Solutions

Tutorial 1

1st Law of thermodynamics and other basic concepts

(04-03-2015)

1. \[ w = nRT \ln \left( \frac{p_1}{p_2} \right) \]
   \[ = 1 \times 8.314 \times 273 \ln \left( \frac{1013.25}{41} \right) \]
   \[ = 7.28 \text{ KJ} \]
   Isothermal process, so, \( dT = 0 \)
   \[ \Delta U = nC_v dT = 0 \]
   \[ \Delta H = nC_p dT = 0 \]
   Now \( q = U + w = w = 7.28 \text{ kJ} \)

2. \[ w = nRT \ln \left( \frac{v_2}{v_1} \right) = 41.96 \text{ KJ} \]

3. \[ w = nRT \ln \left( \frac{v_2}{v_1} \right) \]
   \[ = 4 \times 1.98 \times T \times \ln \left( \frac{10v_1}{v_1} \right) \]
   \[ 40000 \text{ Cal} = 4 \times 1.98 \times T \times \ln \left( \frac{10v_1}{v_1} \right) \]
   Or, \( T = 2193.4 \text{ K} \)
   \[ V_1 = nRT_1/P_1 \]
   \[ = 7.202 \text{ lit.} \]

4. \[ \begin{align*}
   \text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) &= 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \\
   2\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g}) &= 2\text{H}_2\text{O}(\text{l}) \\
   2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) &= 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})
\end{align*} \]

\[(i) + (ii)/2 - (iii)/2
\]
\[ \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) = \text{C}_2\text{H}_6(\text{g}) \]

\[ \Delta H = \Delta H_{(i)} + \Delta H_{(ii)/2} - \Delta H_{(iii)/2} \]
\[ = -32.8 \text{ Kcal.} \]

5. The reaction is

\[ \text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2 \]

Hence 1 mole \( \text{H}_2 \) gas is liberated for every 1 mole \( \text{Zn} \) used.
Therefore work done at constant pressure is given by

\[ w = -p\Delta V = -pV_{\text{gas}} = -nRT = \left( \frac{5g}{65.4 \text{ g mol}^{-1}} \right) \times (8.3145 \text{ JK}^{-1} \text{ mol}^{-1}) \times (23 + 273) \text{ K} = -188J \]

6. \( \Delta n = 1 - 1.5 = -0.5 \)

\[ \Delta H = \Delta U + \Delta (PV) \]
\[ \Delta H = \Delta U + \Delta nRT \]
\[ \Delta U^\circ = \Delta H^\circ - \Delta nRT \]
\[ = (-282.97 \text{ kJ mol}^{-1}) - (-0.5 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}) \]
\[ = -281.73 \text{ KJmol}^{-1} \]

7. Final volume of the cylinder is

\[ V(\text{final}) = \frac{(1.000 \text{ mol})(8.314 \text{ KJ mol}^{-1})(273.15)}{1.50 \times 10^5 \text{ Pa}} = 0.0151 \text{ m}^3 \]

Since \( P \) (transmitted) cannot exceed \( P_{\text{ext}} \),

\[ W \text{ (max.)} = -P_{\text{ext}} \Delta V = -(1.50 \times 10^5 \text{ Pa}) (0.0151 \text{ m}^3 - 0.0224 \text{ m}^3) = 2270 \text{ J} \]

Since \( P \) (transmitted) will exceed the equilibrium pressure that the gas would have at any volume,

\[ W \text{ (min.)} = - (1.000 \text{ mol}) \times (8.314 \text{ KJ mol}^{-1}) \times \frac{\ln(0.0151 \text{ m}^3)}{(0.0224 \text{ m}^3)} \times (273.15) \]
\[ = 890 \text{ J} \]

(The actual value must lie between these values, since it depends on the rate of the process and other things that we cannot evaluate using thermodynamics)

