

A GRAPHICAL REPRESENTATION

For the Fugacity of a Pure Substance

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The traditional development presents the fugacity^[1] of a pure substance as a mathematical translation to the Gibbs energy.

$$f_i \equiv P_R \exp\left(\frac{G_i - G_{i,R}^\circ - \Delta G_{i,\Delta T}^\circ}{RT}\right) \quad (1)$$

The most frequent expression is the equivalent implicit form or a variant thereof:

$$G_i = G_{i,R}^\circ + \Delta G_{i,\Delta T}^\circ + RT \ln\left(\frac{f_i}{P_R}\right) \quad (2)$$

For example, Smith, Van Ness, and Abbott,^[2] Tester and Modell,^[3] and Kyle^[4] use nomenclature of the form:

$$G_i \equiv \Gamma_i \{T\} + RT \ln(f_i) \quad (3)$$

The function of system temperature is:

$$\Gamma_i \{T\} = G_{i,R}^\circ + \Delta G_{i,\Delta T}^\circ - RT \ln(P_R) \quad (4)$$

The inclusion of the reference pressure term in the temperature function leaves the defining equation with an apparent infeasibility since fugacity has units of pressure and the argument of the logarithm must be dimensionless. Prausnitz, Lichtenthaler, and de Azevedo^[5] use nomenclature of the form:

$$G_i - G_{i,R} = RT \ln\left(\frac{f_i}{f_{i,R}}\right) \quad (5)$$

The values at the reference point are:

$$\begin{aligned} f_{i,R} &= P_R \\ G_{i,R} &= G_{i,R}^\circ + \Delta G_{i,\Delta T}^\circ \end{aligned} \quad (6)$$

Others (Winnick,^[6] Kyle,^[4] and Elliott and Lira^[9]) define fugacity in differential form at constant temperature:

$$dG_i = RT d \ln(f_i) \quad (7)$$

Integration from the arbitrary reference point at the system temperature gives the Prausnitz, et al. form. Sandler^[7] defines

the fugacity as a transformation to the residual Gibbs energy:

$$f_i = P \exp\left(\frac{\bar{G}_{i,P}}{RT}\right) \quad (8)$$

All authors use this equation as the basis for computing the value of the fugacity. This equation does not contain the reference state or the ideal gas Gibbs energy change.

A graphical representation of the rigorous mathematical definitions is described that explains the relationship between fugacity and Gibbs energy for a pure substance. The graphical representation provides students with a visual interpretation that aids in their comprehension of the definitions and the methods for determining the value of the fugacity.

PG DIAGRAM FOR A PURE SUBSTANCE

A PG diagram demonstrates the physics underlying the definitions for the fugacity. Figure 1 is a semi-logarithmic PG diagram for argon. The PG diagram was developed using data from the NIST Chemistry WebBook (<<http://webbook.nist.gov/chemistry/>>). The solid lines are the solid/liquid and the liquid/vapor coexistence curves. The vapor/liquid coexistence curve ends at the critical point (150.687 K and 48.630 bar). The solid/liquid and vapor/liquid coexistence curves would intersect at the triple point (83.8 K and 0.689 bar). The solid squares represent the data for the critical isotherm (150.687 K). The solid diamonds and solid circles are data on the 135 K and 120 K subcritical isotherms, respectively, in the vapor and liquid regions. The solid triangular data points represent the 180 K supercritical isotherm.

