Chapter 1

Gases and the Zeroth Law of Thermodynamics

1.2. A system is any part of the universe under observation. The “surroundings” includes everything else in the universe. Consider a solution calorimeter in which two aqueous solutions are mixed and temperature changes are recorded. In this case the solutes (reactants and products) would be considered the “system”. The water, calorimeter, and rest of the lab and world would be the “surroundings”.

1.4. (a) $12.56\ \mathrm{L}\times\frac{1000\ \mathrm{mL}}{1\ \mathrm{L}}\times\frac{1\ \mathrm{cm}^3}{1\ \mathrm{mL}}=12{,}560\ \mathrm{cm}^3\ =1.256\times10^4\ \mathrm{cm}^3$

(b) 45°C + 273.15 = 318 K

(c) $1.055\ \mathrm{atm}\times\frac{1.01325\ \mathrm{bar}}{1\ \mathrm{atm}}\times\frac{100{,}000\ \mathrm{Pa}}{1\ \mathrm{bar}}=1.069\times10^5\ \mathrm{Pa}$

(d) $1233\ \mathrm{mmHg}\times\frac{1\ \mathrm{torr}}{1\ \mathrm{mmHg}}\times\frac{1\ \mathrm{atm}}{760\ \mathrm{torr}}\times\frac{1.01325\ \mathrm{bar}}{1\ \mathrm{atm}}=1.644\ \mathrm{bar}$

(e) $125\ \mathrm{mL}\times\frac{1\ \mathrm{cm}^3}{1\ \mathrm{mL}}=125\ \mathrm{cm}^3$

(f) 4.2 K – 273.15 = –269.0°C

(g) $25750\ \mathrm{Pa}\times\frac{1\ \mathrm{bar}}{100{,}000\ \mathrm{Pa}}=0.2575\ \mathrm{bar}$

1.6. $p_{atm} = p_{mouth} + \rho hg$, where ρhg correspond to the pressure exerted by the liquid

$p_{atm} - p_{mounth} = \rho hg = (1.0\mathrm{x}10^3\ \mathrm{kg/m^3})(0.23\mathrm{m})(9.80\mathrm{m/s^2}) = 2254\ \mathrm{N/m^2} = 2.3\ \mathrm{x}10^3\ \mathrm{Pa}$

1.8. In terms of the zeroth law of thermodynamics, heat will flow from the (hot) burner or flame on the stove into the (cold) water, which gets hotter. Then heat will move from the hot water into the (colder) egg.

1.10. For this sample of gas under these conditions, $F(T)$ = 2.97 L × 0.0553 atm = 0.164 L·atm. If the pressure were increased to 1.00 atm: 0.164 L·atm = (1.00 atm) × V; therefore V = 0.164 L.

1.12. $V=R\cdot\frac{nT}{p}$, which rearranges to $R=\frac{pV}{nT}$.

Therefore: $R = \dfrac{(2.66\,\text{bar})(27.5\,\text{L})}{(1.887\,\text{mol})(466.9\,\text{K})} = 0.0830\dfrac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}}$

1.14. V_1=67 L, p_1=1.04 atm.

$\dfrac{x\,\text{atm}}{64.0\,\text{m}} = \dfrac{1\,\text{atm}}{10.1\,\text{m}}$; x = 6.34 atm. Therefore p_2 = 1.04 atm + 6.34 atm = 7.38 atm.

$p_1V_1 = p_2V_2$; so $V_2 = \dfrac{(1.04\,\text{atm})(67\,\text{L})}{(7.38\,\text{atm})} = 9.4\text{L}$

1.16. $1.82\times10^{13}\,\text{g}\,SO_2 \times \dfrac{1\,\text{mole}\,SO_2}{64.07\,\text{g}} = 2.84\times10^{11}\ \text{moles}\,SO_2$

$$p = \frac{nRT}{V} = \frac{(2.84\times10^{11}\ \text{moles}\,SO_2)(0.0821\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(273.15-17.0\text{K})}{8\times10^{21}\,\text{L}} = 7\times10^{-10}\,\text{atm}$$

1.18. $0.0821\dfrac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\times\dfrac{5/9\,\text{K}}{1\,^{\circ}\text{R}} = 0.0456\dfrac{\text{L}\cdot\text{atm}}{\text{mol}\cdot^{\circ}\ \text{R}}$

1.20. Calculations using STP and SATP use different numerical values of *R* because the sets of conditions are defined using different units. It's still the same *R*, but it's expressed in different units of pressure, atm for STP and bar for SATP.

