Fugacity calculation for gases and liquids

We shall study how to calculate the fugacity of a pure gas or liquid component.

We will see why the Gibbs function is called the generating function.

We shall see how to calculate the fugacity of a gaseous component using the vdW cubic EOS and also using the Virial EOS and the Pitzers correlation.

For a liquid component we follow a different procedure, because for liquids reliable cubic EOS dont exist.

At the end we shall solve GATE problems on fugacity.

We saw one reason why the thermodynamic function G is so important in our last module. Namely because it has P and T as its independent variables which we can easily manipulate.
In this chapter we shall see the second reason why the Gibbs free energy is the most sought after function in all of Thermodynamics.

We shall see why G/RT is called the generating function. Specifically we shall show that knowing the functional form for G/RT we can calculate all other thermodynamic functions namely V, U, H and S.

we have the two equations

$$dG = VdP - SdT \quad \text{and} \quad G = H - TS$$

Take the equality

$$d\left(G/RT\right) = \frac{1}{RT} dG - \frac{G}{R} \frac{1}{T^2} dT$$

$$d\left(G/RT\right) = \frac{1}{RT}\left(VdP - SdT\right) - \left(\frac{H - TS}{RT^2}\right) dT$$

$$= \frac{V}{RT} dP - \frac{S}{RT} dT - \frac{H}{RT^2} dT + \frac{S}{RT} dT$$

$$\therefore d\left(G/RT\right) = \frac{V}{RT} dP - \frac{H}{RT^2} dT$$

$$\therefore \; d\left(G/RT\right) = \frac{V}{RT}\,dP - \frac{H}{RT^2}\,dT$$

$$\therefore \quad \left.\frac{d\left(G/RT\right)}{dP}\right|_{T=\text{Const}} = \frac{V}{RT}$$

<u>or</u> Since T = const on differentiation

and $$\left.\frac{d\left(G/RT\right)}{dT}\right|_{P=\text{Const}} = -\frac{H}{RT^2}$$

Again Since

$$G = H - TS$$

$$S = -\frac{G}{T} + \frac{H}{T}$$

and $U = H - PV$

So if we know the G/RT functional form
we can differentiate it wrt P and get V
we can differentiate it wrt T and get H
then get S and then U !!

So if the functional form for G/RT is known the full information of all thermo. properties are known !!

Is this the end of the story !

NO

Thermo. does not give us this functional dependence or relation.

Then what is the way.

If we assume this Virial expansion is a valid representation of the gas phase behavior then all thermodynamic quantities can be exactly evaluated.

The Virial equation holds advantage over the cubic EOS. For a cubic EOS we need to solve the cubic equation for V given P and T. Then knowing P, T, and V we calculate Z. The Virial equation gives us an explicit equation for Z.

Virial EOS an alternative to Cubic EOS

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$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots$$

B = second virial coeff

C = third virial coeff

For vapor phase we normally use a one term approximation

$$Z \simeq 1 + \frac{B}{V} \simeq 1 + \frac{BP}{RT}$$

B is a function of Temperature only and can be either negative or positive. If B is positive Z > 1 and if negative Z < 1.

we arrange it as

$$Z = 1 + \left(\frac{BP_c}{RT_c}\right)\left(\frac{P/P_c}{T/T_c}\right)$$; P_c, T_c are critical P and T

$$= 1 + \left(\frac{BP_c}{RT_c}\right) \cdot \frac{P_r}{T_r}$$; $P_r = P/P_c$ reduced Pressure

$T_r = T/T_c$ reduced temp

We correlate $\frac{BP_c}{RT_c}$ using Pitzers Correlation

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1 \quad \text{where} \quad B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

ω = acentric factor

So if we know P and T

we can Calculate $\frac{BP_c}{RT_c}$,

then calc Z

then $V = \frac{ZRT}{P}$

This one term virial eqn is one approach to Calculate all thermodynamic properties exactly.

Let us see why.

If we assume the gas obeys the virial EOS we can do a lot then.