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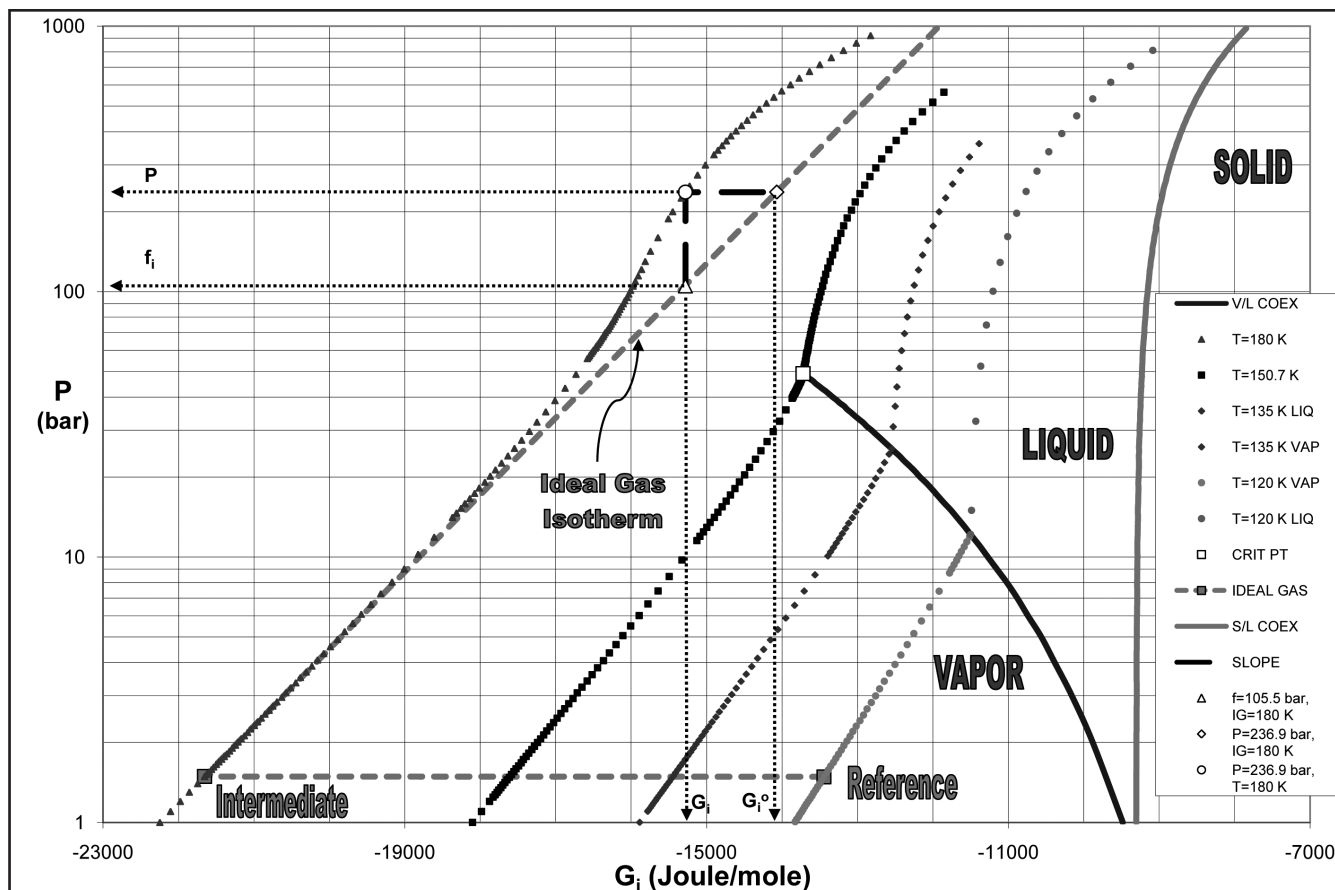


Figure 1. PG diagram for argon.

Suppose that the fugacity of the unfilled circular point at 180 K and 236.9 bar with Gibbs energy of -15,280 Joule/mole is to be determined.

$$G_{AR, 180 \text{ K}, 236.9 \text{ bar}} = -15,280 \frac{\text{Joule}}{\text{mole}} \quad (9)$$

GIBBS ENERGY FOR A SUBSTANCE BEHAVING AS AN IDEAL GAS

The Gibbs energy of a substance behaving as an ideal gas can be determined at any temperature and pressure provided that:

The absolute (or standard) entropy of the ideal gas is known at some reference state, and

The ideal gas heat capacity is known over the range from the reference temperature to the system temperature.