1.22. The partial pressure of N_2 = $0.80\times\dfrac{14.7\,\text{lb}}{\text{in.}^2} = 11.8\dfrac{\text{lb}}{\text{in.}^2}$

The partial pressure of O_2 = $0.20\times\dfrac{14.7\,\text{lb}}{\text{in.}^2} = 2.9\dfrac{\text{lb}}{\text{in.}^2}$

1.24.

$$pV = \left(\frac{m}{M}\right)RT;\quad \frac{m}{V} = \frac{pM}{RT} = \frac{(4.50\text{torr})(44.01\text{g}/\text{mole})}{(62.36\frac{\text{L}\cdot\text{torr}}{\text{mol}\cdot\text{K}})(273.15-87\text{K})} = 0.01706\ \text{g}/\text{L} = 1.71\times10^{-5}\,\text{g}/\text{cm}^3$$

1.26. Using the ideal gas law, the number of moles of CO_2 =

$$\frac{(.965\ \text{atm})(1.56\ \text{L})}{(0.0821\ \frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}})(273.15\text{K}+22.0\text{K})} = 0.0621\ \text{moles}$$

$$0.0622\ \text{moles}\ CO_2 \times \frac{1\ \text{mole}\ C_6H_{12}O_6}{2\ \text{moles}\ CO_2} \times \frac{180.16\ \text{g}}{1\ \text{mole}\ C_6H_{12}O_6} = 5.60\ \text{g}\ C_6H_{12}O_6$$

1.28. Following the normal rules of derivation: (a) $3y^2 - \frac{y^2z^3}{w}$ (b) $\frac{3w^2z^3}{32y} + \frac{xy^2z^3}{w^2}$ (c) $6xy - \frac{w^3z^3}{32y^2} - \frac{2xyz^3}{w}$ (d) Using the answer from part a, we get $-\frac{3y^2z^2}{w}$ (e) $-\frac{3y^2z^2}{w}$ (f) Using the answer from part e, we get $\frac{3y^2z^2}{w^2}$.

1.30 (a) $\left(\frac{\partial n}{\partial V}\right)_{T,P} = \frac{p}{R \cdot T}$

(b) $\left(\frac{\partial T}{\partial p}\right)_{V,n} = \frac{V}{n \cdot R}$

(c) $\left(\frac{\partial n}{\partial T}\right)_{P,V} = \frac{-pV}{RT^2}$

(d) $\left(\frac{\partial p}{\partial n}\right)_{T,V} = \frac{RT}{V}$

1.32. (a) $V(T,p) = \frac{nRT}{p}$

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

(c)

$$dV = \left(\frac{nR}{p}\right)dT + \left(\frac{-nRT}{p^2}\right)dp = \left(\frac{(1\,\text{mole})\left(0.0821\frac{\text{Latm}}{\text{Kmole}}\right)}{1.08\,\text{atm}}\right)(10.0\text{K}) - \left(\frac{(1\text{mole})\left(0.0821\frac{\text{Latm}}{\text{Kmole}}\right)(350\text{K})}{(1.08\text{atm})^2}\right)(0.10\text{atm})$$

= -1.70 L

1.34. (a) $\left(\frac{\partial V}{\partial p}\right)_{n,T} = \frac{-nRT}{p^2}; \left(\frac{\partial^2 V}{\partial p^2}\right)_{n,T} = \frac{2nRT}{p^3}$

(b) $\left(\frac{\partial p}{\partial T}\right)_{n,V} = \frac{nR}{V}; \left(\frac{\partial^2 p}{\partial T^2}\right)_{n,V} = 0$

1.36. (a) Z=1 for an ideal gas. (b) If the gas truly follows the ideal gas law, Z will always be 1 regardless of the pressure, temperature, or molar volume.

