

# Chapter 4 Part 2

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# Gibbs-Helmholtz equation

- It can be found that as temperature changes, the change in free energy is equal to the negative of the entropy of the system

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

- This implies that as temperature goes up, the free energy decreases
- Free energy and temperature change can be related to enthalpy change with the Gibbs-Helmholtz equation below

$$\left(\frac{\Delta \frac{\Delta G}{T}}{\Delta \frac{1}{T}}\right)_p = \Delta H$$

- This shows that a plot of  $\frac{\Delta G}{T}$  versus  $\frac{1}{T}$  would be equal to  $\Delta H$  as slope

# Gibbs-Helmholtz equation

Predict the value of  $\Delta G$  (100 °C, 1 atm) of the reaction



Given that  $\Delta G$  (25 °C, 1 atm) =  $-474.36 \text{ kJ}$  and  $\Delta H = -571.66 \text{ kJ}$ .

Assume constant pressure and  $\Delta H$ .

# Gibbs-Helmholtz equation

$$\Delta \frac{1}{T} = \frac{1}{373 \text{ K}} - \frac{1}{298 \text{ K}} = -0.000674 \frac{1}{\text{K}}$$

$$\left( \frac{\Delta \frac{\Delta G}{T}}{-0.000674 \text{ K}} \right)_p = -571.66 \text{ kJ}$$

$$\Delta \frac{\Delta G}{T} = 0.386 \frac{\text{kJ}}{\text{K}}$$

$$\left( \frac{\Delta G}{373 \text{ K}} \right)_{final} - \left( \frac{-474.36 \text{ kJ}}{298 \text{ K}} \right)_{initial} = 0.386 \frac{\text{kJ}}{\text{K}}$$

$$\Delta G_{final} = -450. \text{ kJ}$$

# Relating $\Delta G$ and pressure

- We can relate  $\Delta G$  and pressure with the equation below

$$\Delta G = nRT \ln \frac{p_f}{p_i}$$

- ▣ The above equation is only applicable for isothermal changes

# Relating $\Delta G$ and pressure

What is the change in  $G$  for a process in which 0.22 mole of an ideal gas goes from 2505 psi (pounds per square inch) to 14.5 psi at a room temperature of 295 K?

## Relating $\Delta G$ and pressure

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$$\Delta G = (0.022 \text{ mol}) \left( 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (295 \text{ K}) \ln \frac{14.5 \text{ psi}}{2505 \text{ psi}} = -278 \text{ J}$$

# Chemical Potential

- The chemical potential,  $\mu$ , is defined as the change in the Gibbs free energy with respect to amount at constant temperature and pressure:

$$\mu \equiv \left( \frac{\partial G}{\partial n} \right)_{T,p}$$

- Chemical potential is referred to as a partial molar quantity since it expresses the change in a state variable, the Gibbs free energy, versus molar amount.
- For pure substances, the chemical potential is equal to the change in the Gibbs free energy of the system as the amount of material changes.



# Chemical Potential of Mixtures

- For systems that have more than one chemical component, the chemical potential for component  $i$  is expressed as

$$\mu_i \equiv \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_j(j \neq i)}$$

- For systems of more than one component, the chemical potential does not equal the change in free energy of the pure material because each component interacts with the other, which affects the total energy of the system.
- If all components were ideal, this wouldn't happen, and partial molar quantities would be the same for any component of the system.

# Varying $\mu$ and $\Delta G$ with pressure

$$\Delta G = nRT \ln \frac{p_f}{p_i}$$

$$\Delta \mu = RT \ln \frac{p_f}{p_i}$$

# Chemical Potential, Reactivity, and Equilibrium

- Chemical potential is a measure of how much a species wants to undergo a physical or chemical change.
- If two or more substances exist in a system and have different chemical potentials, some process would occur to equalize the chemical potentials.
- Thus, chemical potential allows us to begin consideration of chemical reactions and chemical equilibrium.

# Fugacity

- Fugacity,  $f$ , is a measure of the nonideality of real gases.
- The fugacity can be thought of as a scaled pressure of the gas that increases as the gas becomes less ideal.