8. Balanced equation of the reaction is

\[ \text{CH}_4 (g) + 2\text{O}_2 (g) \rightarrow \text{CO}_2 (g) + 2\text{H}_2\text{O (l)} \]
\[ 0 = \text{CO}_2 (g) + 2\text{H}_2\text{O} (l) - \text{CH}_4 (g) - 2\text{O}_2 (g) \]

So,

\[ -890.36 \text{ KJ mol}^{-1} = \Delta H^\circ (\text{CO}_2) + 2\Delta H^\circ (\text{H}_2\text{O}) + (-1) \Delta H^\circ (\text{CH}_4) + (-1) \Delta H^\circ (\text{O}_2) \]

Since standard enthalpy of gaseous \( \text{O}_2 \) \[ \Delta H^\circ (\text{O}_2) \] = 0, at 273.15 \( K \), and applying the given enthalpy values of \( \text{CH}_4 \) and \( \text{H}_2\text{O} \).

\[ \Delta H^\circ (\text{CH}_4) = -890.36 \text{ KJ mol}^{-1} + (-393.522 \text{ KJ mol}^{-1}) + 2(-285.830 \text{ KJ mol}^{-1}) + (-2) (0) \]

\[ = -74.82 \text{ KJ mol}^{-1} \]

9. Assume supercooled water is metastable and treat it as though it were at equilibrium. We calculate \( \Delta H \) along the reversible path.

Step 1 is the reversible heating of the supercooled liquid to 0 \( ^\circ \text{C} \), the equilibrium freezing temperature.

Step 2 is the reversible freezing of the system at 0 \( ^\circ \text{C} \), and

Step 3 is the reversible cooling of the solid to −15 \( ^\circ \text{C} \). The enthalpy change for the irreversible process is equal to the enthalpy change of this reversible process.

(Figure taken from text book)

Enthalpy change in step 1:

\[ \Delta H_1 = \int_{258.15 \text{ K}}^{273.15 \text{ K}} C_p(l) \, dT = C_p(l) \Delta T \]

\[ = (2.000 \text{ mol}) (75.48 \text{ KJ mol}^{-1}) (15 \text{ K}) = 2264 \text{ J} \]

Enthalpy change in step 2:

\[ \Delta H_2 = (2.000 \text{ mol}) (18.02) (-333.5 \text{ KJ mol}^{-1}) = -12020 \text{ J} \]
Enthalpy change in step 3:
\[
\Delta H_3 = \int_{273.15 \text{ K}}^{298.15 \text{ K}} C_p(s) \,dT = C_p(s) \Delta T
\]
\[
= (2.000 \text{ mol}) \times (37.15 \text{ KJ mol}^{-1}) \times (15 \text{ K}) = 1114 \text{ J}
\]

The enthalpy change of total process is
\[
\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -10.87 \text{ kJ}
\]

Since process is at constant pressure, \( q = \Delta H \)

10.
\[
\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right) \left( \frac{R}{C_{v,m} + R} \right) = \left( \frac{1.000 \text{ atm}}{0.81 \text{ atm}} \right) \frac{2}{7} = 1.062
\]

\( T_2 = (1.062) \times (298 \text{ K}) = 316 \text{ K} \)

\( t_{C,2} = 43 \degree C \)

**Tutorial 2**

**Phase Equilibria, 2\textsuperscript{nd} law, chemical equilibria**

**Solution 11:**

\[
\Delta_{\text{vap}} H_m = T \Delta_{\text{vap}} S_m \approx (334.8 \text{ K})(88 \text{ J K}^{-1} \text{ mol}^{-1}) = 2.95 \times 10^4 \text{ J mol}^{-1}
\]

\[
\ln \left( \frac{P_2}{P_1} \right) \approx \frac{\Delta_{\text{vap}} H_m}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

\[
\ln \left( \frac{P_2}{1.00 \text{ atm}} \right) \approx -\frac{29500 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{323.15 \text{ K}} - \frac{1}{334.8 \text{ K}} \right) \approx -0.382
\]