1.38. Using equation 1.23, $T_B = \frac{a}{bR}$, and using data from Table 1.6, we have:

for CO_2: $$T_B = \frac{3.592\ \frac{\mathrm{L^2 atm}}{\mathrm{mol^2}}}{(0.04267\ \mathrm{L/mol})\left(0.08205\frac{\mathrm{L\ atm}}{\mathrm{mol\ K}}\right)} = 1026\ \mathrm{K}$$

for O_2: $$T_B = \frac{1.360\ \frac{\mathrm{L^2 atm}}{\mathrm{mol^2}}}{(0.03183\ \mathrm{L/mol})\left(0.08205\frac{\mathrm{L\ atm}}{\mathrm{mol\ K}}\right)} = 521\ \mathrm{K}$$

for N_2: $$T_B = \frac{1.390\ \frac{\mathrm{L^2 atm}}{\mathrm{mol^2}}}{(0.03913\ \mathrm{L/mol})\left(0.08205\frac{\mathrm{L\ atm}}{\mathrm{mol\ K}}\right)} = 433\ \mathrm{K}$$

1.40. The C term is $\frac{C}{\overline{V}^2}$. In order for the term to be unitless, C should have units of $(\text{volume})^2/(\text{moles})^2$, or $\mathrm{L^2/mol^2}$. The C' term is $C'p^2$, and in order for this term to have the same units as $p\overline{V}$ (which would be L·atm/mol), C' would need units of $\frac{L\cdot mol}{atm}$. (The unit bar could also be substituted for atm if bar units are used for pressure.)

1.42. Gases that have lower Boyle temperatures will be most ideal (at least at high temperatures). Therefore, they should be ordered as He, H_2, Ne, N_2, O_2, Ar, CH_4, and CO_2.

1.44. (a) He: b= $\frac{0.0237\mathrm{L}}{\mathrm{mole}} \times \frac{1\,\mathrm{m^3}}{1000\,\mathrm{L}} = 2.37\times10^{-5}\,\frac{\mathrm{m^3}}{\mathrm{mole}}$

$$2.37\times10^{-5}\,\frac{\mathrm{m^3}}{\mathrm{mole}} \times \frac{1\mathrm{mole}}{6.02\times10^{23}\ \mathrm{atoms}} = 3.94\times10^{-29}\,\frac{\mathrm{m^3}}{\mathrm{atom}}$$

$$\mathrm{V} = \frac{4}{3}\pi \mathrm{r}^3 = 3.94\times10^{-29}\,\frac{\mathrm{m^3}}{\mathrm{atom}};\mathrm{r} = 2.11\times10^{-10}\,\mathrm{m\ or\ 2.11\ Å}$$

(b) H_2O: b= $\frac{0.03049\mathrm{L}}{\mathrm{mole}}$; using a similar method to part a, r = 2.30 Å

(c) C_2H_6: b= $\frac{0.0638\text{L}}{\text{mole}}$; using a similar method to part a, r = 2.94 Å

1.46. Let us assume standard conditions of temperature and pressure, so $T = 273.15$ K and $p = 1.00$ atm. Also, let us assume a molar volume of 22.412 L = 2.2412×10^4 cm^3. Second virial coefficient terms can be calculated using values in Table 1.6.

Therefore, we have for hydrogen:

$$\frac{pV}{RT} = 1 + \frac{B}{\overline{V}} = 1 + \frac{15.7\,cm^3/mol}{2.2412 \times 10^4\,cm^3/mol} = 1.00070$$

, which is a 0.070% increase in the compressibility.

For H_2O, we have:

$$\frac{pV}{RT} = 1 + \frac{B}{\overline{V}} = 1 + \frac{-213.3\,cm^3/mol}{2.2412 \times 10^4\,cm^3/mol} = 0.9905$$

, which is a 0.95% decrease in the compressibility with respect to an ideal gas.

1.48. By comparing the two expressions from the text

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}} + \left(\frac{b}{\overline{V}}\right)^2 + \cdots \quad \text{and} \quad Z = 1 + \frac{B}{\overline{V}} + \frac{C}{\overline{V}^2} + \cdots$$

it seems straightforward to suggest that, at the first approximation, $C = b^2$. Additional terms involving $\overline{V}^2$ may occur in later terms of the first expression, necessitating additional corrections to this approximation for C.