Gibbs energy is a state (point) function. As such, any convenient path between two states determines the difference in the Gibbs energy. Select a path from the ideal gas reference state to a hypothetical ideal gas state that is composed of: 1) an isobaric step at the reference state pressure from the reference state temperature to the ideal gas state temperature (details of the ideal gas reference state and the computation

of the Gibbs energy change for the isobaric step are contained in the Appendix) and 2) an isothermal step at the ideal gas state temperature from the reference state pressure to the ideal gas state pressure.

$$G_i^{\circ} - G_{i,R}^{\circ} = \Delta G_{i,\Delta T}^{\circ} + \Delta G_{i,\Delta P}^{\circ} \quad (10)$$

Rearranging:

$$G_i^{\circ} = G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + \Delta G_{i,\Delta P}^{\circ} \quad (11)$$

The fundamental property relationship for the Gibbs energy is:

$$dG = -SdT + VdP \quad (12)$$

For the isothermal step, the Gibbs energy change is:

$$\Delta G_{i,\Delta P}^{\circ} = \int_{P_R}^P V^{\circ} dP = \int_{P_R}^P \frac{RT}{P} dP = RT \ln \left(\frac{P}{P_R} \right) \quad (13)$$

Rearranging:

$$\ln \left(\frac{P}{P_R} \right) = \frac{\Delta G_{i,\Delta P}^{\circ}}{RT} = \frac{G_i^{\circ} - G_{i,R}^{\circ} - \Delta G_{i,\Delta T}^{\circ}}{RT} \quad (14)$$

The isotherm for a pure substance behaving as an ideal gas

is a straight line with slope of $1/RT$ on the semi-logarithmic PG diagram. It is a fundamental axiom of thermodynamics that all substances behave as an ideal gas as the pressure approaches zero on an isotherm, therefore, every isotherm becomes asymptotic to a straight line with this slope as the pressure approaches zero. Note that the four isotherms on Figure 1 become asymptotic to a straight line at low pressure and that the slope of the line decreases with increasing temperature. The dashed line, asymptotic at low pressure to the 180 K isotherm, is the 180 K isotherm for argon behaving as an ideal gas. At 180 K and 236.9 bar, argon has a significant deviation from ideal gas behavior (unfilled circle for argon as a real gas and unfilled diamond for argon as an ideal gas).

Suppose that the Gibbs energy for argon as an ideal gas at 180 K and 236.9 bar relative to the ideal gas reference state taken to be 120 K and 1.5 bar with an ideal gas absolute entropy of 132.35 Joule/mole K and Gibbs energy of -13,444 Joule/mole is to be determined. The ideal gas reference state is not on the 120 K isotherm for argon. It is an ideal gas reference state, therefore it is located on the 120 K isotherm for argon behaving as an ideal gas that is asymptotic to the real isotherm as the pressure approaches zero. At the low pressure of the reference state, there is little difference between the real isotherm and the ideal gas isotherm.

The two-step path is depicted on Figure 1 by a dashed line that begins at the reference state and proceeds horizontally (isobaric) to an intermediate state on the 180 K isotherm for the ideal gas and then proceeds from the intermediate state along the ideal gas isotherm to the ideal gas state (unfilled diamond). The Gibbs energy of argon behaving as an ideal gas at 180 K and 236.9 bar is -14,070 Joule/mole.

$$G_{\text{Ar},180\text{ K},236.9\text{ bar}}^{\circ} = -14,070 \frac{\text{Joule}}{\text{mole}} \quad (15)$$

Substituting for the isothermal step and rearranging:

$$G_i^{\circ} - G_{i,R}^{\circ} = \Delta G_{i,\Delta T}^{\circ} + \Delta G_{i,\Delta P}^{\circ} = \Delta G_{i,\Delta T}^{\circ} + RT \ln \left(\frac{P}{P_R} \right)$$

$$G_i^{\circ} = G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left(\frac{P}{P_R} \right) \quad (16)$$

