CH8 The Behavior of Real Gases

§1. * Ideal gas: $\begin{cases}\text{No interactions between molecules}\\ \text{volumeless for molecules}\end{cases}$

* Real gas

2. Ideal gas equation: PV=RT

Equation of state for real gas?

3. Fugacity (f)

$$\begin{cases}\text{Ideal gas: } f=P\\ \text{Real gas: } f = P\cdot e^{\frac{-1}{RT}\int \alpha dP}\end{cases}$$

$$\begin{cases}\text{Ideal gas: } dG = RTd\ln P\\ \text{Real gas: } dG = RTd\ln f\end{cases}$$

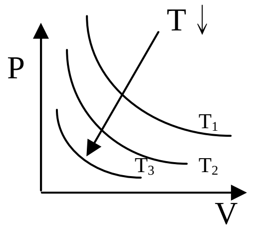
P-V-T Relationships of Gases

* Experiment: all gases (one mole)

$$\lim_{p\to 0}\left(\frac{PV}{RT}\right)\to 1 \quad \text{, where } P\to 0$$

* Ideal gas: PV=RT (perfect gas)

one mole



$T_1 > T_2 > T_3$ (isotherm)

any T

* Real gas, Fig 8.1

$T_1 > T_{cr} > T_2$

(1) isotherm, at $T=T_{cr}$

inflexion points (P_{cr}, V_{cr})

$$\left(\frac{\partial P}{\partial V}\right)_{T_{cr}} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_{cr}} = 0$$

(2) $T < T_{cr}$, e.g. $T=T_2$

with P ↑ $\Rightarrow$ $\begin{cases}\text{A}\to\text{B at point B}\\ \text{vapor condenses and liquid forms}\end{cases}$

B$\longleftrightarrow$C, vapor and liquid coexist
(P=constant, two phases eqquil)
at point C, all vapor condenses and only liquid exists

$$\left[-\left(\frac{\partial P}{\partial V}\right)_T\right] \text{ at A (for vapor) } < \left[-\left(\frac{\partial P}{\partial V}\right)_T\right] \text{ at D (liquid)}$$

i.e. $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ (vapor) $>$ β (liquid)

(3) At $T=T_{cr}$, $V_{liquid}=V_{vapor}$

(4) $T>T_{cr}$, e.g. $T=T_1$

Vapor (gas) cannot be liquefied by isothermal compression alone.
Liquefaction requires cooling. (1→2)

Where $T>T_{cr}$ or $P>P_{cr}$, no distinction can be made between liquid and gas.

Deviation From Ideality (Equations of State of Real Gas)

compressibility factor: Z

$$Z \equiv \frac{PV}{RT} \quad , Z=Z(P,T)$$

ideal gas: Z=1

real gas: Fig. 8.3 for $P<10$ atm , T=0℃

$Z=mP+1$ (experimental data)

$$\therefore \frac{PV}{RT} = mP + 1$$

$P(V-mRT)=RT$

or $P(V-b')=RT\cdots$ ⊛

(1) deviation from ideal behavior can be dealt with by making a correction to volume term.
$b'<0$ for must gases, except H_2 (at low P)

(2) Eg⊛ is empirical, for $P<10$ atm, T=0℃ or $P>300$ atm, $b'>0$

(3) when Z is plotted versus $P_R = \frac{P}{P_{cr}}$

at fixed $T_R = \frac{T}{T_{cr}}$, then all gases lie on a single curve. Fig. 8.4

van der Waals Gas

1. Ideal gas
   - * U=U(T) only
   - * U is entirely the (kinetic + rot. + vib.) energy of particle
   - * noninteracting particles
   - * particles can be considered as volumeless

2. Modification for real gas * particle occupy a finite volume→修正 V
   * interaction exists→修正 P

   Consider: one mole of gas

   Ideal gas: PV=RT

   Van der Waals gas: $(P+\frac{a}{V^2})(V-b)=RT$

   Concepts:

   (1) b is a correction term for the finite volume of the particles

   * When two spherical particles collide, they exclude a volume:

   $$\frac{4}{3}\pi(2r)^3$$

   * excluded volume per particle: $\frac{1}{2}\times\left[\frac{4}{3}\pi(2r)^3\right]=4\times\left(\frac{4}{3}\pi\ r^3\right)$

   $$\therefore b\cong N_A\times 4\times\frac{4}{3}\pi\ r^3 \sim \text{volume}$$

   * Videal=(V－b) is the volume available for the movement of gas particles

   (2) $\frac{a}{V^2}$ is a correction term for particle interaction

   * pressure exerted on the vessel wall

   ~ number of particles is the “surface layer”

   ~ gas density $\left(\frac{N_A}{V}\right)$

   * Attractive force between the “surface layer” and the “next-to-surface layer”

   ~ gas density $\left(\frac{1}{V}\right)$

   * Therefore , net inward pull due to interaction

   $\sim \frac{1}{V^2}$

   $\left(P+\frac{a}{V^2}\right) \Longleftrightarrow$ ideal gas pressure P_{ideal}

   P: measured pressure of real gas

3. Values of a, b for any gas are evaluated from experimental determination of T_{cr}

and P_{cr} (V_{cr})

$$\because (P+\frac{a}{V^2})(V-b)=RT$$

$$\therefore P=\frac{RT}{(V-b)}-\frac{a}{V^2}$$

when T=Tcr

$$\begin{cases} \left(\frac{\partial P}{\partial V}\right)_{T_{cr}} = \frac{-RT_{cr}}{(V_{cr}-b)^2}+\frac{2a}{V^3{}_{cr}}=0 \\ \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_{cr}} = \frac{2RT_{cr}}{(V_{cr}-b)^3}-\frac{6a}{V^4{}_{cr}}=0 \end{cases}$$

$$\therefore \begin{cases} T_{cr}=\frac{8a}{27bR} \\ V_{cr}=3b \\ P_{cr}=\frac{a}{27b^2} \end{cases}$$

4. Consider $T_2 < T_{cr}$, P-V-T carve

   * $\left(\frac{\partial P}{\partial V}\right)_T < 0$ is a condition of intrinsic stability of gas system. However, in region JHF, elnis condition is violated and has no physical significance.

   * Gibbs Free Energy ⟺ Equilibrium state

   ∵ dG=－SdT+VdP

   Isothermal compression from A (constant T_2)

   dG=VdP

   $$\therefore G-G_A=\int_{P_A}^{P}VdP$$

   (1) For $P < P_4$
       $\overline{ABCD}$ is the stable vapor phase
   (2) For $P > P_4$
       $\overline{LMND}$ is the stable liquid
   (3) $\overline{DEF}$ is unstable vapor
       $\overline{JKL}$ is unstable liquid
   (4) $\overline{JHF}$ is unstable
   (5) $P_2 < P < P_6$, three states may exist, however, only lowest G states cure stable
   (6) For vapor and liquid, (two phases) is equilibrium, i.e. $G_{vapor}=G_{liquid}$ occurs at $P=P_4$ (i.e. D=L), and area HFD=area LJH

5. <u>Example:</u> CO_2 $\left\{\begin{array}{l} T_{cr}=31^\circ C \\ P_{cr}=72.9 \text{ atm} \\ V_{cr}=95.7 \text{ cm}^3/\text{mole} \end{array}\right\}$ experiment

$$\therefore \quad b=\frac{RT_{cr}}{8P_{cr}}=0.0427 \ ltr=42.7 \ cm^3$$

$$a=27b^2P_{cr} \ =3.59 \ l^2-atm$$

$$\therefore \quad \left(P+\frac{3.59}{V^2}\right)(V-0.0427)=RT$$

* $\left\{\begin{array}{l}\text{P-V-T curves (isotherms) see Fig. 8.9} \\ \text{G-P curves at const T, see Fig. 8.10}\end{array}\right.$

* For $T<T_{cr}=304$ K, (liquid+vapor) two phase equilibrium, ⇨ saturated vapor pressure (over liquid) at T

Plot log P_{sat} versus 1/T

(1) P_{sat} (van der Waals) ＞ P_{sat} (experiment)

(△P) ↑ when T ↓

(2) Heat of Evaporation, $\triangle H_{evap}$

∵Clausius-Clapeyron Eq.

$$d\ln P=\frac{\Delta H}{RT^2}dT$$

或 $\ln P=\frac{-\Delta H}{RT}+constant$

∴slope of lnP versus 1/T ~ $\frac{-\Delta H}{R}$

∴△H (van der Waals) ＜ △H (experiment)

i.e. van der Waals binding force is not adequate for the correction for deviation from ideal behavior

6. Since a, b are determined by experimental values of T_{cr} P_{cr} (V_{cr}) , therefore van der Waals equation is an "empirical" equation.

