Worked Solutions to the Problems

Solution problem 1: Combustion Energy

1.1 $1\ C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(l)$

$2\ C_4H_{10}(g) + 13\ O_{2(g)} \longrightarrow 8\ CO_2(g) + 10\ H_2O(l)$

1.2 Combustion energy (reaction enthalpy): $\Delta_c H^0 = \Sigma_p \Delta_f H^0\ (p) - \Sigma_r \Delta_f H^0\ (r)$

$\Delta_c H^0$(propane) = $3\cdot(-393.5\ \text{kJ mol}^{-1}) + 4\cdot(-285.8\ \text{kJ mol}^{-1}) - (-103.8\ \text{kJ mol}^{-1})$

$\Delta_c H^0$(propane) = $-2220\ \text{kJ mol}^{-1}$

$\Delta_c H^0$(butane) = $4\cdot(-393.5\ \text{kJ mol}^{-1}) + 5\cdot(-285.8\ \text{kJ mol}^{-1}) - (-125.7\ \text{kJ mol}^{-1})$

$\Delta_c H^0$(butane) = $-2877\ \text{kJ mol}^{-1}$

1.3 On the assumption that oxygen and nitrogen behave like ideal gases, the volume is proportional to the molar amount:

$$n_{N_2} = n_{O_2}\frac{V_{N_2}}{V_{O_2}} = n_{O_2}\cdot 3.76\,.$$

5 mol of O_2 and 18.8 mol of N_2 are needed for the burning of 1 mol of propane.

6.5 mol of O_2 and 24.4 mol of N_2 are needed for the burning of 1 mol of butane.

When $V = n\cdot R\cdot T\cdot p^{-1}$, the volumes of air are:

propane: $V_{air} = (5 + 18.8)\ \text{mol}\cdot 8.314\ \text{J (K mol)}^{-1}\cdot 298.15\ \text{K}\cdot(1.013\cdot 10^5\ \text{Pa})^{-1}$

$V_{air} = 0.582\ \text{m}^3$

butane: $V_{air} = (6.5 + 24.4)\ \text{mol}\cdot 8.314\ \text{J (K mol)}^{-1}\cdot 298.15\ \text{K}\cdot(1.013\cdot 10^5\ \text{Pa})^{-1}$

$V_{air} = 0.756\ \text{m}^3$

1.4 Under these circumstances, water is no longer liquid but gaseous. The combustion energies change due to the enthalpy of vaporization of water and higher temperature of the products.

Energy of vaporization of water at 25^0C:

$\Delta_v H^0(H_2O) = \Delta_f H^0(H_2O(l)) - \Delta_f H^0(H_2O(g)) = -285.8\ \text{kJ mol}^{-1} - (-241.8\ \text{kJ mol}^{-1})$

$\Delta_v H^0(H_2O) = 44\ \text{kJ mol}^{-1}$

The energy needed to increase the temperature of the products up to 100^0C is:

$\Delta H(T) = (T-T^0)\sum_i n_i C_p(i)$

The energy E released by burning of 1 mol of gas is:

E(propane, T) = $(-2220 + 4\cdot 44)\ \text{kJ} + (T-T^0)\ (3\cdot 37.1 + 4\cdot 33.6 + 18.8\ \text{mol}\cdot 29.1)\ \text{JK}^{-1}$

E(propane, T) = $-2044\ \text{kJ} + (T-T^0)\cdot 792.8\ \text{JK}^{-1}$ (1)

E(propane, 373.15 K) = $-1984.5\ \text{kJ mol}^{-1}$.

E(butane, T) = $(-2877 + 5\cdot 44)\ \text{kJ} + (T-T^0)\ (4\cdot 37.1 + 5\cdot 33.6 + 24.4\ \text{mol}\cdot 29.1)\ \text{JK}^{-1}$

E(butane, T) = $-2657\ \text{kJ} + (T-T^0)\cdot 1026.4\ \text{JK}^{-1}$ (2)

E(butane, 373.15 K) = $-2580.0\ \text{kJ mol}^{-1}$.

1.5 Efficiency of propane: $\eta_{\text{propane}} = \dfrac{E(propane,\ 373.15\ K)}{\Delta_c H^0}$ = 1984.5/2220 = 89.4%.

$\eta_{\text{butane}} = \dfrac{E(butane,\ 373.15\ K)}{\Delta_c H^0}$ = 2580.0/2877 = 89.7%.

The energy is stored in the thermal energies of the products.