Remember

$$V^R = V - V^{ig}$$

$$\therefore V^R = \frac{ZRT}{P} - \frac{RT}{P} = (Z-1)\frac{RT}{P}$$

but virial EOS

$$Z = 1 + \frac{BP}{RT}$$

$$\therefore (Z-1)\frac{RT}{P} = B \Rightarrow \text{function of } T \text{ only}$$

$$\therefore V^R = B \Rightarrow V = V^{ig} + B$$

↓ correction for ideal gas volume !!

now we have the eqn

$$dG = VdP - SdT$$

writing once for ideal gas

$$dG^{ig} = V^{ig}dP - S^{ig}dT$$

and subtracting

$$d(G - G^{ig}) = (V - V^{ig})dP - (S - S^{ig})dT$$

$$dG^{R} = V^{R}dP - S^{R}dT$$

$$d G^R = V^R dP - S^R dT$$

$$\therefore V^R = \left(\frac{\partial G^R}{\partial P}\right)_{T=\text{const}}$$

$$= B$$

$$\therefore \frac{dG^R}{dP} = B \qquad T = \text{constant Process}$$

Integrating from $P = 0$ to $P = P$

$$G^R(P) - \underbrace{G^R(P=0)}_{\approx 0} = B(P-0)$$

$$\therefore G^R(P) = BP$$

$$\therefore \boxed{\frac{G^R}{RT} = \frac{BP}{RT}}$$

Now we have

$$\frac{-H}{RT^2} = \frac{d}{dT}\left(G/RT\right) \qquad (P = \text{const})$$

writing this for residual property

$$\frac{-H^R}{RT^2} = \frac{d}{dT}\left(\frac{G^R}{RT}\right) \qquad (P = \text{const})$$

$$= \frac{d}{dT}\left(\frac{BP}{RT}\right) \qquad (P = \text{const})$$

$$\therefore \quad \frac{-H^R}{RT^2} = \frac{P}{RT}\frac{dB}{dT} - \frac{BP}{RT^2}$$

hence if virial EoS is seem to be accepted then we have the thermodynamic props

$$\frac{U^R}{RT} = B$$

$$\frac{G^R}{RT} = \frac{BP}{RT}$$

$$\frac{H^R}{RT^2} = \frac{BP}{RT^2} - \frac{P}{RT}\frac{dB}{dT}$$

} full knowledge about the system!!

and since

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT}$$

Substituting for H^R and G^R

$$\frac{S^R}{R} = -\frac{P}{B}\frac{dB}{dT}$$

This is the reason why G/RT is called the generating function. Once we have the eqn (functional form) for G/RT all other thermodynamic props are known!

But the Virial EoS is only applicable for low to moderate pressures. For high pressures its applicability is rather poor..

Hence another approach the fugacity approach has been introduced to overcome these limitations.

Fugacity of a pure component

We have the relation

$$dG = VdP - SdT$$

@ constant Temp process ($T = \text{const}$)

$$dG = VdP$$

For an ideal gas undergoing a process

$$dG^{ig} = V^{ig} dP$$

$$\therefore dG^{ig} = \frac{RT}{P} dP = RT \, d\ln P$$

For a real gas we define a similar relation

$$dG = RT \, d\ln f \quad , \; f = \text{fugacity}$$

Subtracting one from the other

$$d(G - G^{ig}) = RT\, d\ln(f/P) \qquad (T = \text{const})$$

Integrate $\equiv dG^R$

from $P = 0$ to P

$$\int_{P=0}^{P} dG^R = \int_{P=0}^{P} RT\, d\ln(f/P)$$

$$\int_{P=0}^{P} d G^R = \int_{P=0}^{P} RT \, d \ln (f/p)$$

$$G^R(P) - \underbrace{G^R(P=0)}_{\text{at } P=0 \text{ ie at low pressures Residual props} \to 0 \text{ since real prop} \to \text{ideal prop}} = RT \ln f/p \qquad (15)$$

$$G^R = RT \ln f/p = RT \ln \phi$$

$\phi = f/p \rightarrow$ fugacity coeff.

we have defined fugacity how do we calculate it.

Relating f and Z

$$dG = V\,dP$$
$$dG^{ig} = V^{ig}\,dP$$

} at T = Const.

$$d(G - G^{ig}) = (V - V^{ig})\,dP$$

$$dG^{R} = \left(\frac{ZRT}{P} - \frac{RT}{P}\right) dP$$

$$dG^{R} = (Z-1)\frac{RT}{P}\,dP$$

Integrate from $P=0$ to P

Both f and Z measure the deviation of the gas from ideality. So they must be related.

$$G^R(P) - G^R(P=0) = \int_0^P (Z-1)\frac{RT}{P}\,dP \qquad (T = \text{const.})$$

$$\therefore\ G^R = \int_0^P (Z-1)\frac{RT}{P}\,dP$$

$$\equiv RT \ln\left(f/P\right)$$

$$\therefore\ \ln\left(f/P\right) = \ln\phi = \int_0^P \frac{(Z-1)}{P}\,dP$$

This is the relation between f and Z

hence if we Z vs P data we can easily calc f at every P.

we see that if $Z > 1 \Rightarrow f > P$

if $Z < 1 \Rightarrow f < P$

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We have derived the relation

$$\ln \phi = \ln\left(\frac{f}{P}\right) = \int_{P=0^+}^{P} \frac{Z-1}{P}\, dP \qquad (T = \text{const})$$

What if the Virial EoS is used for the gas phase!

