

Chapter 4 Part 1

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Additional notes on spontaneity

- Recall from the last chapter, an isolated ($q = 0, w = 0$) system is spontaneous if

$$\Delta S > 0$$

- This may also be written as

$$\Delta S_{U,V} > 0$$

Two additional spontaneity condition

- A system is spontaneous if

$$\Delta U_{V,S} \leq 0$$

$$\Delta H_{p,S} \leq 0$$

- These conditions are less useful because they require the system to be isentropic ($\Delta S = 0$). It is quite difficult to perform a process on a system and ensure that the order, on an atomic and molecular level, does not change.

Spontaneity

State whether the following processes can be labelled spontaneous under the following conditions.

- A. A process in which ΔH is positive at constant V and p
- B. An isobaric process in which ΔU is negative and ΔS is 0
- C. An adiabatic process in which ΔS is positive and the volume does not change
- D. An isobaric, isentropic process in which ΔH is negative

Spontaneity Parts A and B

- A. Spontaneity requires that ΔH be negative if pressure and entropy are constant. Since we do not know the constraints on p and S , there is no requirement that the process must be spontaneous.
- B. An isobaric process has $\Delta p = 0$. We are also given a negative ΔU and $\Delta S = 0$. Unfortunately, the negative ΔU spontaneity condition requires an isochoric (that is, $\Delta V = 0$) condition. Therefore, we cannot say this condition must be spontaneous.

Spontaneity Parts C and D

- A. An adiabatic process implies that $q = 0$, and with volume not changing, we have $V = 0$; therefore $w = 0$ and thus $\Delta U = 0$. The constant U and V allow us to apply the strict entropy spontaneity test: if $\Delta S > 0$, the process is spontaneous. Since we are given that ΔS is positive, this process must be spontaneous.
- B. Isobaric and isentropic imply $\Delta p = \Delta S = 0$. These are the proper variables for using the enthalpy spontaneity test, which requires that ΔH be less than zero. This is in fact the case, so the process must be spontaneous.

Helmholtz Energy

- The Helmholtz energy, A , is defined as maximum amount of pressure-volume work that a system can do on the surroundings during an isothermal and isochoric process such that

$$\Delta A_{T,V} \leq w$$

- For a reversible process, the Helmholtz energy is equal to the pressure-volume work that a system does on the surroundings

$$\Delta A_{T,V} = w$$

- A process must be spontaneous if

$$\Delta A_{T,V} \leq 0$$

- The Helmholtz energy may also be written in terms of temperature, internal energy, and entropy such that

$$\Delta A = \Delta U - T\Delta S$$

Gibbs Free Energy

- The Gibbs free energy, G , is defined as maximum amount of non-pressure-volume work that a system can do on the surroundings during an isothermal and isobaric process such that

$$\Delta G_{T,p} \leq w_{non-pV}$$

- For a reversible process, the Gibbs free energy is equal to the non-pressure-volume work that a system does on the surroundings

$$\Delta G_{T,p} \leq w_{non-pV}$$

- A process must be spontaneous if

$$\Delta G_{T,p} \leq 0$$

- The Gibbs free energy may also be written in terms of temperature, enthalpy, and entropy such that

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

Comparing ΔA and ΔG

- Since maintaining a constant pressure and temperature for a process is easier than maintaining a constant volume and temperature, the Gibbs free energy is generally more useful than the Helmholtz energy.
- However, there are certain scenarios, such as bomb calorimetry, where Helmholtz energy is useful.

ΔA and ΔG and as state functions

- Since ΔA and ΔG are state functions, the Helmholtz and Gibbs free energies of a reaction can be determined from the products-minus reactants method using Helmholtz or Gibbs free energies of formation.
- Like ΔH , the $\Delta_f A$ and $\Delta_f G$ values of elements in their standard states is exactly zero.
- Hess's law may also be used with Helmholtz and Gibbs free energies.

Helmholtz Energy

Calculate the change in the Helmholtz energy for the reversible isothermal compression of 1 mole of an ideal gas from 100.0 L to 22.4 L. Assume that the temperature is 298 K.

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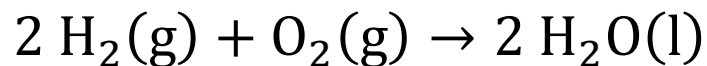
Since the process is reversible, the relationship $\Delta A = w$ applies

$$w = nRT \ln \frac{V_f}{V_i} = -(1 \text{ mole}) \left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (298 \text{ K}) \ln \left(\frac{22.4 \text{ L}}{100.0 \text{ L}} \right) \\ = 3610 \text{ J}$$

$$w = \Delta A = 3610 \text{ J}$$

Determining $\Delta_{\text{rxn}}G$

Determine $\Delta_{\text{rxn}}G$ ($25^\circ\text{C} = 298.15\text{ K}$) for the following chemical reaction using both methods for determining $\Delta_{\text{rxn}}G$ and show that they yield the same answer. Assume standard conditions.



	$\text{H}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{H}_2\text{O}(\text{l})$
$\Delta_f H$ (kJ/mol)	0	0	-285.83
S (J/mol · K)	130.68	205.14	69.91
$\Delta_f G$ (kJ/mol)	0	0	-237.13

Determining $\Delta_{\text{rxn}}G$

$$\Delta_{\text{rxn}}H = 2(-285.83) - 2(0) - 1(0) = -571.66 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_{\text{rxn}}S = 2(69.91) - 2(130.68) - 1(205.14) = -326.68 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\begin{aligned}\Delta G = \Delta H - T\Delta S &= -571.66 \frac{\text{kJ}}{\text{mol}} - (298.15 \text{ K}) \left(-0.32668 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \\ &= -474.26 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

$$\Delta_{\text{rxn}}G = 2(-237.13) - 2(0) - 1(0) = -474.26 \frac{\text{kJ}}{\text{mol}}$$

Maxwell Relations

- The following are known as the Maxwell relations

$$\begin{aligned}\left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\ \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\ \left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

Maxwell Relations

- The Maxwell relations are generally applicable, meaning they are not restricted to ideal gases, or even just gases. They apply to solid and liquid systems as well.
- They also express certain relationships in terms of variables that are easier to measure. This is particularly helpful for entropy.

Maxwell Relations

What is $\left(\frac{\partial S}{\partial V}\right)_T$ for a gas that follows the van der Waals equation of state?

Maxwell Relations

What is $\left(\frac{\partial S}{\partial V}\right)_T$ for a gas that follows the van der Waals equation of state?

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V - nb}$$
$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V - nb}$$

Maxwell Relations

In Chapter 1, we showed that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa}$$

where α is the expansion coefficient and κ is the isothermal compressibility. For mercury, $\alpha = 1.82 \times 10^{-4} \frac{1}{K}$ and $\kappa = 3.87 \times 10^{-5} \frac{1}{\text{atm}}$ at 20°C. Determine how entropy changes with volume under isothermal conditions at this temperature.

Maxwell Relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa} = \frac{1.82 \times 10^{-4} \frac{1}{\text{K}}}{3.87 \times 10^{-5} \frac{1}{\text{atm}}} = 4.70 \frac{\text{atm}}{\text{K}}$$

$$4.70 \frac{\text{atm}}{\text{K}} \left(\frac{101.32 \text{ J}}{\text{L} \cdot \text{atm}} \right) = 476 \frac{\text{J}}{\text{K} \cdot \text{L}}$$