RESIDUAL GIBBS ENERGY

The residual Gibbs energy at constant pressure is the difference between the Gibbs energy of the system and the Gibbs energy of a system of the same chemical composition and at the same temperature and pressure but behaving as an ideal gas.

$$\hat{G}_{i,P} \equiv G_i - G_i^{\circ} \quad (17)$$

An important attribute of residual properties is that the calculation only requires PVT data and/or equations of state applicable on the system isotherm from a pressure that approaches zero to the system pressure. These calculations do not require heat capacity or absolute entropy. On the PG diagram, the residual Gibbs energy for argon at 180 K and 236.9 bar represents a process from

the 180 K ideal gas isotherm at 236.9 bar (unfilled diamond) to the real 180 K isotherm at 236.9 bar (unfilled circle). The residual Gibbs energy for argon at 180 K and 236.9 bar is:

$$\hat{G}_{i,P} \equiv G_i - G_i^{\circ} = -15,280 - (-14,070) = -1,210 \frac{\text{Joule}}{\text{mole}} \quad (18)$$

PHYSICAL DEFINITION OF THE FUGACITY FOR A PURE SUBSTANCE

The fugacity of a pure substance at a temperature and pressure is the pressure at which the substance behaving as an ideal gas at the same temperature has the same Gibbs energy as the system. On Figure 1, the Gibbs energy of a system containing argon at 180 K and 236.9 bar is -15,280 Joule/mole. The pressure of argon behaving as an ideal gas at 180 K that has a Gibbs energy of -15,280 Joule/mole is 105.5 bar. This is the fugacity of argon at 180 K and 236.9 bar. The fugacity is easily determined on Figure 1 as the pressure where a vertical line through the point at 180 K and 236.9 bar intersects the 180 K ideal gas isotherm (unfilled triangle).

$$G_{\text{Ar},180\text{ K},105.5\text{ bar}}^{\circ} = -15,280 \frac{\text{Joule}}{\text{mole}} \quad (19)$$

The fugacity is a point located on the ideal gas isotherm. The two-step path from the reference state gives the implicit form for the definition.

$$G_i = G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left(\frac{f_i}{P_R} \right) \quad (20)$$

DETERMINING THE FUGACITY FOR A PURE SUBSTANCE

Consider the Gibbs energy changes for a three-step process from the reference state to the system state that is composed of: 1) an isobaric step for the substance behaving as an ideal gas at the reference state pressure from the reference state temperature to the intermediate state at the system temperature, 2) an isothermal step for the substance behaving as an ideal gas at the system temperature from the reference state pressure to the system pressure, and 3) an isobaric step from the ideal gas isotherm to the real isotherm. The first two steps are the Gibbs energy changes for the two-step process from the reference state to the ideal gas state at the system temperature and pressure (unfilled diamond for a system at 180 K and 236.9 bar). The Gibbs energy change for the third step is the residual Gibbs energy.

$$G_i^{\circ} = G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left(\frac{P}{P_R} \right)$$

$$\hat{G}_{i,P} \equiv G_i - G_i^{\circ}$$

$$G_i = G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left(\frac{P}{P_R} \right) + \hat{G}_{i,P} \quad (21)$$

Equating with the implicit form for the definition of the fugacity gives the Sandler definition:

$$\begin{aligned}
G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left(\frac{f_i}{P_R} \right) &= G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left(\frac{P}{P_R} \right) + \widehat{G}_{i,P} \\
RT \ln \left(\frac{f_i}{P} \right) &= \widehat{G}_{i,P} \\
f_i &= P \exp \left(\frac{\widehat{G}_{i,P}}{RT} \right) \quad (22)
\end{aligned}$$

This is the equation that is used to compute the value of the fugacity of a pure substance. The residual Gibbs energy at constant pressure is determined from PVT data and/or equations of state for the pure substance. Since the ideal gas reference state is not specified, the absolute entropy at the reference state is not required. The isobaric ideal gas Gibbs energy change cancels and this eliminates the need for the ideal gas heat capacity.