For the Virial EoS

$$Z = 1 + \frac{BP}{RT} \quad \Rightarrow \quad \frac{Z-1}{P} = \frac{B}{RT} = f(T)$$

$$\therefore \ln\left(\frac{f}{P}\right) = \int_{P=0^+}^{P} \frac{Z-1}{P}\, dP = \int_{P=0^+}^{P} \frac{B}{RT}\, dP$$

$$= \frac{B}{RT}\int_{0}^{P} dP = \frac{BP}{RT}$$

$$\therefore \ln\left(f/P\right) = \frac{BP}{RT}$$ for a gas phase obeying the virial EOS !

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and here we see, if $B = 0$ (no molecular interactions)

$\ln f/P = 0 \Rightarrow f = P$ an ideal gas

Prob 11.18 (4)

Van Ness Calculate the fugacity of isobutylene gas at 280°C and 20 bar, using Pitzers EOS.

Soln We have the data

$$\omega = 0.194, \quad T_c = 417.9\ K, \quad P_c = 40\ bar$$

$$\therefore P_r = P/P_c = 0.5, \quad T_r = T/T_c = 1.324$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.186$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.086$$

$$\frac{BP}{RT} = \left(B_0 + \omega B_1\right)\frac{P_r}{T_r} = -0.064 = \ln\phi$$

$$\phi = \exp(-0.064) = 0.938$$

$$\therefore \frac{f}{P} = \phi \Rightarrow f = P\cdot\phi = (20\,\text{bar})(0.938)$$

$$\therefore f = 18.758\,\text{bar}.$$

Because f < P, the gas is showing a negative deviation from ideality ie Z < 1 over most of the pressure range of integration.

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For a vdW EOS

$$\ln \phi = \ln\left(\frac{f}{P}\right) = (Z-1) - \ln Z + \ln\left(\frac{V}{V-b}\right) - \frac{a}{VRT}$$

Similarly you can derive relations for any cubic EOS.

Since cubic EOS can describe both gaseous and liquid phases, this relation is applicable for both phases. For ex for vdW EOS

For a vapor phase

$$\ln\left(\frac{f^V}{P}\right) = (Z^V - 1) - \ln Z^V + \ln\left(\frac{V^V}{V^V - b}\right) - \frac{a}{V^V RT}$$

and for liquid phase

$$\ln\left(\frac{f^L}{P}\right) = (Z^L - 1) - \ln Z^L + \ln\left(\frac{V^L}{V^L - b}\right) - \frac{a}{V^L RT}$$

where V^V = vapor phase molar volume

V^L = Liquid phase molar volume

$Z^V = \frac{PV^V}{RT}$ – vapor phase compressibility

$Z^L = \frac{PV^L}{RT}$ – Liquid phase compressibility

How to calculate the vapor and liquid phase fugacities from vdW EOS

Given T and P use the EOS and calculate the volume, V if a single phase is only present.

Calculate the compressibility factors

$$Z = \frac{PV}{RT}$$

Then calculate the fugacity :

$$\ln \frac{f}{P} = (Z-1) - \ln Z + \ln \frac{V}{V-b} - \frac{a}{VRT}$$

If two phases can exist at these P and T, you get three roots for the EOS. Then take the largest volume as the vapor volume, V^V and the smallest volume as the liquid volume, V^L. Calculate the liquid and vapor phase compressibility factors.

$$Z^V = \frac{PV^V}{RT}, Z^L = \frac{PV^L}{RT}$$

$$\ln\frac{f^V}{P} = (Z^V - 1) - \ln Z^V + \ln\frac{V^V}{V^V - b} - \frac{a}{V^V RT}$$

$$\ln\frac{f^L}{P} = (Z^L - 1) - \ln Z^L + \ln\frac{V^L}{V^L - b} - \frac{a}{V^L RT}$$

