

Chapter 5:

Simple applications of macroscopic thermodynamics

Zhi-Jie Tan

Wuhan University

2019 spring semester

- Important relationships between macroscopic quantities
- Based on the fundamental thermodynamic laws (0th, 1st, 2nd, 3rd)
- Quantities such as p , E always are mean values

Independent variables:

- Most of systems only have the external para V ;
- two independent variables can specify the system, such as E and V ; or E and P ; or T and V ... Other variables can be determined by the two independent variables;

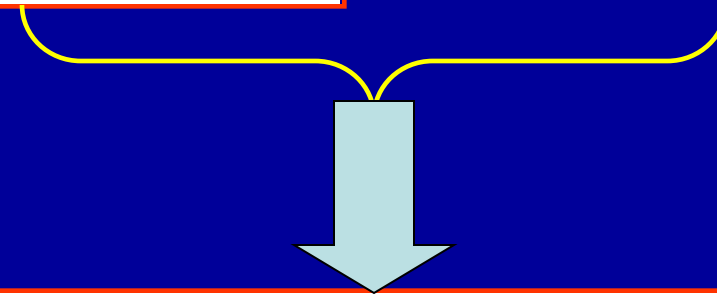
Fundamental equations:

1st law

$$dQ = dE + dW$$

2nd law

$$dQ = T dS$$



$$T dS = dE + p dV$$

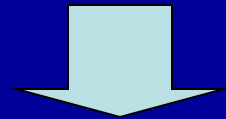
Properties of ideal gas

5.1 Equation of state and internal energy



$$pV = \nu RT$$

$$\begin{aligned}\Omega &\propto V^N \chi(E) \\ \beta &= \frac{\partial \ln \chi(E)}{\partial E} \\ \beta &= \beta(E)\end{aligned}$$



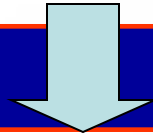
$$E = E(T) \quad \text{independent of } V$$

Properties of ideal gas

5.1 Equation of state and internal energy

Generally,

$$E = E(T, V)$$

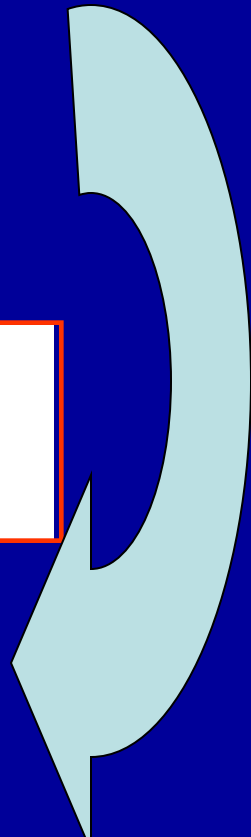


$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

Fundamentally,

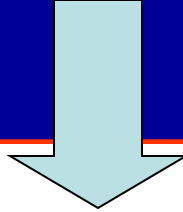
$$T dS = dQ = dE + p dV$$

$$dS = \frac{1}{T} dE + \frac{pR}{V} dV$$



Properties of ideal gas

5.1 Equation of state and internal energy



$$dS = \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_V dT + \left[\frac{1}{T} \left(\frac{\partial E}{\partial V} \right)_T + \frac{\nu R}{V} \right] dV$$

Because

$$S = \bar{S}(T, V)$$

Thus

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



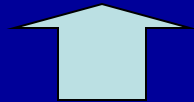
Properties of ideal gas

5.1 Equation of state and internal energy

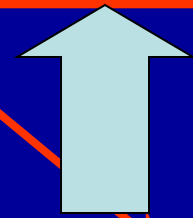


$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V$$
$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}$$

$$E = E(T)$$



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



Because

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}$$

Thus

$$\frac{1}{T} \left(\frac{\partial^2 E}{\partial V \partial T}\right) = \left[-\frac{1}{T^2} \left(\frac{\partial E}{\partial V}\right)_T + \frac{1}{T} \left(\frac{\partial^2 E}{\partial T \partial V}\right) \right] + 0$$

Properties of ideal gas

5.2 Specific heats

1st law

$$dQ = dE + p dV$$

At constant volume

$$dQ = dE$$

$$c_V \equiv \frac{1}{\nu} \left(\frac{dQ}{dT} \right)_V = \frac{1}{\nu} \left(\frac{\partial E}{\partial T} \right)_V$$