\( P_2 = (1.00 \text{ atm})e^{-0.382} = 0.68 \text{ atm} = 520 \text{ torr} = 69 \text{ kPa} \)
Solution 12:

a. Since the activities of the solids are nearly equal to unity,

\[ K = \frac{a_{eq}(CaO) a_{eq}(CO_2)}{a_{eq}(CaCO_3)} \approx a_{eq}(CO_2) \approx \frac{P_{eq}(CO_2)}{P^o} \]

b. From the Gibbs energy changes of formation

\[ \Delta G^o = (1)(-603.501 \text{ kJ mole}^{-1}) - 394.389 \text{ kJ mole}^{-1} + (-1)(-1128.79 \text{ kJ mole}^{-1}) \]
\[ = 130.90 \text{ kJ mole}^{-1} \]

\[ K = \exp \left[ \frac{-130900 \text{ J mole}^{-1}}{6.3145 \text{ J K}^{-1} \text{ mole}^{-1} (298.15 \text{ K})} \right] \]
\[ = 1.17 \times 10^{-23} \]

\[ P_{eq}(CO_2) = (P^o) \left( 1.17 \times 10^{-23} \right) \]
\[ = 1.17 \times 10^{-23} \text{ bar} = 1.15 \times 10^{-23} \text{ atm} \]

This equilibrium constant is strongly temperature-dependent and becomes much larger at higher temperatures. At high temperatures this reaction is used to make CaO(s) ("quicklime") commercially from limestone.

Solution 13:

Spontaneous means \( \Delta G \) should be negative

\[ \Delta G = nRT \ln(p_2/p_1) \]
\[ = 2.0 \times 8.314 \times 273 \times \ln(1/2) \]
\[ = -3.147.06 \text{ J} \]

Solution 14:

We have 50 g copper at 393 K and 100 g copper at 303 K. The temperature of the two bodies when they have come to thermal equilibrium can be calculated as follows.

Heat gain = Heat loss

\[ m_1C_p(\Delta T_1) = m_2C_p(\Delta T_2) \]

i.e. \( m_1\Delta T_1 = m_2\Delta T_2 \)

\[ 100 \text{ g} \times (T-303 \text{ K}) = 50 \text{ g} \times (393 \text{ K}-T) \]

\[ T = 333 \text{ K} \]

\[ \Delta S_h = nC_{p,m} \ln \left( \frac{T}{T_h} \right) \]
\[
\Delta S = nC_p\ln(T/T_c)
\]
\[
= (100 \text{g/63 mol}^{-1})[(0.4184 \text{ J g}^{-1} \text{K}^{-1})(63 \text{ mol}^{-1})] \times 2.303 \log(333/393)
\]
\[
= 3.951 \text{ JK}^{-1}
\]
\[
\Delta S_{\text{total}} = \Delta S_c + \Delta S_h = 0.485 \text{ JK}^{-1}
\]

**Solution 15:**

a) \(\Delta S_{\text{(gas)}} = nR\ln(V_f/V_i) = (21 \text{g/39.95 g mol}^{-1}) \times (8.314 \text{ JK}^{-1} \text{mol}^{-1}) \ln(4.6/1.2) = +5.867 \text{ JK}^{-1}\)

\(\Delta S_{\text{(surrounding)}} = -\Delta S_{\text{(gas)}} = -5.867 \text{ JK}^{-1}\) (REVERSIBLE)

\(\Delta S_{\text{(total)}} = 0\)

b) \(\Delta S_{\text{(gas)}} = +5.867 \text{ JK}^{-1}\) (S is a state function)

\(\Delta S_{\text{(surrounding)}} = 0\) (no change in surroundings)

\(\Delta S_{\text{(total)}} = +5.867 \text{ JK}^{-1}\)

c) \(q_{\text{rev}} = 0\) so \(\Delta S_{\text{(gas)}} = 0\)