Peng–Robinson EOS

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

$$a = a_C\alpha, a_C = 0.45724R^2\frac{T_C{}^2}{P_C}, \alpha = \left[1+\kappa(1-T_r{}^{0.5})\right]^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.269932\omega^2$$

$$b = 0.07780R\frac{T_C}{P_C}$$

$$\ln\frac{f}{P} = (Z-1) - \ln(Z-B) - \frac{A}{B2\sqrt{2}}\ln\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}$$

$$A = \frac{aP}{R^2T^2}, B = \frac{bP}{RT}$$

The saturation vapor pressure of water at 200 C is 1.555 MPa. Estimate the fugacity of water at these conditions using the PR EOS?

Algorithm

1) For this T and P calculate the V.
2) Calculate the liquid and vapor volumes.
3) Calculate the liquid and vapor phase Z.
4) Calculate f for liquid and vapor phases.

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

$$a = a_C\alpha, a_C = 0.45724R^2\frac{T_C^{\,2}}{P_C}, \alpha = \left[1+\kappa(1-T_r^{0.5})\right]^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.269932\omega^2$$

$$b = 0.07780R\frac{T_C}{P_C}$$

$$\ln\frac{f}{P} = (Z-1) - \ln(Z-B) - \frac{A}{B2\sqrt{2}}\ln\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}$$

$$A = \frac{aP}{R^2T^2}, B = \frac{bP}{RT}$$

$Tc := 647.3 \quad Pc := 22.12 \cdot 10^6 \quad \omega := 0.344$

$T := 473.15 \quad P := 1.555 \cdot 10^6 \quad R := 8.314$

$k := 0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2 \quad \alpha := \left(1 + k \cdot \left(1 - \sqrt{\frac{T}{Tc}}\right)\right)^2 = 1.269$

$a := 0.45724 \cdot \left(\frac{R^2 \cdot Tc^2}{Pc}\right) \cdot \alpha \quad b := 0.07780 \cdot \left(\frac{R \cdot Tc}{Pc}\right) = 1.893 \cdot 10^{-5}$

Calc all the parameters needed for the PR EOS, namely a,α, k and b knowing the critical properties and the acentric factor.

$$c := \begin{bmatrix} b^3 \cdot P + b^2 \cdot R \cdot T - b \cdot a \\ a - 3 \cdot P \cdot b^2 - 2 \cdot b \cdot R \cdot T \\ P \cdot b - R \cdot T \\ P \end{bmatrix}^T$$

$$volu := polyroots(c) = \begin{bmatrix} 0.000025 \\ 0.00014 \\ 0.002345 \end{bmatrix}$$

$Vg := \max(volu) = 0.002345 \qquad Vl := \min(volu) = 0.000025$

Solve the cubic equation for the three specific volumes the lowest specific volume corresponds to the liquid and the largest to the vapor specific volume.

$$Zg := \frac{P \cdot Vg}{R \cdot T} = 0.927 \qquad Zl := \frac{P \cdot Vl}{R \cdot T} = 0.01$$

Calc the vapor phase and liquid phase compressibility.

$$A := \frac{a \cdot P}{R^2 \cdot T^2} = 0.076 \qquad B := \frac{b \cdot P}{R \cdot T} = 0.007$$

Calc the factors A and B

$$fg\_fac := \left((Zg - 1) - \ln(Zg - B) - \frac{A}{2 \cdot B \cdot \sqrt{2}} \cdot \ln\left(\frac{Zg + \left(1 + \sqrt{2}\right) \cdot B}{Zg + \left(1 - \sqrt{2}\right) \cdot B} \right) \right) = -0.071$$

$$fl\_fac := \left((Zl - 1) - \ln(Zl - B) - \frac{A}{2 \cdot B \cdot \sqrt{2}} \cdot \ln\left(\frac{Zl - \left(1 + \sqrt{2}\right) \cdot B}{Zl - \left(1 - \sqrt{2}\right) \cdot B} \right) \right) = -0.068$$

$$fug\_vap := P \cdot \exp(fg\_fac) = 1.449 \cdot 10^6 \qquad fug\_liq := P \cdot \exp(fl\_fac) = 1.453 \cdot 10^6$$

Calc the vapor phase and liquid phase fugacities.

Since at 200 C and 1.555 Mpa conditions water exists in two phases, vapor and liquid have same fugacities !!

For calculating liquids fugacity another approach is usually followed.