At 180 K and 236.9 bar, the residual Gibbs energy is -1210 Joule/mole. Substitution gives the fugacity:

$$f_i = P \exp \left(\frac{\widehat{G}_{i,P}}{RT} \right) = 236.9 \text{ bar} \exp \left(\frac{-1210 \frac{\text{Joule}}{\text{mole}}}{\left(8.3143 \frac{\text{Joule}}{\text{mole K}} \right) 180 \text{ K}} \right) = 105.5 \text{ bar} \quad (23)$$

The PG diagram also reveals this definition for the fugacity. Rearranging:

$$\frac{\ln \left(\frac{P}{f_i} \right)}{-\widehat{G}_{i,P}} = \frac{1}{RT} \quad (24)$$

The slope of the ideal gas isotherm is equal to the “rise” over the “run.” The slope of the 180 K isotherm for argon behaving as an ideal gas at 180 K and 236.9 bar is indicated on the diagram. The rise on the semi-logarithmic PG diagram (unfilled triangle to unfilled circle) is the numerator and the run (unfilled circle to unfilled diamond) is the denominator. The residual Gibbs energy and the fugacity are measures of the deviation from ideal gas behavior. The fugacity is a measure of the vertical distance (on a logarithmic scale) from ideal gas behavior to the system state. The residual Gibbs energy is a measure of the horizontal distance (on a linear scale) from ideal gas behavior to the system state.

PHASE COEXISTENCE FOR A PURE SUBSTANCE

The temperature, pressure, and Gibbs energy of a pure substance must be equal in each phase for two or more phases to coexist.

$$G_{i(\alpha)} = G_{i(\beta)} \quad (25)$$

The implicit form for the definition of the fugacity produces the equivalent requirement for fugacity.

$$\begin{aligned}
G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left(\frac{f_{i(\alpha)}}{P_R} \right) &= G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left(\frac{f_{i(\beta)}}{P_R} \right) \\
f_{i(\alpha)} &= f_{i(\beta)} \quad (26)
\end{aligned}$$

Since the fugacity can be determined from PVT information for a substance, it is more convenient for phase coexistence calculations than Gibbs energy. Lewis^[1] used this requirement coupled with the low pressure limit as the definition when developing the concept of fugacity.

STUDENT COMPREHENSION

Lewis described the concept of fugacity that he developed as “abstruse” and most students in the intervening century would agree. The PG diagram demonstrates the equivalence of the various definitions and gives insight to the advantages of fugacity over Gibbs energy. Students prefer the physical definition for fugacity that is also demonstrated on the diagram. It explains why two quantities with the same units but different values, pressure and fugacity, are equal when two phases of a pure substance are in equilibrium. Fundamental comprehension leads to increased confidence and fewer errors when applying fugacity.

CONCLUSIONS

The semi-logarithmic PG diagram for a pure substance with superimposed isotherms for the substance behaving as an ideal gas provides physical descriptions for the equations used to define and compute the value of the fugacity. The PG diagram clearly demonstrates that the fugacity of a pure substance at a temperature and pressure is the pressure at which the substance behaving as an ideal gas at the same temperature has the same Gibbs energy as the system. This physical definition eliminates much of the “abstruse” nature^[1] of the fugacity.

NOMENCLATURE

- $C_{p,i}^{\circ}$ Ideal gas heat capacity at constant pressure for the pure substance
- f_i Fugacity of the pure substance at the system temperature and pressure
- $f_{i,R}$ Fugacity of the pure substance at an arbitrary reference point at the system temperature
- G_i Gibbs energy of the pure substance at the system temperature and pressure
- $G_{i,I}^{\circ}$ Gibbs energy for a hypothetical ideal gas at the intermediate state (system temperature and reference state pressure)
- $G_{i,R}$ Gibbs energy of the pure substance at the arbitrary reference point at the system temperature
- $G_{i,R}^{\circ}$ Gibbs energy for a hypothetical ideal gas at the reference state for the Gibbs energy relative to the reference state for the enthalpy
- $G_{i(\alpha)}$ Gibbs energy of pure substance in phase α
- $G_{i(\beta)}$ Gibbs energy of pure substance in phase β
- G_i° Gibbs energy of the pure substance as a hypo-

theoretical ideal gas at the system temperature and pressure

$\Delta G_{i,\Delta P}^\circ$ Ideal gas Gibbs energy change at constant temperature from the reference state pressure to the system pressure

