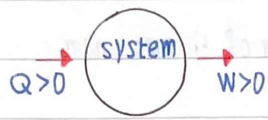
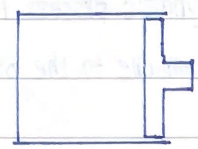
The First Law of Thermodynamics



Work Done During Volume Changes



$dW = F\,dx \qquad A\,dx = dV$

$\Rightarrow dW = P\,dV$

$\Rightarrow W = \int_{V_1}^{V_2} P\,dV = nRT\int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1}$

Paths Between Thermodynamic States

work done by the system depends not only on the initial and final states, but also on the intermediate states-path

experiments have shown when an ideal gas undergoes a free expansion, there is no temperature change

heat depends only on the initial and final states but also on the path

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Internal Energy and the First Law of Thermodynamics

$$U_2 - U_1 = \Delta U = Q - W$$ first law of thermodynamics

$$Q = \Delta U + W$$

while Q and W depend on the path, $\Delta U = Q - W$ is independent of path

the change in internal energy of a system during any thermodynamic process depends only on the initial and final states, no on the path leading from one to the other

the internal energy of ideal gas only depends on the temperature

$$F(U,V,T)=0$$

$$dF = \frac{\partial F}{\partial U}dU + \frac{\partial F}{\partial V}dV + \frac{\partial F}{\partial T}dT = 0$$

if V is fixed, then $dV=0$

$$dF = \frac{\partial F}{\partial U}dU + \frac{\partial F}{\partial T}dT = 0, \quad \left(\frac{\partial U}{\partial T}\right)_V = -\frac{\left(\frac{\partial F}{\partial T}\right)_{U,V}}{\left(\frac{\partial F}{\partial U}\right)_{V,T}} \quad \left(\frac{\partial T}{\partial U}\right)_V = -\frac{\left(\frac{\partial F}{\partial U}\right)_{V,T}}{\left(\frac{\partial F}{\partial T}\right)_{U,V}}$$

thus, $\left(\frac{\partial U}{\partial T}\right)_V = -\frac{1}{\left(\frac{\partial T}{\partial U}\right)_V}$

if T is fixed, then $dT=0$

$$dF = \frac{\partial F}{\partial U}dU + \frac{\partial F}{\partial V}dV = 0, \quad \left(\frac{\partial V}{\partial U}\right)_T = -\frac{\left(\frac{\partial F}{\partial U}\right)_{V,T}}{\left(\frac{\partial F}{\partial V}\right)_{U,T}}$$

if $dU=0$

$$dF = \frac{\partial F}{\partial T}dT + \frac{\partial F}{\partial V}dV = 0, \quad \left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial F}{\partial V}\right)_{U,T}}{\left(\frac{\partial F}{\partial T}\right)_{U,V}}$$

$$\Rightarrow \left(\frac{\partial V}{\partial U}\right)_T \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U = -1, \quad \left(\frac{\partial U}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U$$

according to Joule experiment, $\left(\frac{\partial T}{\partial V}\right)_U = 0 \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0$

for non-ideal gas $\left(\frac{\partial T}{\partial V}\right)_U \neq 0$

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a process that eventually returns a system to its initial state is called a cyclic process

$U_1 = U_2 \Rightarrow Q = W$

isolated system : one that does no work on its surroundings and has no heat flow to or from its surroundings

$W = Q = 0$, $\Delta U = 0$

$dU = dQ - dW = dQ - PdV$

Kinds of Thermodynamic Processes

adiabatic process

no heat transfer into or out of a system : $Q = 0$

$\Delta U = -W$

isochoric process (isovolumetric)

constant-volume process $\Rightarrow$ it does no work on its surroundings $\Rightarrow W = 0$

$\Delta U = Q$

isobaric process

constant-pressure process

$W = P(V_2 - V_1)$

isothermal process

constant-temperature process

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Heat Capacities of an Ideal Gas