We have the relation @ const Temp

$$dG = RT\, d\ln f = V^L dP$$

(V^L → liquid phase molar volume)

$$\therefore d\ln f = \frac{V^L}{RT} dP$$

Integrating from $P = P^{Sat}$ to $P = P > P^{Sat}$ so that the phase is liquid along the integration path.

$$\int_{p^{sat}}^{p} \frac{V^L}{RT}\, dP = \int_{f^{sat}}^{f} d\ln f$$

$$\Rightarrow \ln\left(f / f^{sat}\right) = \int_{p^{sat}}^{p} \frac{V^L}{RT}\, dP \simeq \frac{V^L}{RT}\left(P - P^{sat}\right)$$

Since for liquids $V^L \simeq$ constant with moderate change in P

SPECIFIC VOLUME V

	T K	P kPa	sat. liq.	evap.	sat. vap.
0	273.15	0.611	1.000	206300.	206300.
0.01	**273.16**	**0.611**	**1.000**	**206200.**	**206200.**
1	274.15	0.657	1.000	192600.	192600.
2	275.15	0.705	1.000	179900.	179900.
3	276.15	0.757	1.000	168200.	168200.
4	277.15	0.813	1.000	157300.	157300.
65	338.15	25.01	1.020	6201.3	6202.3
66	339.15	26.15	1.020	5947.2	5948.2
67	340.15	27.33	1.021	5705.2	5706.2
68	341.15	28.56	1.022	5474.6	5475.6
69	342.15	29.84	1.022	5254.8	5255.8
70	343.15	31.16	1.023	5045.2	5046.3
71	344.15	32.53	1.023	4845.4	4846.4
72	345.15	33.96	1.024	4654.7	4655.7
73	346.15	35.43	1.025	4472.7	4473.7
74	347.15	36.96	1.025	4299.0	4300.0

$$\ln\left(\frac{f}{f^{sat}}\right) = \frac{V^L}{RT}\left(P - P^{sat}\right) \qquad (17)$$

$$\therefore\ f(P) = f^{sat}(P^{sat}) \cdot \underbrace{e^{\frac{V^L(P-P^{sat})}{RT}}}_{\text{Poynting factor. (PF)}}$$

$$\therefore f(P) = f^{Sat}(p^{Sat}) \cdot \underbrace{e^{\frac{V^L(P-p^{Sat})}{RT}}}_{\text{Poynting factor. (PF)}}$$

PF ~ 1 for P not large compared to p^{Sat}

then

$$f(P) \sim f^{Sat}(p^{Sat})$$

$f(P)$: fugacity of liquid at $P > p^{Sat}$

$f^{Sat}(p^{Sat})$: fugacity of saturated phase, since at saturation $f^V = f^L = f^{Sat}$

$\therefore f(P) \sim f^{Sat}(P^{Sat}) = \phi^{Sat} \cdot P^{Sat}$

if the vapor phase is ideal $\phi^{Sat} = 1$

$\therefore f(P) \sim P^{Sat}$

i.e as a first approximation

fugacity of liquid at $=$ P^{Sat}.
pressure $P > P^{Sat}$

Stability of a phase

Water can exist in any of the three states. At a pressure of 1 atm, why do we see water in the liquid state between 0 C and 100 C and in the vapor phase above 100 C ?

$$dG = RTd\ln f$$

$$G = RT\ln f + \Gamma(T)$$

In this equation remember we have kept T as constant.

For two phases (say vapor and liquid) in equilibrium

$$G^V = RT\ln f^V + \Gamma(T)$$
$$G^L = RT\ln f^L + \Gamma(T)$$

At VLE, $G^V = G^L$

$$G^V = G^L \Rightarrow f^V = f^L$$

Let us check if $G^V = G^L$ at 100 C and 101.325 kPa for water

From steam tables at 100 C and 101.325 kPa we have the following data

	Liquid Phase	Vapor Phase
H (kJ/kg)	419.064	2676
S (kJ/kg K)	1.3069	7.3554

$G^V = H^V - TS^V = 2676 - 373.15*7.3554 = -68.67$

$G^L = H^L - TS^L = 419.064 - 373.15*1.3069 = -68.61$

Of all the phases a component can exist, it chooses the state which has the lowest Gibbs (G) free energy. Since G and fugacity, f are equivalent we can reframe this sentence as:

Of all the phases a component can exist it chooses the state which has the lowest fugacity.

