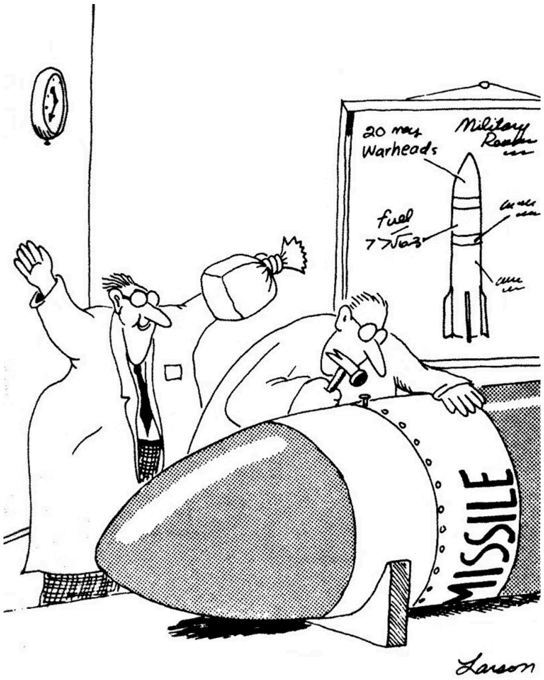
Thermodynamics R and R Worksheet
7/29/24



1.) You and your best friend Greg are building a missile using the chemistry you learned at Bryn Mawr's Post-baccalaureate Program. As Greg is putting the finishing touches on the missile, you decide to harmlessly prank him by popping a paper bag over his head. The mechanism for the explosion of the missile works via the combustion of ethane:

$$C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$$

a.) At room temperature (25 °C) and standard conditions, is the above reaction product-favored at equilibrium? Solve this by calculating the $\Delta S°_{universe}$.

1. **Calculate $\Delta S°_{system}$**

$\Delta S°_{system} = \Sigma S°_{products} - \Sigma S°_{reactants}$

$\Delta S°_{system} = [213.74*2 + 3*69.95] - [7/2 * 205.07 + 1*229.2]$

$\Delta S°_{system} = -309.6$ J/(K*mol)

2. **Calculate $\Delta S°_{surroundings}$**

$\Delta S°_{surroundings} = (-\Delta H°_{reaction})/T$

$\Delta H°_{reaction} = \Sigma\Delta H°_{products} - \Sigma\Delta H°_{reactants}$

$\Delta H°_{reaction} = [2*-393.5 + 3*-285.8] - [7/2 * 0 - 83.85]$

$\Delta H°_{reaction} = -1560.6$ kJ/mol

$\Delta S°_{surroundings} = (-\Delta H°_{reaction})/T = (1560.6\ kJ/mol)/298K$
$\Delta S°_{surroundings} = 5.237\ kJ/(mol*K)$

3. **Calculate $\Delta S°_{universe}$**
$\Delta S°_{universe} = \Delta S°_{system} + \Delta S°_{surroundings}$
$\Delta S°_{universe} = -309.6\ J/(K*mol) + 5.237\ kJ/(mol*K)$
$\Delta S°_{universe} = -309.6\ J/(K*mol) + 5237\ J/(mol*K)$
$\Delta S°_{universe} = 4927\ J/(mol*K)$

Since $\Delta S°_{universe} > 0$, the reaction is product favored.

b.) Alternatively, tell us if the reaction is product favored at equilibrium by calculating the standard Gibbs Free Energy of reaction, $\Delta G°_r$.

$\Delta G° = \Delta H° - T\Delta S°$
$\Delta G° = -1560.6\ kJ/mol - 298K*-309.6\ J/(K*mol)$
$\Delta G° = -1560.6\ kJ/mol + 92260.8\ J/mol$
$\Delta G° = -1560.6\ kJ/mol + 92.26\ kJ/mol$
$\Delta G° = -1468\ kJ/mol$. Since $\Delta G° < 0$, reaction is product favored.

