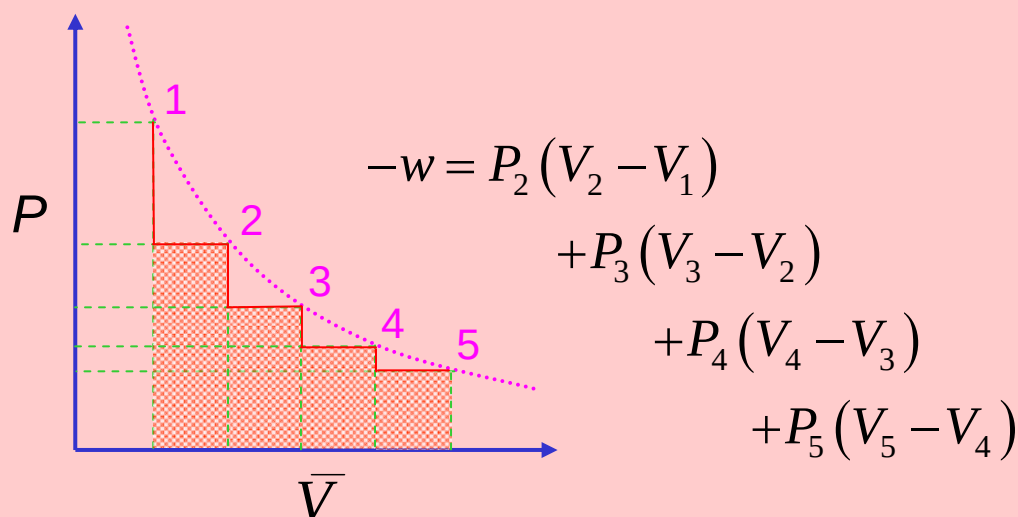


Pressure–Volume Work 2

Multi-stage Expansion



Reversible Expansion

Make steps so small that

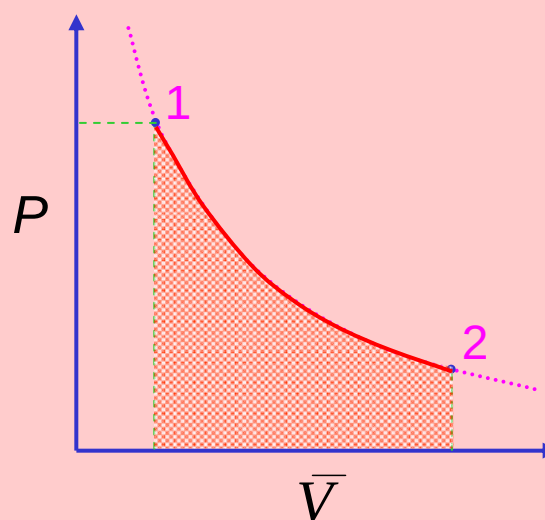
$$dP \rightarrow 0, dV \rightarrow 0$$

Then $-\delta w = P_{\text{ex}} dV$

$$= (P_{\text{int}} + dP) dV$$

$$\rightarrow P_{\text{int}} dV$$

$$w = \int_{\text{path}} dw = - \int_1^2 P_{\text{int}} dV$$



For ideal gases $P_{\text{int}} = nRT / V$

and at fixed temperature $w_{\text{rev}} = -nRT \ln \left(\frac{V_2}{V_1} \right) = nRT \ln \left(\frac{P_2}{P_1} \right)$

Heat Capacity

Transfer of heat to a system *may* result in a rise in T .

$$\delta q = CdT$$

↗ path function, so C depends on conditions.

Define: $\delta q_V = C_V dT$ at constant volume, *no* work

$\delta q_P = C_P dT$ at constant pressure, *only* PV work

From 1st Law, $dU = \delta q + \delta w = \delta q - P_{\text{ex}} dV$

assume no
other work

$$dU = \delta q_V \quad \text{for } dV = 0$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Similarly

$$\begin{aligned} dH &= dU + PdV - VdP \\ &= (\delta q - PdV) + PdV - VdP \\ &= \delta q_P \quad \text{for } dP = 0 \end{aligned}$$