$G_{i,R}^\circ$ Gibbs energy at the ideal gas reference state

$\Delta G_{i,\Delta T}^\circ$ Ideal gas Gibbs energy change at constant pressure from the reference state temperature to the system temperature

$\widehat{G}_{i,P}$ Residual Gibbs energy at constant pressure

$H_{i,R}^\circ$ Enthalpy for a hypothetical ideal gas at the reference state for the Gibbs energy relative to the reference state for the enthalpy

P Absolute pressure of the pure substance

P_R Absolute pressure at the ideal gas reference state

R Gas constant

$S_{i,R}^\circ$ Absolute entropy for a hypothetical ideal gas at the reference state for the Gibbs energy

T Absolute temperature of the pure substance

T_R Absolute temperature at the reference state for the Gibbs energy

$\Gamma_i\{T\}$ A function of system temperature

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APPENDIX

Ideal Gas Reference State

The value of the fugacity can be determined without specifying the ideal gas reference state, however, development of the PG diagram requires a reference state where the absolute entropy is known. The definition for the Gibbs energy is:

$$G \equiv H - TS \quad (27)$$

The Gibbs energy and the enthalpy are relative quantities however the temperature and entropy are absolute quantities. The absolute entropy (relative to the perfect crystalline state at a temperature of absolute zero) for the substance behaving as an ideal gas is required to determine the Gibbs energy at the ideal gas reference state.

$$G_{i,R}^\circ = H_{i,R}^\circ - T_R S_{i,R}^\circ \quad (28)$$

Gibbs energy and enthalpy are relative quantities but are not independent. The definition of the Gibbs energy ties the value of one to the arbitrary reference state for the other. In like fashion, the definitions for the internal energy and the Helmholtz energy make all four quantities interdependent.

The NIST database reports the absolute entropy of argon as an ideal gas at 298.16 K and 1 bar to be 154.84 Joule/mole K. Extensive tabulations of data for absolute entropies do not exist, thus, one of the driving forces to replace Gibbs energy with fugacity. Standard entropies may be reported for the pure substance as a solid or liquid. In principle, the absolute entropy at an ideal gas reference state can be determined from condensed state data. This makes the definitions of the fugacity based on an ideal gas reference state general.

Poling, Prausnitz, and O'Connell^[8] provide methods for estimating absolute entropies in the absence of data.

ISOBARIC GIBBS ENERGY CHANGES FOR A PURE SUBSTANCE

The first step to determine the Gibbs energy change for an ideal gas is an isobaric process. The Gibbs energy change for the process is:

$$\Delta G_{i,\Delta T}^\circ = G_{i,I}^\circ - G_{i,R}^\circ \quad (29)$$

The definition of the Gibbs energy at the intermediate state is:

$$G_{i,I}^\circ = H_{i,I}^\circ - T S_{i,I}^\circ \quad (30)$$

The ideal gas enthalpy at the intermediate state is determined from the ideal gas heat capacity:

$$H_{i,I}^\circ = H_{i,R}^\circ + \int_{T_R}^T C_{p,i}^\circ dT \quad (31)$$

Determination of the value for the absolute entropy at the intermediate state also requires a correlation for the ideal gas heat capacity.

$$S_{i,I}^\circ = S_{i,R}^\circ + \int_{T_R}^T \frac{C_{p,i}^\circ}{T} dT \quad (32)$$

Tabulations of parameter values for correlations of data for the ideal gas heat capacity of pure substances are extensive and there are several group contribution methods^[8] to estimate the heat capacity in the absence of correlations. □