7. $\boxed{\text{When } T\rightarrow T_{cr}\text{ , } \triangle H_{evap}\rightarrow 0}$

<u>Proof:</u> $\because \Delta H_{evap}=H_v-H_l=(U_v-U_l)+P(V_v-V_l)$

$$\because dU=TdS-PdV$$

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

Maxwell Relation $\because \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$\because \left(P+\frac{a}{V^2}\right)(V-b)=RT \quad \therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$

$\therefore \left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{V-b} - P = \frac{a}{V^2}$

$\therefore U = -\frac{a}{V} + const$

$\therefore U_V - U_l = -a\left(\frac{1}{V_V} - \frac{1}{V_l}\right)$

$\therefore$ when T→T_{cr} V_V→V_l U_V→U_l $\therefore \triangle H_{evap} \to 0$

\# Other Equations of State For Nonideal Gas

Dieteria Eq. $P(V-b')e^{a'/RTV} = RT$

Berthelot Eq. $\left(P+\frac{A}{TV^2}\right)(V-B)=RT$

Virial Eq. $\frac{PV}{RT} = 1 + BP + CP^2 + \cdots$

或 $\frac{PV}{RT} = 1 + \frac{B'}{V} + \frac{C'}{V^2} + \cdots$

* All are empirical and obtained by curve fitting.

§ Thermodynamic Treatment of Nonideal Gas (Real Gas)

1. Consider nonideal gas itself, not mixture

Fugacity: $\boxed{dG = RTd\ln f}$

c.p. ideal gas $dG = RT\ln P$

$\therefore \begin{cases} \text{Ideal gas: } f = P \\ \text{Real gas: } P \to 0 \ , \ f \to P \quad \left(f = Pe^{\frac{-\alpha P}{RT}}\right) \end{cases}$

As $P \to 0$, $\left(\frac{f}{P}\right) \to 1$

Deviation $\alpha \equiv -V + \frac{RT}{P} \left(= V^{id} - V\right)$

Const T $dG = VdP = RTd\ln f$

$$\left(-\alpha+\frac{RT}{P}\right)dP = RTd\ln f$$

$$\therefore \quad \int_{P=0}^{P} d\ln\left(\frac{f}{P}\right)=\int_{P=0}^{P}\frac{-\alpha}{RT}dP$$

$$\because \quad P\rightarrow 0 \quad \left(\frac{f}{P}\right)\rightarrow 1 \quad \ln\left(\frac{f}{P}\right)\rightarrow 0$$

$$\therefore \quad \ln\left(\frac{f}{P}\right)=\frac{-\alpha P}{RT} \qquad (\text{If } \alpha=\text{const.})$$

$$\therefore \quad \frac{f}{P}=e^{\frac{-\alpha P}{RT}}$$

$$\text{or} \quad f = Pe^{\frac{-\alpha P}{RT}}$$

$$\text{或} \quad f = Pe^{\frac{-1}{RT}\int_{P=0}^{P}\alpha dP} \quad (\alpha \neq \text{const.})$$

* Calculate f from equation of state of real gas $\begin{cases} Z=Z(P) \\ Z=Z(V) \end{cases}$

$$\because \quad d\ln\left({}^{f}\!/_{P}\right)=\frac{-\alpha}{RT}dP=\left(\frac{V}{RT}-\frac{1}{P}\right)dP \quad \text{constant T}$$

$$Z=\frac{Pv}{Rt}$$

$$\therefore \quad \boxed{d\ln\left(\frac{f}{P}\right)=\frac{Z-1}{P}dP}$$

$$\left[\ln\left(\frac{f}{P}\right)\right]_{P}-\left[\ln\left(\frac{f}{P}\right)\right]_{P=0}=\int_{0}^{P}\frac{Z-1}{P}dP$$

$$\therefore \quad \boxed{d\ln\left(\frac{f}{P}\right)=\int_{0}^{P}\frac{Z-1}{P}dP}$$

<u>EX:</u> one mole N_2 gas at T=273.16K (0℃) $PV=22414.6-10.281P+0.065189P^2+5.2\times 10^{-7}P^4-1.32\times 10^{-11}P^6+1.01\times 10^{-16}P^8$ (atm · cm^3)

When P=100 atm , f=?