1.6. The combustion energies have been calculated in 1.4., equation (1), (2):

E(propane, T) = -2044 kJ + (T-T^0) · 792.8 J K^{-1}

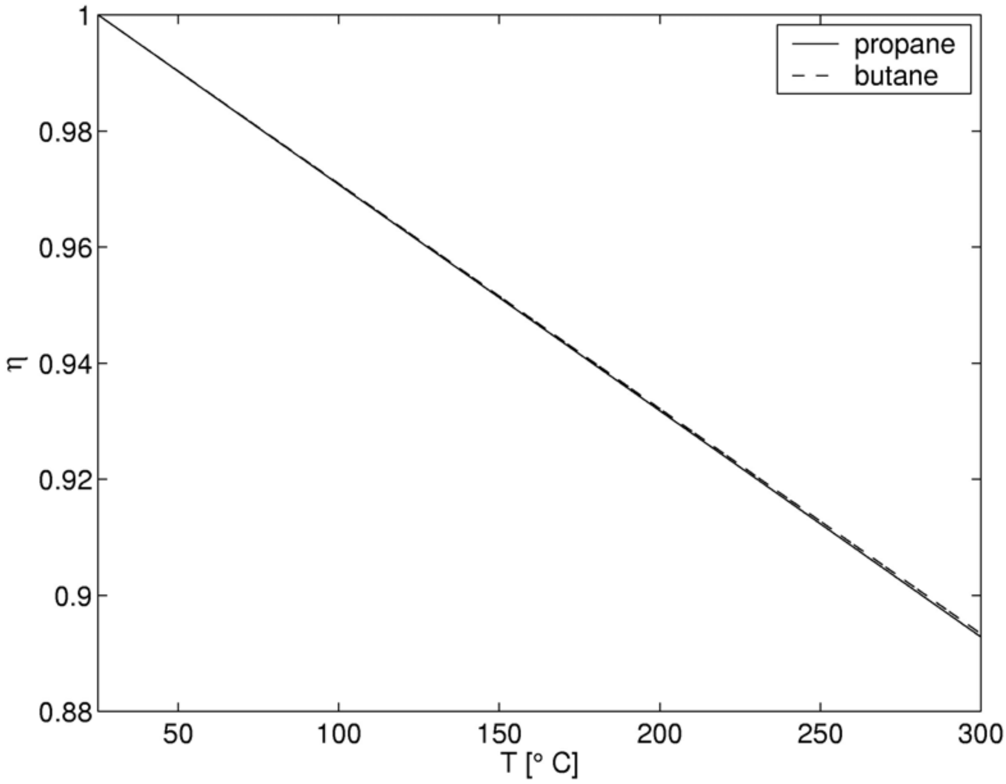
E(butane, T) = -2657 kJ + (T-T^0) · 1026.4J K^{-1}

the efficiencies are given by:

Propane: $\eta_{\text{propane}}(T) = 1 – 3.879 \cdot 10^{-4} \cdot (T-T^0)$

Butane: $\eta_{\text{butane}}(T) = 1 – 3.863 \cdot 10^{-4} \cdot (T-T^0)$

The plot shows that there is really no difference between the efficiencies of burning propane and butane.



1.7 $n_j = \rho_j \dfrac{V_j}{M_j}$

n_{propane} = 0.493 g cm^{-3} · 1000 cm^3 · (44.1 g mol^{-1})$^{-1}$ = 11.18 mol

n_{butane} = 0.573 g cm^{-3} · 1000 cm^3 · (58.1 g mol^{-1})$^{-1}$ = 9.86 mol

$E_i = n_i \cdot E$(propane/butane, 373.15K)

E_{propane} = 11.18 mol ·(-1984.5 kJ mol^{-1}) = -22.19 MJ

E_{butane} = 9.86 mol · (-2580.0 kJ mol^{-1}) = -25.44 MJ

Despite the fact that there is less butane per volume, the energy stored in 1 L of butane is higher than the energy stored in 1 L of propane.

Solution problem 2: Haber-Bosch Process

2.1 $N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$

2.2 $\Delta H^0 = -\ 91.8$ kJ mol^{-1}
$\Delta S^0 = -198.1$ J mol^{-1} K^{-1}
$\Delta G^0 = \Delta H^0 - T\cdot\Delta S^0 = -32.7$ kJ mol^{-1}
The reaction is exothermic and exergonic under standard conditions.

2.3 Ammonia will form instantaneously, but the activation energy for the reaction will be so high that the two gases won`t react. The reaction rate will be very low.

2.4 The enthalpy of formation is described by $\Delta_f H(T) = \Delta_f H^0 + \int_{T^0}^{T} C_P(T)dT$.

For N_2:	$\Delta_f H(800\ K) = 15.1$ kJ mol^{-1},	$\Delta_f H(1300\ K) = 31.5$ kJ mol^{-1}.
For H_2:	$\Delta_f H(800\ K) = 14.7$ kJ mol^{-1},	$\Delta_f H(1300\ K) = 29.9$ kJ mol^{-1}.
For NH_3:	$\Delta_f H(800\ K) = -24.1$ kJ mol^{-1},	$\Delta_f H(1300\ K) = 4.4$ kJ mol^{-1}.

This leads to a reaction enthalpy of:

$\Delta H(800K) = -107.4$ kJ mol^{-1}, $\Delta H(1300K) = -112.4$ kJ mol^{-1}.

