

### C. Entropy Changes in Surroundings

- Heat that flows into or out of the system changes the entropy of the surroundings

↳ For an isothermal process: \*

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T}$$

\* if P is constant,  
 $q_{\text{sys}} = \Delta H^\circ$  for the reaction

- The universe is composed of the system and the surroundings.

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

\* Remember - spontaneous processes  $\Delta S_{\text{univ}} > 0$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T} \quad ; \quad q_{\text{sys}} = \Delta H_{\text{sys}}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \frac{-\Delta H_{\text{sys}}}{T}, \text{ rearrange}$$

$$-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

defined as Gibbs free energy ( $\Delta G$ )

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$\Delta G$  will always be negative if  $\Delta S$  is positive, spontaneous

$$\Delta G^\circ = \sum \Delta G^\circ_{\text{products}} - \sum \Delta G^\circ_{\text{reactants}}$$



(1) How does  $\Delta G^\circ$  change with Temperature?

- (a) If  $\Delta G$  is negative, the forward reaction is spontaneous  
 (b) If  $\Delta G = 0$ , the system is at equilibrium  
 (c) If  $\Delta G$  is positive, the reverse reaction is spontaneous

Effect of Temperature

$\Delta H$	$\Delta S$	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction characteristics	Example
-	+	-	-	Spontaneous at all T.	$2O_3(g) \rightarrow 3O_2(g)$
+	-	+	+	Nonspontaneous at all T.	$3O_2(g) \rightarrow 2O_3(g)$
-	-	-	+ or -	Spontaneous at low T, nonspontaneous at high T	$H_2O(l) \rightarrow H_2O(s)$
+	+	-	+ or -	Spontaneous at high T, nonspontaneous at low T	$H_2O(s) \rightarrow H_2O(l)$

(2) Under any conditions (standard or nonstandard), the free energy can be found this way:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

1.8.314 J/mol K

standard conditions: concentrations = 1M, so  $Q = 1$

at equilibrium,  $Q = K$  &  $\Delta G = 0$

$$0 = \Delta G^\circ + RT \ln K$$

rearranged,

$$\Delta G^\circ = -RT \ln K$$

or

$$K = e^{-\frac{\Delta G^\circ}{RT}}$$

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p 837 - 839

# 56 a & c, 58 c & d, 66, 76, 78, 82