**Lecture 3 Evaluation of Properties of Pure Substances: Ideal and Real Gases, Calculation Methods**

**Goal of the lecture:** To study the fundamental principles of thermodynamics, including the classification of systems, their properties, and parameters used to describe their state.

**Brief lecture notes:** This lecture focuses on the evaluation of thermodynamic properties of pure substances in both ideal and real states. The ideal gas model provides a fundamental understanding of the relationship among pressure, volume, and temperature, while real gases exhibit deviations due to molecular interactions and finite molecular volumes. We will review the basic equations of state, the concept of compressibility factor, generalized correlations, and practical methods used to determine properties such as internal energy, enthalpy, and entropy. The lecture also discusses phase behavior, the use of property tables, and computer-aided estimation of thermodynamic parameters.

**Main part**

**1. Introduction**

The behavior of pure substances under different thermodynamic conditions is fundamental for understanding energy transformations and process design. Depending on temperature, pressure, and intermolecular forces, a substance can behave as an ideal or a real gas. Ideal models are mathematically simple, while real models are necessary for high-pressure or low-temperature systems.

The ideal gas law assumes that gas molecules do not interact and occupy negligible volume.

$$PV = nRT$$

where

$P$— pressure, $V$— volume, $n$— number of moles, $R$— universal gas constant, and $T$— temperature (K).

For one mole of gas, the specific form is $Pv = RT$, where $v$is molar volume. The ideal gas model is valid for low pressures (P < 1 atm) and high temperatures (T > 300 K). The internal energy and enthalpy of an ideal gas depend only on temperature:

$$du = C_v dT, dh = C_p dT$$

where $C_v$and $C_p$are specific heat capacities at constant volume and pressure.

Real gases deviate from ideal behavior because of:

1. Finite molecular volume.
2. Intermolecular forces (attraction and repulsion).

To account for these effects, equations of state (EoS) are introduced.

The most common are:

| Equation of State | Mathematical Form | Application Range |
|---|---|---|
| Van der Waals | $(P + \frac{a}{v^2})(v - b) = RT$ | Moderate pressures |

| Equation of State | Mathematical Form | Application Range |
|---|---|---|
| Redlich–Kwong | $P = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)}$ | Wider range |
| Peng–Robinson | $P = \frac{RT}{v-b} - \frac{a\alpha(T)}{v(v+b)+b(v-b)}$ | Accurate for hydrocarbons |

These equations introduce correction parameters $a$(for intermolecular attraction) and $b$(for molecular volume).

Compressibility Factor (Z)

To quantify deviation from ideality, the compressibility factor is used:

$$Z = \frac{PV}{nRT}$$

For an ideal gas, $Z = 1$.

Values of $Z$are obtained experimentally or from generalized compressibility charts using reduced parameters:

$$P_r = \frac{P}{P_c}, T_r = \frac{T}{T_c}$$

where $P_c$and $T_c$are the critical pressure and temperature of the substance.

Evaluation of Thermodynamic Properties

Thermodynamic properties such as enthalpy (H), internal energy (U), and entropy (S) can be derived from experimental data or correlations. For real gases, these are evaluated as:

$$h = h^{ideal}(T) + h^{res}(P,T)$$
$$u = u^{ideal}(T) + u^{res}(P,T)$$

where the residual terms represent deviations due to non-ideal interactions.

Computer-based programs and property databases (e.g., NIST REFPROP, Aspen Plus) are often used for accurate calculations.

Phase Behavior of Pure Substances

At given $P$and $T$, a pure substance can exist as a solid, liquid, or vapor. The P–T phase diagram (Fig. 1) shows regions of stability and the critical point, where liquid and vapor phases become indistinguishable.

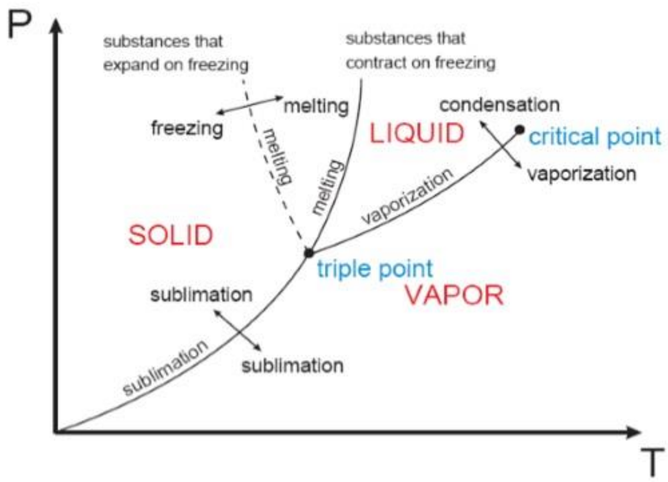

Figure 1. Typical P–T diagram of a pure substance showing solid, liquid, and vapor regions.

Property Tables and Computational Methods

For accurate engineering applications, property tables and charts are used (e.g., for water or refrigerants). These tables give $h, u, s, v$as functions of temperature and pressure.

**Questions for Self-Control**

1. What are the main assumptions of the ideal gas model?
2. Explain the physical meaning of parameters $a$and $b$in the van der Waals equation.
3. What is the compressibility factor, and how is it used?
4. How do real gases deviate from the ideal gas law at high pressures?
5. What is the significance of the critical point in a P–T diagram?

**Literature**


1. Çengel, Y.A., & Boles, M.A. Thermodynamics: An Engineering Approach, 9th ed. McGraw-Hill, 2019.
2. Moran, M.J., & Shapiro, H.N. Fundamentals of Engineering Thermodynamics, Wiley, 2020.
3. Smith, J.M., Van Ness, H.C., & Abbott, M.M. Introduction to Chemical Engineering Thermodynamics, 8th ed. McGraw-Hill, 2017.
4. Koretsky, M.D. Engineering and Chemical Thermodynamics, Wiley, 2013.
5. Lemmon, E.W. et al. NIST REFPROP Database: Reference Fluid Thermodynamic and Transport Properties, NIST, 2022.