2003 GATE

(1)

Prob water at 300°C has a vapor pressure of 8592.7 kPa and fugacity 6738.9 kPa. Under these conditions one mole of water in liquid phase has a volume of 25.28 cm^3 and that in vapor phase has 391.1 cm^3. Fugacity of water (in kPa) at 9000 kPa will be

a) 6738.9 b) 6753.5 c) 7058.3 d) 9000

Soln $f^L = f^{sat} \cdot PF$

$f^L(P) = f^{sat}(P^{sat}) \cdot PF$

here $P = 9000 kPa > P^{sat} = 8592.7 kPa$

hence the phase is liquid water.

given the eqn

$$f^L(P) = f^{sat}(P^{sat}) \cdot \exp\left[\frac{V_L (P - P^{sat})}{RT}\right]$$

given $V_L = 25.28 \ cm^3/mol$

$R = 8314 \ \frac{cm^3 \ kPa}{mol \cdot K}$, $T = 573 \ K$

$f^{sat}(P^{sat}) = 6738.9 \ kPa$

$$f^L(P) = 6738.9 \exp\left[\frac{25.28 * (9000 - 8592.7)}{8314 * 573}\right]$$

$$= 6738.9 \exp(0.00216)$$

$$= 6753.5 \text{ kPa}$$

2015 Gate

Given that the molar residual Gibbs free energy g^R and residual volume v^R are related as

$$\frac{g^R}{RT} = \int_0^P \frac{v^R}{RT}\, dP$$

find g^R at $t = 27^\circ C$ and $P = 0.2 MPa$. The gas follows the EOS $Z = 1 + \frac{BP}{RT}$ where $B = -10^{-4}\ m^3/mol$ and $R = 8.314\ J/mol\,K$.

Soln) $V^R = V - V^{ig} = \frac{ZRT}{P} - \frac{RT}{P}$

$= (Z-1)\frac{RT}{P}$

$= B$

$\therefore$

$$\frac{g^R}{RT} = \int_0^P \frac{V^R}{RT} dP$$

$$= \int_0^P \frac{B}{RT} dP = \frac{B}{RT}\int_0^P dP$$

$$= \frac{BP}{RT}$$

Since $B = f(T)$ only

$$\therefore \quad g^R = BP$$

$$= \left(-10^{-4} \cdot \frac{m^3}{mol}\right) * \left(0.2 \times 10^6 \frac{N}{m^2}\right)$$

$$= \underline{-20 \ J/mol}$$

2017 Gate

(3)

Prob The pressure of a liquid is increased isothermally. The molar volume of the liquid decreases from $50.45 \times 10^{-6} \frac{m^3}{mol}$ to $4.8 \times 10^{-6} \frac{m^3}{mol}$ during this process. The isothermal compressibility of the liquid is $10^{-9}\ Pa^{-1}$, which can be assumed constant. The change in the molar gibbs free energy of the liquid in J/mol is

Soln

Given $\alpha = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$= 10^{-9}\ Pa^{-1}$.

We have the eqn

$dG = VdP - SdT \rightarrow 0$, Since T = Constant along the path

$\therefore dG = VdP$

$= V\left(\frac{\partial P}{\partial V}\right)_T dV$ change variable of integration

$= -\frac{dV}{\alpha}$

$\therefore \Delta G = -\frac{\Delta V}{\alpha}$ Since α = Constant

$= -\left[\frac{48\times10^{-6} - 50.45\times10^{-6}}{10^{-9}}\right]$

2017 Gate

Prob

The vapor pressure of a pure liquid at a temperature T is 30 bar. The actual and ideal gas values of g/RT for the saturated vapor at this temp. T and 30 bar are 7 and 7.7 respectively. The fugacity of the saturated liquid at these conditions in bar is

Soln)

$$dG^R = V^R dP = RT\, d\ln f$$

$$\therefore G^R = RT \ln\left(f/p^{sat}\right) \qquad \left(\text{Eqn } 11.31 \text{ Smith \& VanNess}\right)$$

$$\text{But } \frac{G^R}{RT} = \frac{G}{RT} - \frac{G^{ig}}{RT} = 7 - 7.7 = -0.7$$

$$\therefore \ln\left(\frac{f}{p^{sat}}\right) = \frac{G^R}{RT} = -0.7$$

$$\frac{f}{p^{sat}} = 0.5$$

$$\therefore f = 0.5 * p^{sat} = 0.5 * 30 = 15 \text{ bar}$$