Lecture Notes F: Entropy and Free Energy II

1) **Reversible vs. irreversible isothermal expansion of an ideal gas**

Isothermal expansion of an ideal gas (review from page 8 of lecture notes E)

Irreversible, isothermal expansion of an ideal gas
2) \( \Delta S \) for system plus surroundings, for a reversible vs. irreversible process

Assume the surroundings are sufficiently large that even when the system undergoes an irreversible process, the surroundings absorb the heat reversibly.
3) The Third Law of Thermodynamics: Standard State Entropies

The entropy of any pure substance (element or compound) in its equilibrium state approaches zero at the absolute zero of temperature.

(All substances will form a perfectly ordered solid at 0K.)

\[
\begin{align*}
\text{2CO} \ (g) + \text{O}_2 \ (g) & \rightarrow \text{2CO}_2 \ (g) \\
S^0 \ (J/mol \ K) & = 197.56 + 205.03 \rightarrow 213.63 \\
\Delta S & = 2 \times 213.63 - 2 \times 197.56 - 205.03 = -172.89 \ J/(mol \ K)
\end{align*}
\]

4) Trouton’s rule

\[\Delta S_{\text{vap}} = 88 \pm 5 \ J/(K \ mol) \text{ for most liquids} \]

Exception: \[\Delta S_{\text{vap}}(\text{water}) = 109 \ J/(K \ mol)\]
**Problem**

Consider the reaction:

\[ 2 \text{NO}_2 (g) \rightarrow \text{N}_2\text{O}_4 (g) \]

a) What is the sign of $\Delta H$ for the above reaction?  
(a) positive  
(b) negative

b) What is the sign of $\Delta S$ for the above reaction?  
(a) positive  
(b) negative

c) Using Appendix D of the textbook, calculate $\Delta H$, $\Delta S$ and $\Delta G$ for this reaction at 25°C.

- $\text{NO}_2 (g)$  
  $H_f^{\circ} = 33.18 \text{ kJ/mol}$
- $\text{N}_2\text{O}_4 (g)$
  $H_f^{\circ} = 9.16 \text{ kJ/mol}$

  $S^\circ$  
  $S^\circ = 239.95 \text{ J/(mol K)}$
  $S^\circ = 304.18 \text{ J/(mol K)}$

\[ \Delta H = \Delta H_f^{\circ} \]
\[ \Delta S = \Delta S_f^{\circ} \]
\[ \Delta G = \Delta G_f^{\circ} \]

- $\Delta H_f^{\circ} = -2.58 \text{ kJ/mol}$
- $\Delta S_f^{\circ} = 25.23 \text{ J/(mol K)}$
- $\Delta G_f^{\circ} = -1.27 \text{ kJ/mol}$

d) For what temperature range is this reaction spontaneous?