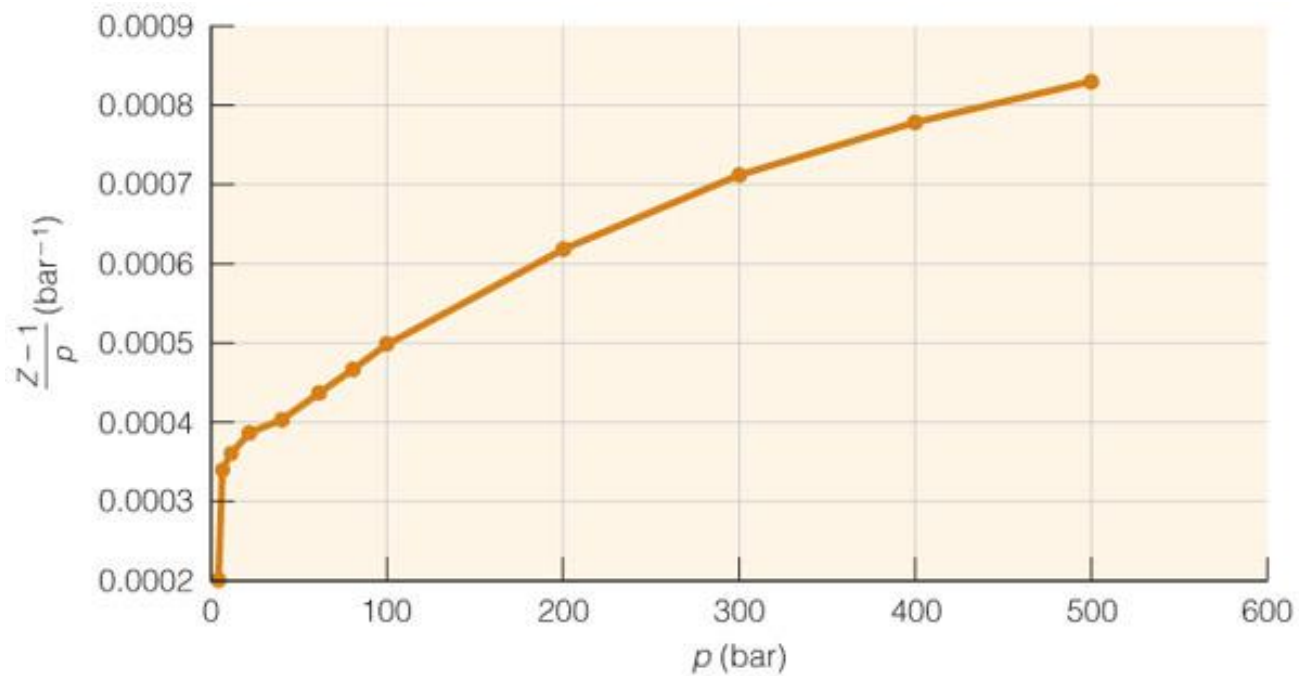
$$f = \phi \cdot p$$

- $f$  is the fugacity (scaled gas pressure)
- $\phi$  is the fugacity coefficient
- $p$  is the pressure of the gas
- The fugacity coefficient can be found by fitting experimental data to the equation

$$\ln \phi = \int_0^p \frac{Z - 1}{p} dp$$

# Fugacity coefficient

$$\ln \phi = \int_0^p \frac{Z - 1}{p} dp$$



# Fugacity

Calculate the fugacity of 100. atm of argon gas at 600. K assuming its compressibility is adequately represented by the truncated virial equation  $Z = 1 + \frac{B'p}{RT}$ .  $B'$  for Ar at 600 K is 0.012 L/mol (from Table 1.4).

# Fugacity

$$\begin{aligned}\ln \phi &= \int_0^{100 \text{ atm}} \frac{1 + \frac{B'p}{RT} - 1}{p} dp = \frac{B'}{RT} \int_0^{100 \text{ atm}} 1 dp \\&= \frac{B'p}{RT} \Big|_0^{100 \text{ atm}} \\&= \frac{B'(100 \text{ atm} - 0 \text{ atm})}{RT} = \frac{\left(0.012 \frac{\text{L}}{\text{mol}}\right) (100 \text{ atm})}{\left(0.08205 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (600 \text{ K})} = 0.024 \\&\ln \phi = 0.024 \\&e^{\ln \phi} = e^{0.024} \\&\phi = 1.024\end{aligned}$$