1.50. The Redlich-Kwong equation of state: $p = \frac{RT}{\overline{V} - b} - \frac{a}{\sqrt{T}\,\overline{V}(\overline{V} - b)}$

$$\left(\frac{\partial p}{\partial \overline{V}}\right)_{T,n} = \frac{-RT}{(\overline{V} - b)^2} + \frac{a}{\sqrt{T}\,\overline{V}(\overline{V} - b)^2} + \frac{a}{\sqrt{T}\,\overline{V}^2(\overline{V} - b)}$$

1.52. The van der Waals equation of state: $(p + \frac{an^2}{V^2})(V - nb) = nRT$; As V approaches ∞, the an^2/V^2 term goes to 0 and the nb term becomes negligible. The equation then reduces to pV=nRT.

1.54. The Redlich-Kwong equation of state: $p = \frac{RT}{\overline{V} - b} - \frac{a}{\sqrt{T}\,\overline{V}(\overline{V} - b)}$

As T approaches infinity, the second term on the right side goes to 0. The molar volume of a gas at high temperature will generally be high so the correction factor, b, is negligible. The equation reduces to $p\overline{V} = RT$

1.56. Using the ideal gas law, $p = \frac{RT}{\overline{V}}, p = \frac{(0.0821\frac{L \cdot atm}{K \cdot mol})(273.15K)}{22.41L} = 1.00atm$

Using the Dieterici equation of state:

$$p = (0.0821\frac{L \cdot atm}{K \cdot mol})(273.15K)\frac{e^{-(10.91atm \cdot L^2)/\left[(22.41L)(0.0821\frac{L \cdot atm}{K \cdot mol})(273.15K)\right]}}{(22.41L - 0.0401L)} = 0.981atm$$

; It varies by ~2%.

1.58. In terms of *p*, *V*, and *T*, we can also write the following two expressions using the cyclic rule:

$\left(\frac{\partial V}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T}$ and $\left(\frac{\partial V}{\partial p}\right)_T = -\frac{\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_p}$. There are other constructions possible that would be reciprocals of these relationships or the one given in Figure 1.11.

1.60. Since the expansion coefficient is defined as $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$, α will have units of $\frac{1}{\text{volume}} \cdot \frac{\text{volume}}{\text{temperature}} = \frac{1}{\text{temperature}}$, so it will have units of K^{-1}. Similarly, the isothermal compressibility is defined as $-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$, so κ will have units of $\frac{1}{\text{volume}} \cdot \frac{\text{volume}}{\text{pressure}} = \frac{1}{\text{pressure}}$, or atm^{-1} or bar^{-1}.

. $\kappa = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ For an ideal gas, $\kappa = \frac{-1}{V}\left(\frac{-nRT}{p^2}\right) = \frac{1}{V}\left(\frac{nRT}{p}\right)\left(\frac{1}{p}\right) = \frac{1}{V}(V)\left(\frac{1}{p}\right) = \frac{1}{p}$

1.62

This is equal to 1 bar-1 at STP and SATP

1.64. For an ideal gas, $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\frac{\partial}{\partial p}\left(\frac{nRT}{p}\right) = \frac{1}{V}\frac{nRT}{p^2}$. Since $\frac{nRT}{p} = V$, this last expression becomes $\frac{1}{V}\frac{V}{p} = \frac{1}{p}$ for an ideal gas. The expression $\frac{T}{p}\alpha$ is evaluated as

$\frac{T}{p}\alpha = \frac{T}{p}\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{T}{pV}\frac{\partial}{\partial T}\left(\frac{nRT}{p}\right) = \frac{T}{pV}\frac{nR}{p}$. For an ideal gas, the ideal gas law can be rearranged to give $\frac{nR}{p} = \frac{V}{T}$, so we substitute to get that this last expression is $\frac{T}{pV}\frac{V}{T}$, which $= \frac{1}{p}$. Thus, the two sides of the equation ultimately yield the same expression and so are equal.

1.66. For an ideal gas, $\overline{V} = \frac{RT}{p}$. Therefore, the expression for density becomes, substituting for the molar volume, $d = \frac{M}{RT/p} = \frac{pM}{RT}$. The derivative of this expression with respect to temperature is $\left(\frac{\partial d}{\partial T}\right)_{p.n} = -\frac{pM}{RT^2}$. Using the definition of $\overline{V}$, this can be rewritten as $\left(\frac{\partial d}{\partial T}\right)_{p.n} = -\frac{M}{\overline{V}T}$.