C_V molar heat capacity at constant volume

C_p molar heat capacity at constant pressure

$dQ = nC_V\,dT = dU$ due to $dW=0$

$dQ = nC_p\,dT$ and $dW = PdV = nR\,dT \Rightarrow nC_p dT = dU + nRdT$

$= nC_V dT + nRdT$

$\Rightarrow C_p = C_V + R$

ratio of heat capacities $\gamma = \frac{C_p}{C_V} = \frac{C_V+R}{C_V} = 1 + \frac{R}{C_V}$

$$C_V = \left[\frac{dQ}{dT}\right]_V = \left[\frac{dU + PdV}{dT}\right]_V = \left[\frac{\partial U}{\partial T}\right]_V$$

$$C_p = \left[\frac{dQ}{dT}\right]_p = \left[\frac{dU+PdV}{dT}\right]_p = \left[\frac{\partial U}{\partial T}\right]_p + P\left[\frac{\partial V}{\partial T}\right]_p$$

$\because H = U + PV,\ \Delta H = \Delta U + P\Delta V$

$$= \left[\frac{\partial H}{\partial T}\right]_p$$

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Adiabatic Processes for an Ideal Gas

$\Delta Q = 0$, $\Delta U = \Delta Q - \Delta W \Rightarrow \Delta U = -\Delta W = -P\Delta V \Rightarrow nC_v\,dT = -PdV$

① $nC_v dT = -\frac{nRT}{V}dV \longrightarrow \frac{C_v}{R}\frac{dT}{T} = -\frac{dV}{V}$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$\frac{1}{\gamma-1}\frac{dT}{T} = -\frac{dV}{V}$

$\frac{dT}{T} + \frac{R}{C_v}\frac{dV}{V} = 0$ and $\frac{R}{C_v} = \gamma - 1$

$\frac{dT}{T} + (\gamma-1)\frac{dV}{V} = 0$

$\Rightarrow \ln T + (\gamma-1)\ln V = \text{constant}$

$\Rightarrow \ln T + \ln V^{\gamma-1} = \text{constant}$

$\Rightarrow \ln(TV^{\gamma-1}) = \text{constant}$

$\Rightarrow T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$\Rightarrow \frac{PV}{nR}V^{\gamma-1} = C_2$

$\Rightarrow PV^{\gamma} = C_3$

$\Rightarrow P_1V_1^{\gamma} = P_2V_2^{\gamma}$

$\downarrow$

$\frac{1}{\gamma-1}\ln T = -\ln V + C$

$\ln T^{\frac{1}{\gamma-1}} + \ln V = C$

$T^{\frac{1}{\gamma-1}}V = e^C = C_1$

$(T^{\frac{1}{\gamma-1}}V)^{\gamma-1} = C_1^{\gamma-1} = C_2 = TV^{\gamma-1}$

$\frac{PV}{nR}V^{\gamma-1} = C_2$

$PV^{\gamma} = nRC_2 = C_3$

$PP^{-\gamma}P^{\gamma}V^{\gamma} = P^{1-\gamma}(nRT)^{\gamma}$

$\Rightarrow P^{1-\gamma}T^{\gamma} = C_4$

② $PV = nRT$ total differention

$\Rightarrow PdV + VdP = nRdT$

$\div PV$ $PdV + VdP = -\frac{R}{C_v}dT$

$\frac{dV}{V} + \frac{dP}{P} = -\frac{C_p - C_v}{C_v}\frac{dV}{V} = (1-\gamma)\frac{dV}{V}$

$\Rightarrow \frac{dP}{P} + \gamma\frac{dV}{V} = 0$

$\Rightarrow \ln P + \gamma\ln V = \text{constant}$, $PV^{\gamma} = \text{constant}$

$P_f = C_3V^{-\gamma}$

$\Delta U = -\Delta W = \int PdV = \int \frac{C_3}{V^{\gamma}}dV = \frac{C_3}{\gamma-1}V^{1-\gamma}\Big|_{V_i}^{V_f} = \frac{1}{\gamma-1}(V_fP_f - V_iP_i)$

$= \frac{1}{\gamma-1}nR(T_f - T_i) = nC_v(T_f - T_i)$