Unit 1 Summary

Partial Derivatives and their use in describing equations of state. You need to be able to obtain the total differential of *P*:

$$dP = \left(\frac{\partial P}{\partial V}\right)_{n,T} dV + \left(\frac{\partial P}{\partial T}\right)_{n,V} dT + \left(\frac{\partial P}{\partial n}\right)_{V,T} dn$$

For an ideal gas $PV = nRT$

$$dP = -\frac{nRT}{V^2}dV + \frac{nR}{V}dT + \frac{RT}{V}dn$$

And for a van der Waals gas, where $\left(P + \frac{a}{\overline{V}^2}\right)\left(\overline{V} - b\right) = RT$

The total differential is: $dP = \frac{R}{\overline{V} - b}dT + \left[-\frac{RT}{\left(\overline{V} - b\right)^2} + \frac{2a}{\overline{V}^3}\right]d\overline{V}$

The useful relations: $\left(\frac{\partial y}{\partial x}\right)_{a,b} = \frac{1}{\left(\partial x/\partial y\right)_{a,b}}$, $\left(\frac{\partial^2 U}{\partial V \partial T}\right)_n = \left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_{V,n}\right]_{T,n}$, and $\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$

Know how to prove exact and inexact differentials.
You should all know the basic equation of state dealing with ideal gases. The other important ones are listed below.

You should be able to derive the cubic form of the van der Waals equation:

$$\overline{V}^3 - \left(b + \frac{RT}{P}\right)\overline{V}^2 + \frac{a}{P}\overline{V} - \frac{ab}{P} = 0$$

In terms of the compressibility factor: $Z = \frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}}$

The Redlich-Kwong equation will be given: $P = \frac{RT}{\overline{V} - B} - \frac{A}{T^{1/2}\overline{V}\left(\overline{V} + B\right)}$

The cubic form is: $\overline{V}^3 - \frac{RT}{P}\overline{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P}\right)\overline{V} - \frac{AB}{T^{1/2}P} = 0$

You should appreciate how cubic equations are solved using the Newton-Raphson method (you will not be asked to actually solve one in an exam).

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$

You need to know the most fundamental equation of sate, the *virial equation of state*. In particular, we consider the second virial coefficient to be the most important.

$$Z = \frac{P\overline{V}}{RT} = 1 + \frac{B_{2V}(T)}{\overline{V}} = 1 + B_{2P}(T)P$$

and $$B_{2V}(T) = RTB_{2P}(T) = -2\pi N_A \int_0^\infty \left[e^{-U(r)/k_BT} - 1\right] r^2 dr = \overline{V} - \overline{V}_{IDEAL}$$

Note: Although not mentioned, $B_{2V}(T) = \overline{V} - \overline{V}_{\text{ideal}}$

Know the various contributions to the Lennard-Jones potential.

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Know the graphical form of the above equation and the interpretation of σ and ε. For the long range attractive interactions, these are usually dipole-dipole, dipole-induced dipole, and London dispersion.

Simple potential models can be used to solve for the second virial coefficient.

For the hard-sphere potential $$\begin{aligned} U(r) &= \infty \quad r < \sigma \\ U(r) &= 0 \quad r > \sigma \end{aligned}$$ and $$B_{2V}(T) = \frac{2\pi\sigma^3 N_A}{3}$$

For the square-well potential $$\begin{aligned} U(r) &= \infty \quad r < \sigma \\ U(r) &= -\varepsilon \quad \sigma < r < \lambda\sigma \\ U(r) &= 0 \quad r > \lambda\sigma \end{aligned}$$

a $$B_{2V}(T) = \frac{2\pi\sigma^3 N_A}{3}\left[1 - \left(\lambda^3 - 1\right)\left(e^{\varepsilon/k_BT} - 1\right)\right]$$

We can write the second virial coefficient in terms of the cubic form of the van der Waals equation. Once this is done, we can use a hard-sphere/Lennard Jones hybrid potential to solve the integral for $B_{2V}(T)$. This allows one to determine the molecular parameters *a* and *b* of the van der Waals equations. Please make sure you understand this process. It's given in pages 84 and 85 in your textbook.

You should know the molecular interpretation of *a* and *b* (including the full derivation based on a hybrid hard-sphere and Lennard-Jones potential).

$$a = \frac{2\pi N_A^2 c_6}{3\sigma^3} \quad \text{and} \quad b = \frac{2\pi\sigma^3 N_A}{3}$$

You need to learn the complete proof for this.

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$

$$\begin{aligned} B_{2V}(T) &= -2\pi N_{\mathrm{A}} \int_0^\sigma [0-1] r^2 dr - 2\pi N_{\mathrm{A}} \int_\sigma^{\lambda\sigma} [e^{\varepsilon/k_{\mathrm{B}}T} - 1] r^2 dr \\ &\quad -2\pi N_{\mathrm{A}} \int_{\lambda\sigma}^\infty [e^0 - 1] r^2 dr \\ &= \frac{2\pi\sigma^3 N_{\mathrm{A}}}{3} - \frac{2\pi\sigma^3 N_{\mathrm{A}}}{3} (\lambda^3 - 1)(e^{\varepsilon/k_{\mathrm{B}}T} - 1) \\ &= \frac{2\pi\sigma^3 N_{\mathrm{A}}}{3} [1 - (\lambda^3 - 1)(e^{\varepsilon/k_{\mathrm{B}}T} - 1)] \end{aligned}$$

$$\begin{aligned} P &= \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2} \\ &= \frac{RT}{\overline{V}} \frac{1}{(1 - \frac{b}{\overline{V}})} - \frac{a}{\overline{V}^2} \end{aligned}$$

$$B_{2V}(T) = b - \frac{a}{RT}$$

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\frac{c_6}{r^6} & r > \sigma \end{cases}$$

$$\begin{aligned} B_{2V}(T) &= \frac{2\pi\sigma^3 N_{\mathrm{A}}}{3} - \frac{2\pi N_{\mathrm{A}} c_6}{k_{\mathrm{B}}T} \int_\sigma^\infty \frac{r^2 dr}{r^6} \\ &= \frac{2\pi\sigma^3 N_{\mathrm{A}}}{3} - \frac{2\pi\sigma^3 N_{\mathrm{A}} c_6}{3k_{\mathrm{B}}T} \end{aligned}$$