\(\Delta S_{\text{(surrounding)}} = 0\) (no heat is transferred to the surroundings)

\(\Delta S_{\text{(total)}} = 0\)

**Solution 16:**

a) \(\varepsilon = 1 - T_c/T_h = 1 - (500 \text{K}/1000 \text{K}) = 0.5\)

b) Maximum work = \(\varepsilon q_h \uparrow = 0.5 \times 1 \text{ kJ} = 0.5 \text{ kJ}\)

c) \(\varepsilon_{\text{max}} = \varepsilon_{\text{rev}}\) \(\downarrow w_{\text{max}} \uparrow = \downarrow q_h \uparrow - \downarrow q_c,\text{min} \uparrow\)

\(\downarrow q_c,\text{min} \uparrow = \downarrow q_h \uparrow - \downarrow w_{\text{max}} \uparrow\)

\(= 1.0 \text{ kJ} - 0.5 \text{ kJ} = 0.5 \text{kJ}\)

**Solution 17:**

\[
dP/dT = \Delta_{\text{vap}}H/ T (V_g-V_l)\] (Clapeyron Equation)

\[
= (40,690 \text{ J mol}^{-1})/ (373.15 \text{ K})(30.180 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})
\]

\[
= 3613 \text{ Pa K}^{-1}
\]
Thus \( \frac{dT}{dP} = \frac{1}{3613} = 2.768 \times 10^{-4} \text{ K Pa}^{-1} \)

**Solution 18:**

![Phase diagram]

**Tutorial 3**

**Elementary kinetics & Stat. Thermodynamics**

**Solution 19:**

a) \( \frac{d\xi}{dt} = 0.001 \text{ mol} / 0.01 \text{ s} = 0.1 \text{ mol s}^{-1} \)

b) \( v = \frac{1}{V} \frac{d\xi}{dt} = 0.1 \text{ mol s}^{-1} / 0.25 \text{ L} = 0.4 \text{ mol L}^{-1} \text{ s}^{-1} \)
c) \[ \frac{d[H_2]}{dt} = -0.4 \text{ mol L}^{-1} \text{ s}^{-1} \]
\[ \frac{d[Br_2]}{dt} = -0.4 \text{ mol L}^{-1} \text{ s}^{-1} \]
\[ \frac{d[HBr]}{dt} = 0.8 \text{ mol L}^{-1} \text{ s}^{-1} \]

**Solution 20:**

The rate law is

\[ v = k[A]^a \propto p^a = \{p_0(1-f)\}^a \]

where \( a \) is the reaction order, and \( f \) the fraction reacted (so that \( 1-f \) is the fraction remaining). Thus

\[ \frac{v_1}{v_2} = \frac{\{p_0(1-f_1)\}^a}{\{p_0(1-f_2)\}^a} = \left( \frac{1-f_1}{1-f_2} \right)^a \]

and

\[ a = \frac{\ln(v_1/v_2)}{\ln \left( \frac{1-f_1}{1-f_2} \right)} = \frac{\ln(9.71/7.67)}{\ln \left( \frac{1-0.100}{1-0.200} \right)} = \boxed{2.00} \]

**Solution 21:**

The half life in seconds will be

\[ 1600 \times 325.25 \times 24 \times 60 \times 60 = 5.049 \times 10^{10} \text{ s} \]

\[ k = \frac{0.693}{t_{1/2}} = 1.37 \times 10^{-11} \text{ s}^{-1} \]

the number of nuclei present in 1 g of radium is

\[ \frac{6.023 \times 10^{23} \text{ mol}^{-1}}{226 \text{ g/mol}} = 2.666 \times 10^{21} \text{ g}^{-1} \]

the number of disintegration, is therefore:

\[ 1.37 \times 10^{-11} \text{ s}^{-1} \times 2.67 \times 10^{21} \text{ g}^{-1} = 3.66 \times 10^{10} \text{ g}^{-1} \text{ s}^{-1} \]
Solution 22:

The rate constant is given by

\[ k = A \exp \left( \frac{-E_a}{RT} \right) \] [22.31]

so at 24°C it is

\[ 1.70 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = A \exp \left( \frac{-E_a}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [(24 + 273) \text{ K}]} \right) \]

and at 37°C it is

\[ 2.01 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = A \exp \left( \frac{-E_a}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [(37 + 273) \text{ K}]} \right) \]

Dividing the two rate constants yields

\[ \frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}} = \exp \left[ \left( \frac{-E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left( \frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}} \right) \right] \]

so

\[ \ln \left( \frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}} \right) = \left( \frac{-E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left( \frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}} \right) \]

and

\[ E_a = -\left( \frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}} \right)^{-1} \ln \left( \frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}} \right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \]

\[ = 9.9 \times 10^3 \text{ J mol}^{-1} = 9.9 \text{ kJ mol}^{-1} \]

With the activation energy in hand, the prefactor can be computed from either rate constant value

\[ A = k \exp \left( \frac{E_a}{RT} \right) = (1.70 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times \exp \left( \frac{9.9 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (297 \text{ K})} \right) \]

\[ = 0.94 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \]

Here solution method is same, but the values given in problem sheet are different. Please substitute those values and get answer.
Solution 23:

\[
\frac{\ln 2}{t^{1/2}} = A \exp^{-E_a/RT}
\]

\[T = 269.5 \text{ K}\]

Substitute half-life in sec and all other values and solve for T.

Solution 24:

Number of configurations of combined system \(W = W_1W_2\)

\[W = 2 \times 10^4\]

\(S = k \ln W; \quad S_1 = k \ln W_1; \quad S_2 = k \ln W_2\)

\[S = k \ln(2 \times 10^4) = 92.8k = 1.282 \times 10^{-21} \text{ J K}^{-1}\]

\[S_1 = k \ln(10^{20}) = 0.637 \times 10^{-21} \text{ J K}^{-1}\]

\[S_2 = k \ln(2 \times 10^{20}) = 0.645 \times 10^{-21} \text{ J K}^{-1}\]

Solution 25:

\[
\frac{n_1}{n_n} = \frac{g_1 e^{-\varepsilon_1/kT}}{g_n e^{-\varepsilon_n/kT}} = 3 e^{-\hbar c B/kT}
\]

\[\frac{n_1}{n_n} = 1/e \text{ and solve for } T\]

\[T = 7.26 \text{ K}\]

Solution 26:

a) The ratio of populations is given by the Boltzmann factor

\[
\frac{n_2}{n_1} = \exp\left(-\frac{\Delta \varepsilon}{kT}\right) = e^{-25k/25k} \quad \text{and} \quad \frac{n_3}{n_1} = e^{-50k/25k}
\]

At 25 K \(\frac{n_2}{n_1} = 0.368\) and \(\frac{n_3}{n_1} = 0.135\)

b) The molecular partition function is
\[ q = \sum e^{-E_{\text{state}}/kT} = 1 + e^{-25K/T} + e^{-50K/T} \]

At 25 K \[ q = 1.503 \]

c) The molar internal energy is

\[ U_m = U_m(0) - \frac{N\Delta}{q} \left( \frac{\partial q}{\partial \beta} \right) \] where \( \beta = (kT)^{-1} \)

At 25 K \[ U_m = U_m(0) = 88.3 \text{ J mol}^{-1} \]

Solution 27:

The relative population of states is given by Boltzmann distribution

\[ \frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(\frac{-\hbar c^2}{kT}\right) \] and solve for \( T \)

Having 15% of the molecules in the upper level means

\[ \frac{2n_2}{n_1} = \frac{0.15}{1 - 0.15} \]

Hence \( T = 213 \text{ K} \)

**Tutorial 4**

Kinetics of complex rxns, Reaction rate theories & Surface chemistry

Solution 28:

In the following exercises and problems, it is recommended that rate constants are labeled with the number of the step in the proposed reaction mechanism and that any reverse steps are labeled similarly but with a prime.

