HWK #1 Key

QM

1. $\tilde{\nu} = 2349.16\ cm^{-1}$

$\tilde{\nu}$	λ	E
$\nu = c/\lambda$	$\lambda = 1/\tilde{\nu} = 0.0004257$ cm	$E = h\nu$
$c = 2.9979\times10^{10}$ cm/s, $\lambda = 0.0004257$ cm	1 cm = 10^7 nm	$\nu = 7.04255\times10^{13}$, $h = 6.626076\times10^{-34}$
$\nu = 7.04255\times10^{13}$ Hz	$\lambda = 4256.84$ nm	$E = 4.66645\times10^{-20}$ J

2. H electronic energy levels:

$$\varepsilon_{el} = \frac{-2.17869\times10^{-18}}{n^2}\ J$$

$$\Delta\varepsilon_{el} = 2.17869\times10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\ J$$

First photon absorbed, $\lambda = 97.2$ nm $= \Delta\lambda$

$$\Delta\varepsilon = 2.04363\times10^{-18}\ J$$

$$2.04363\times10^{-18} = 2.17869\times10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$0.938 = \frac{1}{1^2} - \frac{1}{n_2^2}$$

$$n_2 = 4$$

Next photon emitted, $\lambda = 486$ nm $= \Delta\lambda$

$$\Delta\varepsilon = 4.08726\times10^{-19}$$

$$4.08726\times10^{-19} = 2.17869\times10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \left[\text{Note } n_2 > n_1\right]$$

$$0.1876 = \frac{1}{n_1^2} - \frac{1}{4^2}$$

$$\boxed{n_1 = 2}$$

3. $k_{^{79}Br-^{79}Br} = 240\ N\cdot m^{-1}$

$$\mu = \frac{m_1 m_2}{m_1+m_2} = \frac{79\cdot79}{79+79} = 39.5\ \text{amu} \times \frac{1.66\times10^{-27}\ kg}{1\ \text{amu}} = 6.557\times10^{-26}$$

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} = \frac{1}{2\pi}\left(\frac{240}{6.557\times10^{-26}}\right)^{1/2} = 9.63\times10^{12}\ Hz \text{ or } 321.2\ cm^{-1}$$

$$\varepsilon_0 = \frac{1}{2}h\nu = \frac{1}{2}(6.626\times10^{-34}\ J.s)(9.63\times10^{12}\ \tfrac{1}{s}) = 3.19\times10^{-21}\ J$$

4. $\tilde{\nu} = 2330 \text{ cm}^{-1}$, $D_0 = 78715 \text{ cm}^{-1}$ for N_2

$$D_e = D_0 + \frac{h\nu}{2}$$

$$\tilde{\nu} = \nu/c \text{ or } \nu = c\tilde{\nu} = 2.9979 \times 10^{10} \text{ cm/s} \cdot 2330 \text{ cm}^{-1}$$
$$= 6.985 \times 10^{13} \text{ Hz}$$

$$h\nu/2 = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(6.985 \times 10^{13} \text{ 1/s})}{2} = 2.314 \times 10^{-20} \text{ J}$$
or 1165 cm

$$D_0 \Rightarrow E = hc\tilde{\nu} = 1.5636 \times 10^{-18} \text{ J}$$

$$D_e = D_0 + h\nu/2 = 1.5867 \times 10^{-18} \text{ J} \text{ or } 79880 \text{ cm}^{-1}$$

5.

	part	Molecule	Total DOF ~~Trans~~	Trans	Rot	Vib
	a	CH_3Cl	15	3	3	15−6=9
Linear	b	OCS	9	3	2	9−5=4
	c	C_6H_6	36	3	3	36−6=30
	d	H_2CO	12	3	3	12−6= 6

6. a) $\varepsilon_0 = 0$, $\varepsilon_1 = \hbar^2/I$, $\varepsilon_2 = 3\hbar^2/I$