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT$$



$$dE = \nu c_V dT$$

Properties of ideal gas

5.2 Specific heats

1st law

$$dQ = \nu c_V dT + p dV$$

For ideal gas at constant pressure



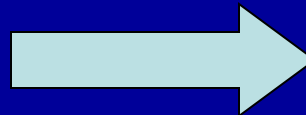
$$p dV = \nu R dT$$

← Equation of state



$$dQ = \nu c_V dT + \nu R dT$$

$$c_p = \frac{1}{\nu} \left(\frac{dQ}{dT} \right)_p$$



$$c_p = c_V + R$$

Properties of ideal gas

5.2 Specific heats

$$\gamma \equiv \frac{c_p}{c_v} = 1 + \frac{R}{c_v}$$

Table 5·2·1 Specific heats of some gases (at 15°C and 1 atm)*

Gas	Symbol	c_v (experimental) (joules mole ⁻¹ deg ⁻¹)	γ (experimental)	γ (computed by (5·2·9))
Helium	He	12.5	1.666	1.666
Argon	Ar	12.5	1.666	1.666
Nitrogen	N ₂	20.6	1.405	1.407
Oxygen	O ₂	21.1	1.396	1.397
Carbon dioxide	CO ₂	28.2	1.302	1.298
Ethane	C ₂ H ₆	39.3	1.220	1.214

* Experimental values taken from J. R. Partington and W. G. Shilling, "The Specific Heats of Gases," p. 201, Benn, London, 1924.

Properties of ideal gas

Microscopic calculations of specific heats

For monatomic gas

$$\Omega(E, V) = B V^N E^{3N/2}$$

$$\ln \Omega = \ln B + N \ln V + \frac{3N}{2} \ln E$$

$$\beta = (kT)^{-1} \quad \beta = \frac{\partial \ln \Omega}{\partial E} = \frac{3N}{2} \frac{1}{E}$$

$$E = \frac{3N}{2\beta} = \frac{3N}{2} kT$$

Relation between internal energy and T

Properties of ideal gas

Microscopic calculations of specific heats

ν is the molar,

$$E = \frac{3}{2}\nu(N_A k)T = \frac{3}{2}\nu RT$$

Thus,

$$c_V = \frac{1}{\nu} \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2} R$$

$$c_V = 12.47 \text{ joules deg}^{-1} \text{ mole}^{-1}$$

$$c_P = \frac{3}{2}R + R = \frac{5}{2}R$$

$$\gamma \equiv \frac{c_P}{c_V} = \frac{5}{3} = 1.667$$

Properties of ideal gas

Table 5·2·1 Specific heats of some gases (at 15°C and 1 atm)*

Gas	Symbol	c_v (experimental) (joules mole ⁻¹ deg ⁻¹)	γ (experimental)	γ (computed by (5·2·9))
Helium	He	12.5	1.666	1.666
Argon	Ar	12.5	1.666	1.666
Nitrogen	N ₂	20.6	1.405	1.407
Oxygen	O ₂	21.1	1.396	1.397
Carbon dioxide	CO ₂	28.2	1.302	1.298
Ethane	C ₂ H ₆	39.3	1.220	1.214

* Experimental values taken from J. R. Partington and W. G. Shilling, "The Specific Heats of Gases," p. 201, Benn, London, 1924.

Properties of ideal gas

5.3 Adiabatic expansion or compression

Keep a heat contact with a heat reservoir. The gas is allowed to expansion under isothermal. Thus,

$$pV = \text{constant}$$

If the gas is thermally insulated,

$$dQ = 0.$$

$$0 = \nu c_V dT + p dV$$

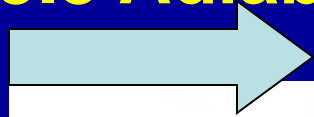
Equation of state

$$p dV + V dp = \nu R dT$$

dT is replaced by dV in the former equation

Properties of ideal gas

5.3 Adiabatic expansion or compression



$$0 = \frac{c_v}{R} (p dV + V dp) + p dV = \left(\frac{c_v}{R} + 1 \right) p dV + \frac{c_v}{R} V dp$$
$$(c_v + R)p dV + c_v V dp = 0$$

$$\gamma \frac{dV}{V} + \frac{dp}{p} = 0$$

$$\gamma \equiv \frac{c_v + R}{c_v} = \frac{c_p}{c_v}$$

γ is T -independent for most gas, and may be a slowly varying function of T

$$\gamma \ln V + \ln p = \text{constant}$$

$$pV^\gamma = \text{constant}$$

Properties of ideal gas

5.3 Adiabatic expansion or compression



$$pV^\gamma = \text{constant}$$

For adiabatic process

$$pV = \text{constant}$$

For isothermal process

$$\gamma > 1$$

p varies more rapidly in adiabatic process

$$\text{since } p = \nu RT/V,$$

Can be V, T; or P, T

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

Properties of ideal gas

5.4 entropy

$$dQ = dE + p dV$$

$$dE = \nu c_V dT$$

$$T dS = \nu c_V(T) dT + \frac{\nu R T}{V} dV$$

$$dS = \nu c_V(T) \frac{dT}{T} + \nu R \frac{dV}{V}$$

From (T_0, V_0) to (T, V) , through quasi-static process

$$S(T, V; \nu) - \nu s_0 = \nu \int_{T_0}^T \frac{c_V(T')}{T'} dT' + \nu R \int_{V_0(\nu/\nu_0)}^V \frac{dV'}{V'}$$

