

CH7001 – Thermodynamics, Reaction Kinetics & Heat Transfer

Problem Set

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1.

(a)

Average/mean velocity

$$v_{avg} = \sqrt{\frac{8RT}{\pi M}}$$

$$T = 25 + 273.15 = 298.15$$

$$M_{He} = 4 \frac{g}{mol}$$

$$M_{Hg} = 200 \frac{g}{mol}$$

Not converting to kg as looking at ratios rather than absolute values.

$$\frac{\sqrt{\frac{8(8.314)(298.15)}{4\pi}}}{\sqrt{\frac{8(8.314)(298.15)}{200\pi}}} = 7$$

$$ke(He) = \frac{1}{2}(4)(v_{avg}(He))^2; ke(Hg) = \frac{1}{2}(4)(v_{avg}(Hg))^2$$

$$\frac{ke(He)}{ke(Hg)} = 1$$

(b)

$$T = 20 + 273.15 = 293.15$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

$$v_{rms}(CO_2) = \sqrt{\frac{3R * 293.15}{\frac{44.01}{1000}}} = 407.6 m/s$$

$$v_{rms}(He) = \sqrt{\frac{3R * 293.15}{\frac{4}{1000}}} = 1352 m/s$$

2.

$$n = 2; p = 1.25 atm; \Delta T = 27 K; C_p = 37.11 \frac{J}{K * mol}$$

At constant pressure heat is the same as change in enthalpy.

$$C_p = \frac{\Delta H}{\Delta T}; \Delta H = 1001.97 J; q_p = \Delta H = 1001.97 J$$

$$\Delta V = 36 - 32.52 = 3.5L \text{ (from the ideal gas equation)} \rightarrow \Delta H = \Delta U - (1.25)(3.5); \Delta U = 1006.36J$$

3.

Mass of benzene: m_b

$$m_b = 0.00075kg * 876.6; M_b = 78.11 \frac{g}{mol}$$

$$n_b = \frac{m_b}{0.001 * M_b} = 0.84moles$$

because the unknown substance is involatile it does not contribute to the vapor pressure

$$25torr = (192torr)x_b \rightarrow x_b = 0.13$$

If 0.84 moles is 0.13 of the total amount of moles there are 6.47 moles in total.

$$20g = 5.63moles \rightarrow 3.55 \frac{g}{mol}$$

4.

$$T = 273.15 + 50 = 323.15K;$$

Assuming that this reaction is taking place at constant pressure so that we can use entropy in the gibbs energy of the reaction.

$$\Delta S_{net} = \frac{\Delta H_{net}}{T} = \frac{-134.47 + 3(-92.31) + 50.72}{323.15} = -1.12 \frac{kJ}{mol * K}$$

$$\Delta_r G = \Delta H_{net} - \Delta T S_{net} = -388 \frac{kJ}{mol}$$

$$\Delta_r G^0 = -73.66 + 3(-95.30) + 50.72 = -308.84 \frac{kJ}{mol}$$

$$K = \exp\left[\frac{-\Delta_r G^0}{0.008314 * 323.15}\right] = 8.38 \times 10^{49}$$

5.

a)

If the bomb calorimeter gains 598 Joules of energy for each K increase then it's gained $598 * 8.1 = 4843.8$ Joules of energy. This is heat lost by the system so

$$\Delta U = q_v = -4843J$$

Molecular weight of glucose

$$M = 179.4 \frac{g}{mol}$$

$$\Delta U^0 = \frac{-4843}{\frac{0.3}{179.4}} = 2900.0479 \frac{kJ}{mol}$$

b)

Because there is no change in volume

$$\Delta H_{com}^0 = -2900 \frac{kJ}{mol}$$

c)

$$\Delta_f H^0(CO_2) = -393.51 \frac{kJ}{mol}$$

$$\Delta_f H^0(H_2O) = -285.83 \frac{kJ}{mol}$$

$$\Delta_f H^0 = 6(\Delta_f H^0(CO_2)) + 6(\Delta_f H^0(H_2O)) = -4079 \frac{kJ}{mol}$$

Gibbs energy of reaction is gibbs energy of the products minus that of the reactants.

$$2900.0479 \frac{kJ}{mol} = -4079 - \Delta_f H^0(C_6H_{12}O_6)$$

$$\Delta_f H^0(C_6H_{12}O_6) = -1179 \frac{kJ}{mol}$$

d)

Unsure as to what quantities to use to analyse combustion in anaerobic glycolysis.