$\Delta\varepsilon_{0\to1} = \hbar^2/I$ $\quad \Delta\varepsilon_{0\to2} = 3\hbar^2/I$

$$\therefore \Delta\varepsilon_{0\to2} = 3\Delta\varepsilon_{0\to1}$$

$$\Delta\nu_{0\to2} = 3(1.153 \times 10^{11} \text{ Hz}) = 3.459 \times 10^{11} \text{ Hz}$$

$$\Delta E_{0\to2} = 2.29 \times 10^{-22} \text{ J} = 2.29 \times 10^{-25} \text{ kJ}$$

$$\Delta\lambda_{0\to2} = 8.66695 \times 10^5 \text{ nm}$$

$$\Delta\tilde{\nu}_{0\to2} = 11.54 \text{ cm}^{-1}$$

(6b) $g_J = 2J+1$

Level	g_J
J=0	1
J=1	3
J=2	5
J=3	7

Gas Laws

16-6. $T = 298\ K$

$P = 10^{-12}$ torr $\rightarrow 1.3158 \times 10^{15}$ atm

$V = 1.00\ cm^3 \rightarrow 1 \times 10^{-3}\ L$

Conversions
760 torr = 1 atm
$1000\ cm^3 = 1L$

Assume ideal gas ($\downarrow P$)...

$P\bar{V} = RT$

$$\bar{V} = \frac{0.08206\ (L\cdot atm/mol\cdot K)\cdot 298\ K}{1.3158\times 10^{15}\ atm} = 1.858 \times 10^{16}\ L/mol$$

$$\left((1.858\times 10^{16})^{-1}\ mol/L\right)(1\times 10^{-3}\ L)\left(6.022\times 10^{23}\ \frac{molecules}{mol}\right) = 3.24\times 10^{4}\ molecu$$

16-7

M, molar mass units = g/mol

$\bar{V} \Rightarrow L/mol \qquad \rho = g/L \qquad \therefore M = \bar{V}\rho \quad$ or $\bar{V} = M/\rho$

use virial expression...

$$\frac{P\bar{V}}{RT} = 1 + \frac{B_{2V}}{\bar{V}} \quad \text{or} \quad \frac{P}{RT}\cdot\frac{M}{\rho} = 1 + B_{2V}\,\rho/M$$

$$\frac{P}{\rho} = \frac{RT}{M} + \frac{RT\,B_{2V}}{M^2}\cdot\rho$$

$$y = b + m\,x \leftarrow \text{Plot}\ \begin{matrix}\rho \text{ on x axis}\\ P/\rho \text{ on y axis}\end{matrix}$$

$b = RT/M,\ M = RT/b \qquad b = 0.5656$ (see attached)

$$M = \frac{(0.08314\ L\cdot bar/mol\cdot K)(300\ K)}{0.5656\ bar\ L/g} = \boxed{44.1\ g/mol}$$

ID = CO_2

16-16. Propane @ 400 K, $\rho = 10.62$ mol/dm^3 $[\bar{V} = 0.094162 \frac{dm^3}{mol}$

$$R = 0.0831451 \frac{dm^3 \cdot bar}{K \cdot mol}$$

a) $P\bar{V} = RT$, $P = \frac{RT}{\bar{V}} = \overset{353.2}{\cancel{375.16}}$ bar, 11.7% error

b) $a = 9.3919 \frac{dm^6 \cdot bar}{mol^2}$, $b = 0.090494$ dm^3/mol

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} = 8008 \text{ bar}, \quad 1901\text{ \% error}$$

c) $A = 183.02 \frac{dm^6 \cdot bar}{mol^2 \; K^{1/2}}$ $B = 0.062723$ dm^3/mol

$$P = \frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} = 438.4 \text{ bar}, \ 9.6\% \text{ error}$$

d) $\alpha = 9.6938 \frac{L^2 \cdot bar}{mol^2}$ $\beta = 0.05632$ L/mol $dm^3 = L$!

$$P = \frac{RT}{\bar{V} - \beta} - \frac{\alpha}{\bar{V}(\bar{V} + \beta) + \beta(\bar{V} - \beta)} = 284.19 \text{ bar}, 28.95\% \text{ err}$$

Redlich-kwong equation gives best results

16-31 $Z = \frac{P\bar{V}}{RT}$ → y-axis

Table 16.5

$\bar{V}_R = \bar{V}/\bar{V}_c$ → x-axis

$\bar{V}_c^{ethane} = 0.1480$ dm^3/mol

$\bar{V}_c^{Ar} = 0.07530$ dm^3/mol

☆ Note... 1st 3 data pts left off graphs for 16-31 to 16-34. See attached.