<u>Soln</u> $Z=\frac{PV}{RT}=\frac{1}{RT}\left(a+bP+cP^2+dP^4+mP^6+nP^8\right)$

$$\therefore \frac{Z-1}{P}=\frac{1}{RT}\left(b+cP+dP^3+mP_5+nP^7\right)$$

$$\therefore \ln\left(\frac{f}{P}\right)=\frac{1}{RT}\left(bP+\frac{c}{2}P^2+\frac{d}{4}P^4+\frac{m}{6}P^6+\frac{n}{8}P^8\right)$$

when P=100 atm

$$\ln\left(\frac{f}{100}\right)=\frac{1}{82.057\times 273.16}\left(10^{2}b+10^{4}\frac{c}{2}+\frac{d}{4}10^{8}+\frac{m}{6}10^{12}+\frac{n}{8}10^{16}\right)$$

$$=-0.03084$$

∴f=0.9696×100=96.96 atm

EX: 同前題 Isothermal compression from P_1=1 atm to P_2=150 atm

△G=? (△G_{id}－△G)=?

Soln $dG=RTd\ln f=VdP$

$$\Delta G=\int_{P_1}^{P_2}VdP=\int_{P_1}^{P_2}\left(\frac{a}{P}+b+cP+dP^{3}+mP^{5}+nP^{7}\right)dP$$

$$=\left(a\ln P+bP+\frac{c}{2}P^{2}+\frac{d}{4}P^{4}+\frac{m}{6}P^{6}+\frac{n}{8}P^{8}\right)\Bigg|_{P_1}^{P_2}$$

=111490 atm · cm^3

$$\Delta G_{id}=\int_{P_1}^{P_2}VdP=\int_{P_1}^{P_2}\frac{RT}{P}dP=RT\ln\left(\frac{P_2}{P_1}\right)=112311\ atm\cdot cm^{3}=+11373\ J$$

$$\therefore(\Delta G_{id}-\Delta G)=+76\ Joul$$

⊛ $\dfrac{\Delta G_{id}-\Delta G}{\Delta G_{id}}\cong+0.7\%$

⊛ △G＜△G_{id} , ⇨ real gas is easier to compress

EX: gas eq. $\dfrac{PV}{RT}=1+BP$ B＞0 $\boxed{\text{usually B＜0}}$ see Fig 8.3 Reversible (isothermal) expansion calculate W_{non} $\begin{cases}(1)P_1\rightarrow P_2\ (100\text{ atm}\rightarrow 50\text{ atm})\\(2)\ V_1\rightarrow V_2\end{cases}$

compare with W_{id}

soln (1) $W=+\int PdV$

$$\begin{cases}\text{ideal gas} \quad PV=RT \quad \therefore dV=\dfrac{-RT}{P^{2}}dP\\[2ex]\text{nonideal gas} \quad \dfrac{PV}{RT}=1+BP \quad dV=\dfrac{-RT}{P^{2}}dP\end{cases}$$

$$\therefore W_{id}=+\int_{P_1}^{P_2}PdV=+\int_{P_1}^{P_2}P\frac{-RT}{P^{2}}dP=RT\ln\left(\frac{P_1}{P_2}\right)$$

$$W_{non} = +\int PdV = +\int_{P_1}^{P_2} P\frac{-RT}{P^2}dP = RT\ln\left(\frac{P_1}{P_2}\right)$$

$\therefore W_{id}=W_{non}$

(2) $$W_{id} = +\int PdV = +\int_{V_1}^{V_2}\frac{RT}{V}dV = RT\ln\left(\frac{V_2}{V_1}\right)$$

$$W_{non} = +\int PdV = +\int_{V_1}^{V_2}\frac{RT}{V-BRT}dV = RT\ln\left(\frac{V_2-BRT}{V_1-BRT}\right)$$

$\therefore W_{non} > W_{id}$

EX1: N_2 Assume van der Waals gas model $P = \frac{RT}{V-b} - \frac{a^2}{V^2}$

a=1.39 *l*-atm$^{1/2}$/mole$^{1/2}$

b=39.1 cm^3/mole=0.0391 l/mole one mole N_2

T=400 K , V_1=1*l* , V_2=2*l* △G=? , △S=?