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

For ideal gases $dH = dU + d(PV) = dU + nRdT$

$$C_P dT = C_V dT + nRdT$$

$$\bar{C}_P = \bar{C}_V + R$$

The Relation Between C_P and C_V

$$C_P - C_V = \left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V$$

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

$H = U + PV$

But since

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

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

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

work needed to overcome

intermolecular forces

expansion

per degree

$$\left(\frac{\partial U}{\partial V} \right)_T = \text{“internal pressure”}$$

For ideal gases

$$\left(\frac{\partial U}{\partial V} \right)_T = 0, \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} \Rightarrow C_P - C_V = nR$$

For liquids and solids

$$\left(\frac{\partial V}{\partial T} \right)_P \text{ is so small that } C_P \approx C_V$$

Adiabatic Expansion 2

Reversible adiabatic expansion of ideal gases:

$$dU = \delta w$$

$$\delta q = 0$$

$$C_V dT = -PdV = -\frac{nRT}{V} dV$$

ideal gases only

$$\bar{C}_V \int_1^2 \frac{1}{T} dT = -R \int_1^2 \frac{1}{V} dV$$

$$\begin{aligned} \bar{C}_V \ln(T_2/T_1) &= -R \ln(V_2/V_1) \\ &= -(\bar{C}_P - \bar{C}_V) \ln(V_2/V_1) \end{aligned}$$

$$\ln(T_2/T_1) = -(\gamma - 1) \ln(V_2/V_1)$$

$$\gamma = \frac{\bar{C}_P}{\bar{C}_V}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

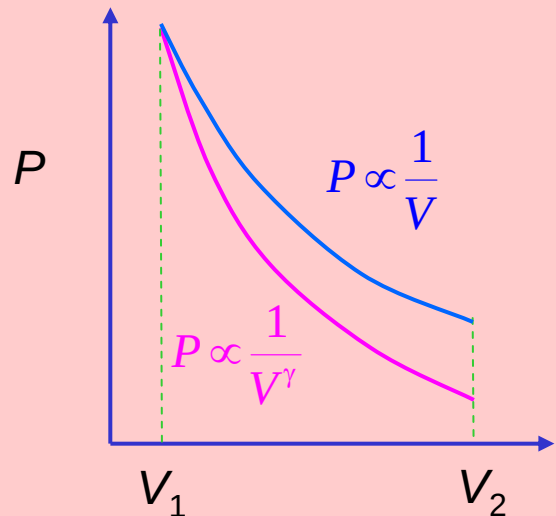
Also, since

$$\frac{P_2 V_2}{P_1 V_1} = \frac{T_2}{T_1}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{\gamma}$$

or $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma}$$



The Clausius Inequality

Given $dS = \frac{\delta q_{\text{rev}}}{T}$ and $\delta w_{\text{rev}} = -PdV$

Substitute into the 1st Law:

$$dU = TdS - PdV$$

Fundamental Equation
of Thermodynamics

All exact differentials, so path independent.

But $dU = \delta q + \delta w = \delta q - P_{\text{ex}} dV$
 $TdS - PdV = \delta q - P_{\text{ex}} dV$

In general,
i.e. any path

$$\Rightarrow dS = \frac{\delta q}{T} + \frac{(P - P_{\text{ex}})}{T} dV$$

If $P > P_{\text{ex}}$, $dV > 0$; if $P < P_{\text{ex}}$, $dV < 0$

$$\therefore (P - P_{\text{ex}})dV \geq 0$$

Clausius Inequality

$$dS \geq \frac{\delta q}{T}$$

Equal for
reversible
change

Even more generally,

$$dS_{\text{univ}} = \left(\frac{T - T_{\text{surr}}}{T} \right) dS_{\text{surr}} + \frac{(P - P_{\text{surr}})}{T} dV$$

Conditions for: thermal equilibrium mechanical equilibrium

The Fundamental Equation of Thermodynamics

Combine $dU = \delta q - PdV$ with $dS = \frac{\delta q_{\text{rev}}}{T}$

Reversible change but true for all paths since dV exact

$$\Rightarrow dU = TdS - PdV$$

$$\text{or } dS = \left(\frac{1}{T}\right)dU + \left(\frac{P}{T}\right)dV$$

This fundamental equation generates many more relationships.

Example 1: Comparison with $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

$$\Rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Example 2: Consider that dU is exact and cross differentiate.