**E23.1(b)** The intermediates are NO and NO\(_3\) and we apply the steady-state approximation to each of their concentrations

\[ k_2 [\text{NO}_2][\text{NO}_3] - k_3 [\text{NO}][\text{N}_2\text{O}_5] = 0 \]

\[ k_1 [\text{N}_2\text{O}_5] - k'_1 [\text{NO}_2][\text{NO}_3] - k_2 [\text{NO}_2][\text{NO}_3] = 0 \]

\[ \text{Rate} = -\frac{1}{2} \frac{d [\text{N}_2\text{O}_5]}{dt} \]

\[ \frac{d [\text{N}_2\text{O}_5]}{dt} = -k_1 [\text{N}_2\text{O}_5] + k'_1 [\text{NO}_2][\text{NO}_3] - k_3 [\text{NO}][\text{N}_2\text{O}_5] \]
From the steady-state equations

\[ k_3 [\text{NO}] [\text{N}_2\text{O}_5] = k_2 [\text{NO}_2] [\text{NO}_3] \]

\[ [\text{NO}_2] [\text{NO}_3] = \frac{k_1 [\text{N}_2\text{O}_5]}{k_1' + k_2} \]

Substituting,

\[ \frac{d [\text{N}_2\text{O}_5]}{dt} = -k_1 [\text{N}_2\text{O}_5] + \frac{k_1' k_1}{k_1' + k_2} [\text{N}_2\text{O}_5] - \frac{k_2 k_1}{k_1' + k_2} [\text{N}_2\text{O}_5] = -\frac{2k_1 k_2}{k_1' + k_2} [\text{N}_2\text{O}_5] \]

Rate = \frac{k_1 k_2}{k_1' + k_2} [\text{N}_2\text{O}_5] = k [\text{N}_2\text{O}_5]

Solution 29:

\(\text{A}_2\) appears in the initiation step only.

\[ \frac{d[A_2]}{dt} = -k_1 [A_2] \]

Consequently, the rate of consumption of \([A_2]\) is first order in \(A_2\) and the rate is independent of intermediate concentrations.

Solution 30:

The collision frequency is

\[ z = \frac{2^{1/2} \sigma \langle \vec{v} \rangle p}{kT} \]  
where \(\sigma = \pi d^2 = 4\pi r^2\) and \(\langle \vec{v} \rangle = \left( \frac{8RT}{\pi M} \right)^{1/2}\)
so \( z = \frac{2^{1/2} p}{kT} \left( \frac{8RT}{\pi M} \right)^{1/2} = \frac{16pN_A r^2 \pi^{1/2}}{(RT)^{1/2}} \)

\[
= 16 \times (100 \times 10^3 \text{ Pa}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (180 \times 10^{-12} \text{ m}^2) \times (\pi)^{1/2} \]
\[
\frac{[(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (28.01 \times 10^{-3} \text{ kg mol}^{-1})]^{1/2}}{2(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}
\]

\[
= 6.64 \times 10^9 \text{ s}^{-1}
\]

The collision density is

\[
Z_{AA} = \frac{1}{2} \frac{zN/V}{Zp} = \frac{zN}{V} = \frac{2}{kT} \left( \frac{6.64 \times 10^9 \text{ s}^{-1}}{2} \right) \times (100 \times 10^3 \text{ Pa}) \times (100 \times 10^3 \text{ Pa})
\]

\[
= 8.07 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1}
\]

Raising the temperature at constant volume means raising the pressure in proportion to the temperature

\( Z_{AA} \propto \sqrt{T} \)

so the percent increase in \( z \) and \( Z_{AA} \) due to a 10 K increase in temperature is 1.6 percent, same as Exercise 24.1(a).