Entropy can be calculated directly with this equation..

For N_2:	$S(800K) = 220.6$ J (mol K)$^{-1}$,	$S(1300\ K) = 236.9$ J (mol K)$^{-1}$.
For H_2:	$S(800K) = 159.2$ J (mol K)$^{-1}$,	$S(1300\ K) = 174.5$ J (mol K)$^{-1}$.
For NH_3:	$S(800K) = 236.4$ J (mol K)$^{-1}$,	$S(1300\ K) = 266.2$ J (mol K)$^{-1}$.

This leads to a reaction entropy of:

$S(800K) = -225.4$ J (mol K)$^{-1}$, $S(1300K) = -228.0$ J (mol K)$^{-1}$.

Gibbs energy is:

$\Delta G(800K) = 72.9$ kJ mol^{-1}, $\Delta G(1300K) = 184.0$ kJ mol^{-1}.

The reaction is still exothermic but now endergonic.

2.5 The equilibrium constant can be calculated from Gibbs energy according to $K_x(T) = \exp(-\Delta G(RT)^{-1})$.
This leads to the following equilibrium constants:
$K_x(298.15K) = 5.36\cdot10^5$,
$K_x(800K) = 1.74\cdot10^{-5}$,
$K_x(1300K) = 4.04\cdot10^{-8}$.

Using $K_x = \dfrac{x_{NH_3}^2}{x_{H_2}^3 \cdot x_{N_2}}$, $x_{H_2} = 3x_{N_2}$, and $1 = x_{NH_3} + x_{N_2} + x_{H_2}$

we obtain $K_x = \dfrac{(1-4x_{N_2})^2}{27x_{N_2}^4}$.

This equation can be converted into $x_{N_2}^2 + \dfrac{4}{\sqrt{27K_x}}x_{N_2} - \dfrac{1}{\sqrt{27K_x}} = 0$

which has only one solution, since K_x and x_{N_2} are always positive:

$$x_{N_2} = -\frac{2}{\sqrt{27K_x}} + \sqrt{\frac{4}{27K_x} + \frac{1}{\sqrt{27K_x}}}.$$

We obtain the following table:

$T \cdot K^{-1}$	x_{N_2}	x_{H_2}	x_{NH_3}
298.15	0.01570	0.04710	0.03720
800	0.24966	0.74898	0.00136
1300	0.24998	0.74994	0.00008

2.6 The catalyst reduces the activation energy of the process and increases the reaction rate. The thermodynamic equilibrium is unchanged.

2.7 Higher pressures will result in a higher mol fraction of NH_3, since $K_x = K_p \cdot p^2$ increases. An increase in pressure shifts the equilibrium toward the products but does not change the reaction rate.

2.8 The best conditions are: high pressure, temperature as low as possible and the presence of a catalyst. The temperature has to be optimized such that the turnover is fast and the yield still acceptable.

Solution Problem 3: Thermodynamics in Biochemistry

3.1 $\Delta G^0 = - RT \ln K$

$$= - RT \ln \frac{c(lactate) \cdot c(NAD^+)}{c(pyruvate) \cdot c(NADH) \cdot c(H^+)}$$

$$= - RT \ln \frac{c(lactate) \cdot c(NAD^+)}{c(pyruvate) \cdot c(NADH)} - RT \ln \frac{1}{c(H^+)}$$

$$\Delta G^{0'} = - RT \ln \frac{c(lactate) \cdot c(NAD^+)}{c(pyruvate) \cdot c(NADH)}$$

$$\Delta G^0 = \Delta G^{0'} - RT \cdot \ln(c(H^+)^{-1})$$

$$= - 25100 \text{ J mol}^{-1} - 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 298.15 \text{ K} \cdot \ln 10^7$$

$$= - 25.1 \text{ kJ mol}^{-1} - 40.0 \text{ kJ mol}^{-1}$$

$$= - 65.1 \text{ kJ mol}^{-1}$$

3.2 $\Delta G^{0'} = - RT \ln K'$ $\qquad K' = e^{-\Delta G^{\circ'}/(RT)}$

$K' = e^{25100 / (8.314 \cdot 298.15)}$ $\qquad K' = 2.5 \cdot 10^4$

3.3 $\Delta G' = \Delta G^{0'} + RT \ln \frac{c(prod.)}{c(react.)}$

$$= \Delta G^{0'} + RT \ln \frac{c(lactate) \cdot c(NAD^+)}{c(pyruvate) \cdot c(NADH)}$$

$$= - 25100 \text{ J mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 298.15 \text{ K} \cdot \ln(3700 \cdot 540/(380 \cdot 50))$$

$$= - 25.1 \text{ kJ mol}^{-1} + 11.5 \text{ kJ mol}^{-1}$$

$$= - 13.6 \text{ kJ mol}^{-1}$$