Sol: (1) $dG = -SdT + VdP \quad \therefore dG_T = VdP$

$$\because P = \frac{RT}{V-b} - \frac{a^2}{V^2}$$

$$\therefore dP = -\frac{RTdV}{(V-b)^2} + \frac{RdT}{(V-b)} + \frac{2a^2dV}{V^3}$$

$$= \frac{RdT}{(V-b)} + \left[\frac{2a^2}{V^3} - \frac{RT}{(V-b)^2}\right]dV \ldots ⊛$$

const T $$dP = \frac{1}{V}\left[\frac{2a^2}{V^2} - \frac{RTV}{(V-b)^2}\right]dV$$

$$\therefore dG = VdP = \left[\frac{2a^2}{V^2} - \frac{RTV}{(V-b)^2}\right]dV \ldots ⊛$$

$$\therefore \Delta G = \int_{V_1}^{V_2}\left[\frac{2a^2}{V^2} - \frac{RTV}{(V-b)^2}\right]dV$$

$$= \left[-\frac{2a^2}{V} + \frac{RTb}{V-b} - RT\ln(V-b)\right]_{V_1}^{V_2}$$

$$= -2a^2\left(\frac{1}{V_2}-\frac{1}{V_1}\right)+RTb\left[\frac{1}{(V_2-b)}-\frac{1}{(V_1-b)}\right]-RT\ln\left(\frac{V_2-b}{V_1-b}\right)$$

$$= -2636\ \text{J}$$

(2) S=S(P, T)

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

const T $\quad dS=\left(\frac{\partial S}{\partial P}\right)_T dP$

$$dS=-\left(\frac{\partial V}{\partial T}\right)_P dP$$

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

$$\therefore dS=-V\alpha dP$$

From⊛ $\left(\frac{\partial V}{\partial T}\right)_P=\dfrac{\dfrac{-R}{(V-b)}}{\dfrac{2a^2}{V^3}-\dfrac{RT}{(V-b)^2}}=\dfrac{-RV^3(V-b)}{2a_2(V-b)^2-RTV^3}$

$$\therefore \alpha=\frac{-RV^2(V-b)}{2a^2(V-b)^2-RTV^3}$$

$$\therefore dS=\left[\frac{-RV^2(V-b)}{2a^2(V-b)^2-RTV^3}\right]\left[\frac{2a^2}{V^2}-\frac{RTV}{(V-b)^2}\right]dV$$

$$dS=+\frac{R}{(V-b)}dV$$

$$\therefore \Delta S=+\int_{V_1}^{V_2}\frac{R}{(V-b)}dV=-R\ln(V-b)\Big|_{V_1}^{V_2}$$

$$=R\ln\frac{V_2-b}{V_1-b}$$

$$\therefore \Delta S=8.314\ln\frac{(2-0.0391)}{(1-0.0391)}=5.93(J/K)$$

<u>EX2:</u> n-butane(異丁烷) one mole T=460 K V_1=400 cm^3 V_2=200 cm^3 △G=?

$Z=1+A/V+\dfrac{B}{V^2}$ A=−265 cm^3/mole B=30250 cm^6/mole

<u>soln:</u> $\dfrac{PV}{RT}=1+\dfrac{A}{V}+\dfrac{B}{V^2}$

$$\therefore P = RT\left(\frac{1}{V} + \frac{A}{V^2} + \frac{B}{V^3}\right)$$

const T, $dP = RT\left(\frac{-1}{V^2} - \frac{2A}{V^3} - \frac{3B}{V^4}\right)dV$

$$dG = VdP = RT\left(-\frac{1}{V} - \frac{2A}{V^2} - \frac{3B}{V^3}\right)dV$$

$$\therefore \Delta G = -RT\left(\ln V - \frac{2A}{V} - \frac{3B}{2V^2}\right)\Big|_{V_1}^{V_2}$$

$$= -RT\left[\ln\left(\frac{V_2}{V_1}\right) - 2A\left(\frac{1}{V_2} - \frac{1}{V_1}\right) - \frac{3B}{2}\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right)\right]$$

∴△G=838 J