2.) After the missile explodes (for the sake of the story, you both survive), Greg is really upset at you, but you can't understand why. You refuse to apologize, since it was just a harmless office prank. Out of spite, Greg decides to synthesize some hydrogen iodide (HI), a strong acid, to dissolve into your water bottle. He synthesizes it via the mechanism:

$$\frac{1}{2} H_2 (g) + \frac{1}{2} I_2 (g) \Leftrightarrow HI (g)$$

a.) Suppose Greg were to add 0.132 bar of H_2, 0.295 bar of I_2 and 1.61 bar of HI (these are all partial pressures) into a reaction chamber at 350 °C. Assume the system is in equilibrium. Calculate the standard Gibbs Free energy of formation, $\Delta G°_f$ of HI(g). Is the formation of HI under standard conditions product or reactant favored?

Given that in this reaction, the chemical equation is a formation reaction, $\Delta G°_f$ is equal to $\Delta G°_r$, we can use the following equation:
$\Delta G_r° = -RT\ln(K)$.

Therefore, $\Delta G_f° = -RT\ln(K)$.

1. Calculate K
$K_p = (1.61\ bar)/[(0.132\ bar)^{\wedge}½ * (0.295\ bar)^{\wedge}½]$

K_p = 8.16

2. Calculating $\Delta G_f°$:
$\Delta G_f°$ = -8.314 J/(mol*K) * 623K * ln(8.16)
$\Delta G_f°$ = -10.9 kJ/mol. Since $\Delta G_f° < 0$, formation of HI under standard conditions is product favored.

b.) Suppose Greg decided to double the initial partial pressures of the reactants, while keeping the initial partial pressure of HI constant (hint: we are no longer in equilibrium). Suppose he also decides to increase the temperature of the reaction by 100 °C. What is the non-standard Gibbs free energy of this modified reaction?

$\Delta G = \Delta G° + RT\ln(Q)$

Q_p = (1.61 bar)/[(0.132 bar * 2)^½ + (0.295 bar * 2)^½]
Q_p = 4.08
$\Delta G = \Delta G° + RT\ln(Q)$ = -10.9 kJ/mol + 8.314 J/(mol*K) * 723K * ln(4.08)
ΔG = -10.9 kJ/mol + 8.45 kJ/mol = **-2.45 kJ/mol**

3) It turns out the paper bag contained an allotrope of sulfur which undergoes a phase transition between 80 °C and 100 °C.

$$S_8(\text{rhombic}) \rightarrow S_8(\text{monoclinic})$$

$$\Delta_r H° = 3.213 \text{ kJ/mol-rxn}$$
$$\Delta_r S° = 8.7 \text{ J/K} \cdot \text{mol-rxn}$$

a) Estimate $\Delta_r G°$ for the transition at 80.0 °C and 110.0 °C. What do these results tell you about the stability of the two forms of sulfur at each of these temperatures?

$\Delta_r G° = \Delta_r H° - T\Delta_r S°$

At 80.0 °C:

$\Delta_r G°$ = 3.213 kJ/mol-rxn − (353 K)(8.7x10^{-3} kJ/K · mol-rxn)

$\Delta_r G°$ = 0.1419 kJ/mol-rxn

At 110 °C:

$\Delta_r G° = 3.213$ kJ/mol-rxn $- (383\text{ K})(8.7\text{x}10^{-3}$ kJ/K · mol-rxn)

$\Delta_r G° = -0.1191$ kJ/mol-rxn

At 80.0 °C rhombic sulfur is more stable, but at 110 °C monoclinic sulfur is more stable.

b) Calculate the temperature at which $\Delta_r G° = 0$. What is the significance of this temperature?

$\Delta_r G° = \Delta_r H° - T\Delta_r S°$

$T = (\Delta_r G° - \Delta_r H°) / -\Delta_r S°$

T = (0 kJ/mol-rxn - 3.213 kJ/mol-rxn) / ($-8.7\text{x}10^{-3}$ kJ/K · mol-rxn)

T = 369.3 K = 96.3 °C

This is the temperature in which the two forms of sulfur are at equilibrium under standard conditions.