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

a Maxwell relation

Example 3: $\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial S}{\partial T}\right)_V$ cyclic rule

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

and again!

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

$$= \alpha / \kappa$$

How Entropy Depends on T and V

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV$$

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

$$\Rightarrow dS = \frac{C_V}{T} dT + \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right] dV$$

Compare with $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\Delta S_V = \int \frac{C_V}{T} dT$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

0 for ideal gases

$$\begin{aligned} \Delta S_T &= \int \frac{P}{T} dV = nR \int \frac{1}{V} dV \\ &= nR \ln(V_2 / V_1) \end{aligned}$$

For any substance, $dS = \frac{C_V}{T} dT + \frac{\alpha}{\kappa} dV$

For ideal gases, $\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$
(eqs 3.7.4, 6.1.6)

assuming C_V is
 T independent

Entropy Depends on T and P (not in text)

$$dS = \left(\frac{1}{T}\right)dU + \left(\frac{P}{T}\right)dV$$

First problem: replace dU ; second problem: replace dV .

Use $dU = dH - PdV - VdP$ and both are solved!

$$dS = \left(\frac{1}{T}\right)dH - \left(\frac{V}{T}\right)dP$$

But
$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\Rightarrow dS = \frac{C_P}{T} dT + \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right] dP$$

Compare with $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$ unnatural variables

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\Delta S_P = \int \frac{C_P}{T} dT$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

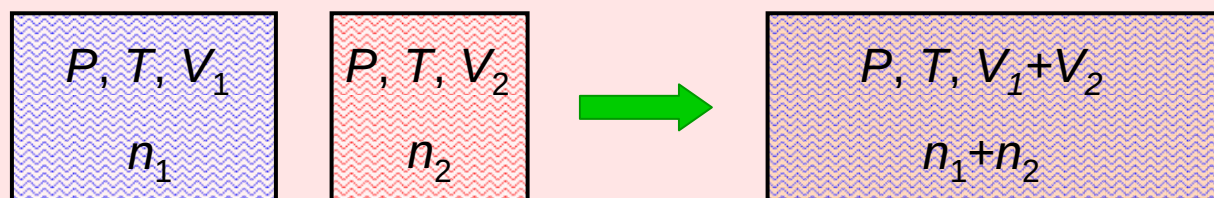
0 for ideal gases

$$\Delta S_T = - \int \frac{V}{T} dP = -nR \int \frac{1}{P} dP$$

$$\Delta S_T = -nR \ln(P_2 / P_1) = nR \ln(V_2 / V_1)$$

Entropy of Mixing

❖ Consider the mixing of two ideal gases :



$$\Delta S_1 = -n_1 R \ln \frac{V_1}{V_1 + V_2} = -n_1 R \ln \frac{n_1}{n_1 + n_2} = -n_1 R \ln \chi_1$$

$$\Delta S_2 = -n_2 R \ln \frac{V_2}{V_1 + V_2} = -n_2 R \ln \frac{n_2}{n_1 + n_2} = -n_2 R \ln \chi_2$$

$$\Delta S_{\text{mix}} = -n_1 R \ln \chi_1 - n_2 R \ln \chi_2 = -(n_1 + n_2) R (\chi_1 \ln \chi_1 + \chi_2 \ln \chi_2)$$

In general

$$\Delta S_{\text{mix}} = -n_{\text{tot}} R \sum_i \chi_i \ln \chi_i$$

This expression applies to the arrangement of objects (molecules) just as well as fluids (gases and liquids).

For example, arrange N identical atoms in N sites in a crystal:

$$\Omega = N! / N! = 1 \quad S = k \ln \Omega = 0$$

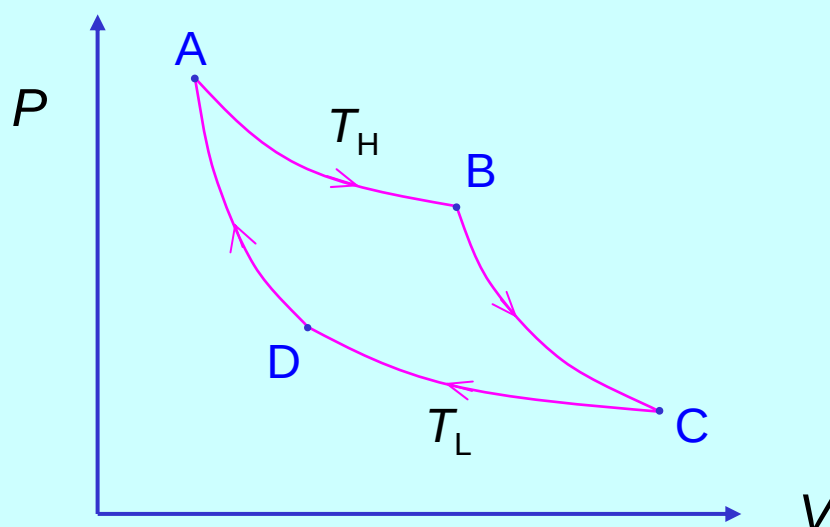
Compare with the arrangement of two types of atom, A and B.

$$\Omega = \frac{N!}{N_A! N_B!} \quad \Delta S = k (\ln N! - \ln N_A! - \ln N_B!)$$

Application of Stirling's approximation $\ln(z!) = z \ln z - z$

leads to $\Delta S_{\text{config}} = -kN (\chi_A \ln \chi_A + \chi_B \ln \chi_B)$

The Carnot Cycle



step	w	q	ΔU
$A \rightarrow B$	$-nRT_H \ln(V_B / V_A)$	$-w_{AB}$	0
$B \rightarrow C$	ΔU_{BC}	0	$-C_V(T_H - T_L)$
$C \rightarrow D$	$-nRT_L \ln(V_D / V_C)$	$-w_{CD}$	0
$D \rightarrow A$	ΔU_{DA}	0	$C_V(T_H - T_L)$
Total	$nR(T_H - T_L) \ln(V_A / V_B)$	$-w_{\text{cyc}}$	0

$$\varepsilon = \frac{w_{\text{out}}}{q_{\text{in}}} = \frac{nR(T_H - T_L) \ln(V_A / V_B)}{nRT_H \ln(V_A / V_B)} = 1 - \frac{T_L}{T_H}$$

$$\varepsilon = \frac{(T_H - T_L)}{T_H}$$

for best efficiency,
maximize T_H
minimize T_L

How Free Energy Depends on T

$$G = H - TS \quad \dots(1) \quad \text{definition}$$

$$\Delta G = \Delta H - T \Delta S \quad \dots(2) \quad \text{constant } T$$

$$dG = VdP - SdT \quad \dots(3) \quad \text{fundamental eqn.}$$

$$\left(\frac{\partial G}{\partial T} \right)_P = -S = \frac{G - H}{T} \quad \text{from (1)}$$

$$\therefore \left(\frac{\partial G}{\partial T} \right)_P - \frac{G}{T} = -\frac{H}{T} \quad \dots(4)$$

$$\text{But} \quad \left(\frac{\partial(G/T)}{\partial T} \right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P - \frac{G}{T^2} \quad \dots(5)$$

Gibbs-Helmholtz
Equation

$$\left(\frac{\partial(G/T)}{\partial T} \right)_P = -\frac{H}{T^2}$$

substitute
(4) in (5)

alternative form:

$$\left(\frac{\partial(G/T)}{\partial(1/T)} \right)_P = H$$

By applying the Gibbs-Helmholtz equation to both reactants and products of a chemical reaction,

$$\Rightarrow \left(\frac{\partial(\Delta G/T)}{\partial T} \right)_P = -\frac{\Delta H}{T^2}$$

How Free Energy Depends on P

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

$$\Delta G = G_2 - G_1 = \int_1^2 V dP$$

For solids and liquids V does not change much with P , so

$$G_2(T) \approx G_1(T) + V(P_2 - P_1)$$

For a perfect gas $V = \frac{nRT}{P}$

$$\Delta G_T = nRT \ln(P_2 / P_1)$$

$$G = G^\circ(T) + nRT \ln(P / P^\circ)$$

where G° is the standard free energy defined at $P^\circ=1$ bar

The chemical potential for a pure substance is the molar Gibbs energy:

$$\mu = \bar{G} = \frac{G}{n}$$

$\therefore$ For a perfect gas

$$\mu = \mu^\circ + RT \ln(P / P^\circ) \quad \text{like eq 5.3.5}$$