Solution 31:

(a) A diffusion-controlled rate constant in decylbenzene is

\[
k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{3 \times (3.36 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})}
\]

\[
= 1.97 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}
\]

(b) In concentrated sulfuric acid

\[
k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{3 \times (27 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})}
\]

\[
= 2.4 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}
\]
Solution 32:

The Gibbs energy of activation is related to the rate constant by

\[ k_2 = B \exp\left(\frac{-\Delta^\dagger G}{RT}\right) \]

where \( B = \frac{kRT^2}{hnp^0} \) so \( \Delta^\dagger G = -RT \ln \frac{k_2}{B} \)

\[ k_2 = (6.45 \times 10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})e^{-\frac{(5375 \text{ K})}{(298 \text{ K})}} = 9.47 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \]

\[ = 947 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \]

Using the value of \( B \) computed in Exercise 27.13(b), we obtain

\[ \Delta^\dagger G = -(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln\left(\frac{947 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}{1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}\right) \]

\[ = 46.8 \text{ kJ mol}^{-1} \]

Solution 33:

The number of collisions of gas molecules per unit surface area is

\[ Z_W = \frac{NAP}{(2\pi MRT)^{1/2}} \]

(a) For \( \text{N}_2 \)

(i) \[ Z_W = \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (10.0 \text{ Pa})}{(2\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})^{1/2}} \]

\[ = 2.88 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1} \]

\[ = 2.88 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1} \]

(ii) \[ Z_W = \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (0.150 \times 10^{-6} \text{ Torr}) \times (1.01 \times 10^5 \text{ Pa/760 Torr})}{(2\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})^{1/2}} \]

\[ = 5.75 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1} \]

\[ = 5.75 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1} \]
(b) For methane

(i) \[ Z_W = \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (10.0 \text{ Pa})}{(2\pi \times (16.04 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})^{1/2}} \]
\[ = 3.81 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1} \]
\[ = 3.81 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1} \]

(ii) \[ Z_W = \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (0.150 \times 10^{-6} \text{ Torr}) \times (1.01 \times 10^5 \text{ Pa/760 Torr})}{(2\pi \times (16.04 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})^{1/2}} \]
\[ = 7.60 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1} \]
\[ = 7.60 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1} \]

Solution 34:

The Langmuir isotherm is

\[ \theta = \frac{Kp}{1 + Kp} \quad \text{so} \quad p = \frac{\theta}{K(1 - \theta)} \]

(a) \[ p = \frac{0.20}{(0.777 \text{ kPa}^{-1}) \times (1 - 0.20)} = 0.32 \text{ kPa} \]

(b) \[ p = \frac{0.75}{(0.777 \text{ kPa}^{-1}) \times (1 - 0.75)} = 3.9 \text{ kPa} \]
Solution 35:

Langmiur isotherm is $\theta = \frac{K_p}{1 + K_p}$

We are looking for $\theta$, so we must first find $K$ or $m_{mon}$

$$K = \frac{\theta}{p(1 - \theta)} = \frac{m/m_{mon}}{p(1 - m/m_{mon})}$$

Setting this expression at one pressure equal to that at another pressure allows solution for $m_{mon}$

$$\frac{m_1/m_{mon}}{p_1(1 - m_1/m_{mon})} = \frac{m_2/m_{mon}}{p_2(1 - m_2/m_{mon})}$$

so

$$\frac{p_1(m_{mon} - m_1)}{m_1} = \frac{p_2(m_{mon} - m_2)}{m_2}$$

$$m_{mon} = \frac{p_1 - p_2}{p_1/m_1 - p_2/m_2} = \frac{(36.0 - 4.0) \text{ kPa}}{(36.0/0.63 - 4.0/0.21) \text{ kPa mg}^{-1}} = 0.84 \text{ mg}$$

So $\theta_1 = 0.63/0.84 = 0.75$ and $\theta_2 = 0.21/0.84 = 0.25$