6. a)

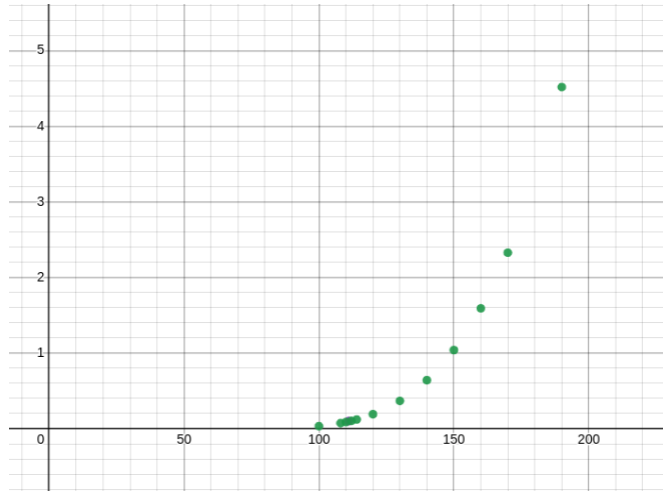


Figure 1: liquid-vapor phase boundary for CH_4

b)

The temperature when the vapor pressure is 1 atm (0.101 MPa) is approximately 111K.

c)

There's no change in temperature so no change in internal energy. Just the work to change the volume against constant pressure (1atm).

$$\Delta V = 9.05 - 4.1 \times 10^{-2} = 9.009 \frac{dm^3}{mol}; \Delta H_{vap} = (-1.013 \times 10^5 Pa)(0.09009 \frac{m^3}{mol}) = -9.126 \frac{kJ}{mol}$$

7.

$$Q = \frac{[C]^2[D]}{[A][B]^3}$$

After reaction the product D increases by 0.2 moles with A losing that amount along with B. The loss $x = 0.2$.

$$\frac{0.2^3}{(4 - 0.2)(2 - 0.2)^3} = 3.6 \times 10^{-4}$$

8.

a)

For each reaction, calculate $\Delta_r G$. The activity of solids are 1.

for $H_2O(g) \rightarrow H_2O(s)$

$$\Delta_r G = -23.6 \frac{kJ}{mol} + (0.008314)(190) \ln\left(\frac{1}{0.13 \times 10^{-6}}\right) = 0.9 \frac{kJ}{mol}$$

for $H_2O(g) + HNO_3(g) \rightarrow HNO_3 \cdot H_2O(s)$

$$\Delta_r G = -57.2 \frac{kJ}{mol} + (0.008314)(190) \ln\left(\frac{1}{0.13 \times 10^{-6} * 0.41 \times 10^{-9}}\right) = 0.7 \frac{kJ}{mol}$$

for $2H_2O(g) + HNO_3(g) \rightarrow HNO_3 \cdot 2H_2O(s)$

$$\Delta_r G = -85.6 \frac{kJ}{mol} + (0.008314)(190) \ln\left(\frac{1}{(0.13 \times 10^{-6})^2 * 0.41 \times 10^{-9}}\right) = -3.2 \frac{kJ}{mol}$$

for $3H_2O(g) + HNO_3(g) \rightarrow HNO_3 \cdot 3H_2O(s)$

$$\Delta_r G = -85.6 \frac{kJ}{mol} + (0.008314)(190) \ln\left(\frac{1}{(0.13 \times 10^{-6})^3 * 0.41 \times 10^{-9}}\right) = -5.8 \frac{kJ}{mol}$$