Properties of ideal gas

5.4 entropy

The last integration is immediate:

$$\int_{V_0(\nu/\nu_0)}^V \frac{dV'}{V'} = [\ln V']_{V_0(\nu/\nu_0)}^V = \ln V - \ln \left(V_0 \frac{\nu}{\nu_0} \right) = \ln \frac{V}{\nu} - \ln \frac{V_0}{\nu_0}$$

Hence (5.4.2) becomes

$$S(T, V; \nu) = \nu \left[\int_{T_0}^T \frac{c_V(T')}{T'} dT' + R \ln \frac{V}{\nu} - R \ln \frac{V_0}{\nu_0} + s_0 \right] \quad (5.4.3)$$

$$\text{or } S(T, V; \nu) = \nu \left[\int \frac{c_V(T')}{T'} dT' + R \ln V - R \ln \nu + \text{constant} \right] \quad (5.4.4)$$

if c_V is constant.

$$\int \frac{c_V}{T'} dT' = c_V \ln T$$

Properties of ideal gas

5.5 Derivation of general relations

Start from

$$dQ = T dS = dE + p dV$$

* Independent variables: S and V

$$dE = T dS - p dV$$

$$E = E(S, V)$$



$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

Combining,



$$\begin{aligned}\left(\frac{\partial E}{\partial S}\right)_V &= T \\ \left(\frac{\partial E}{\partial V}\right)_S &= -p\end{aligned}$$

Properties of ideal gas

5.5 Derivation of general relations

Start from

$$dQ = T dS = dE + p dV$$

* Independent variables: S and V

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}$$
$$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial E}{\partial V}\right)_S$$

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



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

Properties of ideal gas

5.5 Derivation of general relations

Start from

$$dQ = T dS = dE + p dV$$

* Independent variables: S and p

$$p dV = d(pV) - V dp$$

$$dE = T dS - p dV = T dS - d(pV) + V dp$$

$$d(E + pV) = T dS + V dp$$

Define

$$H \equiv E + pV$$



$$dH = T dS + V dp$$

Properties of ideal gas

5.5 Derivation of general relations

* Independent variables: S and p

$$dH = T dS + V dp$$

$$H = H(S, p)$$

$$dH = \left(\frac{\partial H}{\partial S} \right)_p dS + \left(\frac{\partial H}{\partial p} \right)_S dp$$

$$\left(\frac{\partial H}{\partial S} \right)_p = T$$

$$\left(\frac{\partial H}{\partial p} \right)_S = V$$

$$\frac{\partial^2 H}{\partial p \partial S} = \frac{\partial^2 H}{\partial S \partial p}$$

$$\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$$

Properties of ideal gas

5.5 Derivation of general relations

* Independent variables: T and V

Define

$$F \equiv E - TS$$

$$dE = T dS - p dV = d(TS) - S dT - p dV$$

$$dF = -S dT - p dV$$

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

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



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

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

Properties of ideal gas

5.5 Derivation of general relations

* Independent variables: T and V

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V}$$

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

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



$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

Properties of ideal gas

5.5 Derivation of general relations

* Independent variables: T and p

Define

$$G \equiv E - TS + pV$$

$$\begin{aligned} dE &= T dS - p dV = d(TS) - S dT - d(pV) + V dp \\ dG &= -S dT + V dp \end{aligned}$$

$$\begin{aligned} G &= G(T, p) \\ dG &= \left(\frac{\partial G}{\partial T} \right)_p dT + \left(\frac{\partial G}{\partial p} \right)_T dp \end{aligned}$$



$$\begin{aligned} \left(\frac{\partial G}{\partial T} \right)_p &= -S \\ \left(\frac{\partial G}{\partial p} \right)_T &= V \end{aligned}$$

Properties of ideal gas

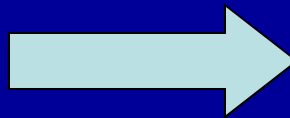
5.5 Derivation of general relations

* Independent variables: T and p

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

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

$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}$$



$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

Properties of ideal gas

5.6 Summary of Maxwell relations and thermodynamic functions

Maxwell relations

$$dE = T dS - p dV$$

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\ \left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

*T, p, V, S are not
completely in-dependent*

???