16-33 $Z = \frac{\bar{V}_R}{\bar{V}_R - 1/3} - \frac{9}{8\bar{V}_R T_R}$

16-34 $Z = \frac{\bar{V}_R}{\bar{V}_R - 0.25992} - \frac{1.2824}{T_R^{3/2}(\bar{V}_R + 0.25992)}$

16-38 O_2 @ 273.15 K SKIPPED

Recall from 16-7... $\frac{P}{\rho} = \frac{RT}{M} + \frac{RT B_{2V}}{M^2}\rho$

intercept, b   slope, m

$m = -0.0004695 \ \frac{dm^3 \cdot atm}{g^2}$ $b = 0.760470 \ atm \cdot L/g$

$R = 0.0820578 \ \frac{dm^3 \cdot atm}{K \cdot mol}$

$T = 273.15 \ K$

$M = 15.9994 \ g/mol$

$B_{2V} = \frac{m M^2}{RT} = -5.3328 \times 10^{-3} \ dm^3/mol$

16-44

$\frac{P\bar{V}}{RT} = 1 + \frac{B_{2V}}{\bar{V}}$ $\bar{V} = \frac{1}{\rho}$

or $P/\rho = RT + RT B_{2V} \rho$ $T = 300.0K$

y axis, intercept, slope, x axis $R = 0.0820578 \ \frac{L \cdot atm}{K \cdot mol}$

Slope = −0.3724   see attached

$-0.3724 = RT B_{2V}$

$B_{2V} = -0.01513 \ L/mol$

$= -15.13 \ cm^3/mol$ more negative than accepted

16-57 Krypton

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

$\sigma = 327.8 \ pm \rightarrow 327.8 \times 10^{-11} \ dm$

$\varepsilon/k_B = 136.5 \ K$ See attached

$\lambda = 1.68$

16-58 $\alpha = \frac{1}{\bar V}\left(\frac{\partial \bar V}{\partial T}\right)_P$ $\quad \bar V = \frac{RT}{P}$ for ideal gas

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

$$\alpha = \frac{1}{\bar V}\cdot\frac{R}{P} = \frac{P}{RT}\cdot\frac{R}{P} = 1/T$$

2. As in slide GAS-11...

cubic VDW EOS $\quad \bar V^3 - \left(b + \frac{RT}{P}\right)\bar V^2 + \frac{a}{P}\bar V - \frac{ab}{P} = 0$

@ $T = T_c$ $\quad \bar V^3 - 3\bar V_c \bar V^2 + 3\bar V_c^2 \bar V - \bar V_c^3 = 0$

$\therefore \quad 3\bar V_c = b + RT_c/P_c \qquad 3\bar V_c^2 = \frac{a}{P_c} \qquad \bar V_c^3 = \frac{ab}{P_c}$

or

$P_c = \frac{a}{3\bar V_c^2}$ $\quad$ substitute $\quad \bar V_c^3 = \frac{ab\cdot 3\bar V_c^2}{a}$

$a = 3\bar V_c^2 P_c$ $\quad$ or $\quad b = \bar V_c/3$

VDW EOS $\quad \left(P + \frac{a}{\bar V^2}\right)(\bar V - b) = RT$

$$\frac{\left(P + \frac{3\bar V_c^2 P_c}{\bar V^2}\right)\left(\bar V - \frac{1}{3}\bar V_c\right)}{P_c V_c} = \frac{RT}{P_c V_c}$$

$P_c \bar V_c = \frac{3ab}{27b^2}$

$RT_c = 8a/27b$

$\therefore P_c \bar V_c = \frac{3}{8} RT_c$

$$\left(\frac{P}{P_c} + 3\frac{\bar V_c^2}{\bar V^2}\right)\left(\frac{\bar V}{\bar V_c} - \frac{1}{3}\right) = \frac{RT}{3/8\, RT_c}$$

Let $P/P_c = P_R$, $\bar V/\bar V_c = V_R$, $T/T_c = T_R$

$$\left(P_R + \frac{3}{V_R^2}\right)\left(V_R - \frac{1}{3}\right) = 8/3\, T_R$$

$V_R = \bar V/\bar V_c \qquad \bar V = \frac{0.009\ dm^3}{0.1113\ mol} = 0.081\ dm^3/mol \qquad \bar V_c = 0.095\ dm^3/mol$

$V_R = 0.853$

$T_R = 300K/304\,k = 0.987$

$\left(P_R + \frac{3}{(0.853)^2}\right)\left(0.853 - \frac{1}{3}\right) = \frac{8}{3}(0.987) \qquad P_R = 0.94$

$P = P_R P_c = 0.94 \cdot 73.84$ bar

$= 69.5$ bar