The last two reactions seem spontaneous, the deepest gibbs energy well being the final reaction $3H_2O(g) + HNO_3(g) \rightarrow HNO_3 \cdot 3H_2O(s)$ the most thermodynamically stable.

b)

If enthalpy of formation is considered $\Delta_r G$ for each solid, from part a.

for $HNO_3 \cdot 2H_2O(s) \rightarrow HNO_3 \cdot 3H_2O(s)$

$$\Delta_r G = -5.8 - (-3.2) = -2.6 \frac{kJ}{mol}$$

for $HNO_3 \cdot 3H_2O(s) \rightarrow HNO_3 \cdot 2H_2O(s)$

$$\Delta_r G = -3.2 - (-5.8) = 2.6 \frac{kJ}{mol}$$

Going from $HNO_3 \cdot 2H_2O(s) \rightarrow HNO_3 \cdot 3H_2O(s)$ is more spontaneous, meaning $HNO_3 \cdot 3H_2O(s)$ is more thermodynamically stable.

9.

a)

From experiment 3 to 2, $[Cl_2]$ is kept constant and $[NO]$ is doubled. This results in the reaction rate increasing by a factor of $8 \frac{2.2 \times 10^{-3}}{2.7 \times 10^{-4}} = 8.1$, this would put a relationship of $r = k[NO]^3$ on the concentration of $[NO]$.

From experiment 1 to 3, $[NO]$ is kept constant and $[Cl_2]$ is doubled. This results in the reaction rate increasing by a factor of $8 \frac{2.7 \times 10^{-4}}{6.7 \times 10^{-5}} = 4$, this would put a relationship of $r = k[Cl_2]^2$ on the concentration of $[Cl_2]$.

the reaction rate law would then be $r = [Cl_2]^3[NO]^2$ an order of 5.

b)

The rate constant k doesn't change for concentrations. From experiment

$$k = \frac{6.7 \times 10^{-5}}{0.015^3 * 0.050^2} = 7940.7 \frac{1}{M^4 s}$$

for experiment 4 then

$$r = k[NO]^3[Cl_2]^2 = 2.4 \times 10^{-3}$$

10.

a)

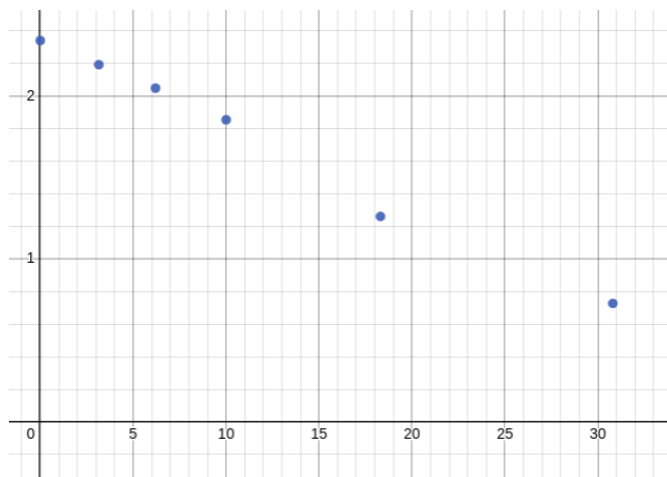


Figure 2: Plot of $\ln[A]$ against time

The rate constant is the slope of the above graph.

$$\ln[A] = \ln[A]_0 - k_{obs}t$$

$$\ln[A]_0 = 2.314 \text{ from the graph}$$

$$k = -0.0486 \text{ picking two points from the graph}$$

b)

$$y = 2.314 - 0.0486t \rightarrow y(t = 43.8) = 0.185$$

$$e^{0.0185} = 1.2 \frac{\times 10^{-2} \text{ mol}}{\text{dm}^3}$$

Taking the mass of $(CH_3)_3CBr = 137 \frac{g}{mol}$ after 43.8 hours we have $137 * 1.2 \times 10^{-2} = 1.6 \frac{grams}{dm^3}$.