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) ΔS for system plus surroundings, for a reversible vs. irreversible process

Universe	
	Surroundings
System	

Assume the surroundings are sufficiently large that even when the system undergoes an irreversible process, the surroudings 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.)

	2CO (g)	+	$O_{2(g)}$	\rightarrow	$2CO_{2(g)}$
S ^o (J/mol K)	197.56		205.03		213.63

 $\Delta S = 2 (213.63) - 2 (197.56) - 205.03 = -172.89 \text{ J/(mol K)}$

4) Trouton's rule

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

Exception: $\Delta S_{vap}(water) = 109 \text{ J/(K mol)}$

Problem

Consider the reaction:

 $2 \operatorname{NO}_{2(g)} \rightarrow \operatorname{N}_2\operatorname{O}_{4(g)}$

a) What is the sign of ΔH for the above reaction? (a) positive (b) negative

b) What is the sign of ΔS for the above reaction? (a) positive (b) negative

c) Using Appendix D of the textbook, calculate ΔH , ΔS and ΔG for this reaction at 25°C.

	$NO_{2 (g)}$	N_2O_4 (g)	
H^{o}_{f}	33.18	9.16	kJ/mol
S°	239.95	304.18	J/(mol K)

d) For what temperature range is this reaction spontaneous?