One can use Ω to give a complete macroscopic description on system

Properties of ideal gas

5.6 Summary of Maxwell relations and thermodynamic functions

Maxwell relations

??? One can use Ω to give a complete macroscopic description on system

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_V \quad \text{and} \quad p = T \left(\frac{\partial S}{\partial V} \right)_E$$

$$\beta = \frac{\partial \ln \Omega}{\partial E}$$

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial E} \right)_V dE + \left(\frac{\partial S}{\partial V} \right)_E dV \\ &= \frac{1}{T} dE + \frac{p}{T} dV \quad \text{by (5.6.6)} \end{aligned}$$

$$\frac{p}{T} = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial V}$$

(T, S)

and

(p, V)

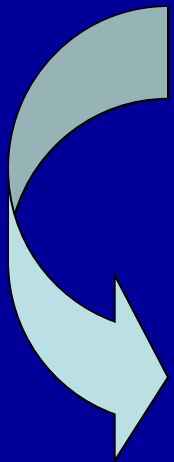
Number of states

generalized force

Properties of ideal gas

5.7 thermodynamic functions

E	$E = E(S, V)$
$H \equiv E + pV$	$H = H(S, p)$
$F \equiv E - TS$	$F = F(T, V)$
$G \equiv E - TS + pV$	$G = G(T, p)$



$dE = T dS - p dV$
$dH = T dS + V dp$
$dF = -S dT - p dV$
$dG = -S dT + V dp$

Properties of ideal gas


5.8 Specific heats

at constant volume

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

at constant pressure

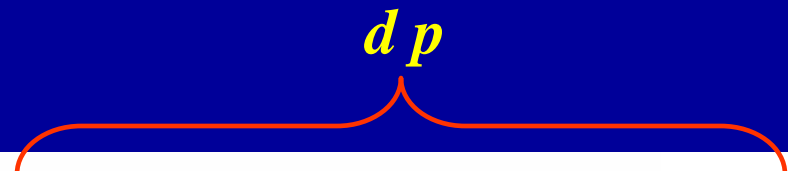
$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p$$


$$dQ = T dS = T \left[\left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp \right]$$

$$dQ = T dS = C_p dT + T \left(\frac{\partial S}{\partial p} \right)_T dp$$

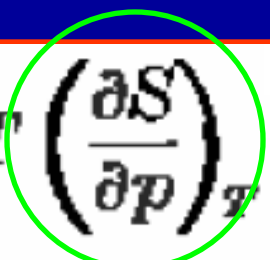
Properties of ideal gas

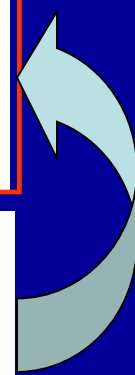
5.8 Specific heats

$$dQ = T dS = C_p dT + T \left(\frac{\partial S}{\partial p} \right)_T \left[\left(\frac{\partial p}{\partial T} \right)_V dT + \left(\frac{\partial p}{\partial V} \right)_T dV \right]$$


when V is constant

$$dQ = C_v dT$$

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_V = C_p + T \left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V$$


$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$$


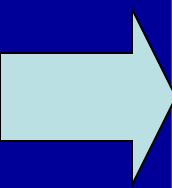
The quantities in the right of equation is easily to be measured

Properties of ideal gas

5.8 Specific heats

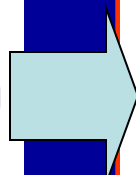
$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

volume coefficient of expansion


$$\left(\frac{\partial S}{\partial p} \right)_T = -V\alpha$$

constant volume

$$dV = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp$$


$$\left(\frac{\partial p}{\partial T} \right)_V = - \frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T}$$

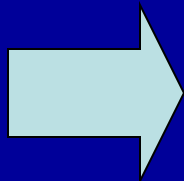
Properties of ideal gas

5.8 Specific heats

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = C_p + T \left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V$$

$$\kappa \equiv - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

isothermal compressibility



$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{\alpha}{\kappa}$$

$$C_V = C_p + T(-V\alpha) \left(\frac{\alpha}{\kappa} \right)$$

$$C_p - C_V = VT \frac{\alpha^2}{\kappa}$$

Class-work

P 192 5.1

Homework

P 192 5.2, 5.3, 5.5, 5.6, 5.7