1.68. $\mathrm{p} = \mathrm{e}^{-\frac{\mathrm{Mgh}}{\mathrm{RT}}}$ $\frac{\mathrm{Mgh}}{\mathrm{RT}} = \frac{\left(\frac{\mathrm{g}}{\mathrm{mol}}\right)\left(\frac{\mathrm{m}}{\mathrm{s}^2}\right)(\mathrm{m})}{\left(\frac{\mathrm{J}}{\mathrm{K}\cdot\mathrm{mole}}\right)(\mathrm{K})}$; If we convert g to kg and recognize that a J= $\frac{\mathrm{kg}\cdot\mathrm{m}^2}{\mathrm{s}^2}$, $\frac{\mathrm{Mgh}}{\mathrm{RT}} = \frac{\left(\frac{\mathrm{kg}}{\mathrm{mol}}\right)\left(\frac{\mathrm{m}^2}{\mathrm{s}^2}\right)}{\left(\frac{\mathrm{J}}{\mathrm{K}\cdot\mathrm{mol}}\right)(\mathrm{K})}$. All of the units cancel and the exponent is unitless.

1.70. If we assume that the average molecular weight of air is 28.967 g/mole, $\mathrm{p} = \mathrm{e}^{-\frac{\mathrm{Mgh}}{\mathrm{RT}}} = \mathrm{e}^{-\mathrm{X}}$

$$\mathrm{X} = \left(0.028967\frac{\mathrm{kg}}{\mathrm{mole}}\right)\left(9.8\frac{\mathrm{m}}{\mathrm{s}^2}\right)(-432\mathrm{m}) \div \left(8.314\frac{\mathrm{J}}{\mathrm{K}\cdot\mathrm{mole}}\right)(273.15+39.0\mathrm{K}) = -0.0473; \mathrm{e}^{-\mathrm{X}} = 1.05\mathrm{atm}$$

1.72. N=7 $\langle\mathrm{score}\rangle = \frac{\left(\frac{4}{7}\right)(5)+\left(\frac{3}{7}\right)(10)}{\left(\frac{4}{7}\right)+\left(\frac{3}{7}\right)} = 7.14$

1.74. The probability that the particle is in the higher state $= \mathrm{e}^{-\Delta\mathrm{E}/\mathrm{RT}}$.

(a) At 200K, probability = $e^{-1000\,\mathrm{J}/\left(\left(8.314\frac{\mathrm{J}}{\mathrm{K\cdot mole}}\right)(200\,\mathrm{K})\right)}$ =0.548

(b) At 500K, probability = $e^{-1000\,\mathrm{J}/\left(\left(8.314\frac{\mathrm{J}}{\mathrm{K\cdot mole}}\right)(500\,\mathrm{K})\right)}$ =0.786

(c) At 1000K, probability = $e^{-1000\,\mathrm{J}/\left(\left(8.314\frac{\mathrm{J}}{\mathrm{K\cdot mole}}\right)(100\,\mathrm{K})\right)}$ =0.887

To calculate ratios we can use the equation: $\frac{\text{probability}}{1-\text{probability}}$. For the three temperatures these ratios equal: 1.21, 3.67, and 7.85; as the temperature goes up.

1.76. (a) $(CN)_2$ is a linear molecule. $\langle E_{\text{trans}}\rangle=\frac{3}{2}RT\,;\langle E_{\text{rot}}\rangle=RT$

(b) H_2O is a non-linear molecule. $\langle E_{\text{trans}}\rangle=\frac{3}{2}RT\,;\langle E_{\text{rot}}\rangle=\frac{3}{2}RT$

(c) Kr is an atom. $\langle E_{\text{trans}}\rangle=\frac{3}{2}RT\,;\langle E_{\text{rot}}\rangle=0$

(d) C_6H_6 is a non-linear molecule. $\langle E_{\text{trans}}\rangle=\frac{3}{2}RT\,;\langle E_{\text{rot}}\rangle=\frac{3}{2}RT$