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Demonstrating the Limitations of the Ideal Gas Law*

A. A. KORNHAUSER†
Department of Mechanical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, U.S.A.

Beginning thermodynamics students often have difficulty in determining when the ideal gas law is an acceptable model for the behavior of substances. The iso-compressibility chart, showing lines of constant compressibility factor in a reduced pressure-reduced temperature plane, clearly demonstrates the limitations of the ideal gas model. It can also be used to develop simple approximate expressions for small errors in the ideal gas law

NOMENCLATURE

- a Constant in Redlich–Kwong equation
- β Constant in Redlich–Kwong equation
- b Constant in Redlich–Kwong equation
- ε Fractional error
- P Pressure
- R Gas constant
- v Specific volume
- Z Compressibility factor
- α Constant in Redlich–Kwong equation

Subscripts
- c Critical property
- r Reduced property

INTRODUCTION

BEGINNING thermodynamics students often have difficulty in determining when the ideal gas law is an acceptable model for the behavior of substances. The ideal gas law is valid when pressures are low and temperatures are high relative to critical pressure and temperature. But how low is 'low', and how high is 'high'? In any engineering thermodynamics course, this question should be answered with another question: 'What accuracy is required?'

The compressibility factor $Z = Pv/Rt$ is a convenient measure of the accuracy of the ideal gas law. For an ideal gas $Z = 1$. For a real gas the error in the ideal gas law is proportional to $Z - 1$.

According to the law of corresponding states, compressibility factor is a function of reduced temperature ($T_r = T/T_c$) and reduced pressure ($P_r = P/P_c$). The law is only approximately correct, since it predicts a single critical compressibility factor ($Z_c = P_c v_c / RT_c$) for all gases while actual values vary from 0.18 to 0.3. It can, however, be used to construct generalized compressibility charts such as those of Nelson and Obert [1]. These charts may be used to find approximate compressibility factor for any gas from T, P, T_c and P_c.

Generalized compressibility charts may thus be used to estimate the error in the ideal gas law. The charts do not, however, provide a good way of demonstrating the conditions at which the ideal gas law is accurate. This paper presents a variation on these charts which is useful for such a demonstration.

THE ISO-COMPRESSIBILITY CHART

The conventional compressibility chart displays Z vs. P_r for various values of T_r. It is proposed that another form would also be useful: an 'iso-compressibility' chart, displaying P_r vs. T_r for various values of Z. If the values of Z were chosen to correspond to certain error levels of the ideal gas law (e.g. ±1%, ±2%) the chart would give a clear visual demonstration of the limitations of the law.

Nelson and Obert's charts were prepared by graphical fitting of experimental data. Such a procedure is very time-consuming. For the purpose of evaluating ideal gas law error, it is felt that a chart generated from an equation of state will be equally useful.

The Redlich–Kwong equation of state [2] was used. It is usually presented as:

$$P = \frac{RT}{v - b} - \frac{a}{v(v+b)\sqrt{T}} \text{ where}$$

$$a = \alpha \frac{R^2 T_c^{5/2}}{P_c} \text{ with } \alpha = \frac{1}{9(2^{1/3} - 1)} \approx 0.4275$$

$$b = \beta \frac{RT_c}{P_c} \text{ with } \beta = \frac{2^{1/3} - 1}{3} \approx 0.08664 \qquad (1)$$

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† Assistant Professor of Mechanical Engineering.

Since all the constants in the equation are based on critical temperature and pressure, rather than evaluated empirically, it is consistent with the law of corresponding states. It gives $Z_c = 0.3$.

The Redlich–Kwong equation can be re-written as a cubic in Z:

$$Z^3 - Z^2 + \left[\frac{\alpha P_r}{T_r^{5/2}} - \frac{\beta P_r}{T_r} - \frac{\beta^2 P_r^2}{T_r^2}\right] Z - \frac{\alpha\beta P_r^2}{T_R^{7/2}} = 0 \qquad (2)$$

For producing the desired P_r vs. T_r chart, this cubic can then be written as a quadratic in P_r:

$$\left[\frac{\beta^2 Z}{T_r^2} + \frac{\alpha\beta}{T_r^{7/2}}\right] P_r^2 + \left[\frac{\beta Z}{T_r} - \frac{\alpha Z}{T_r^{5/2}}\right] P_r + Z^2 - Z^3 = 0 \qquad (3)$$

The iso-compressibility chart (Fig. 1) displays the solution to (3) for various values of Z. For $Z < 1$ and small values of T_r the equation has two physically significant solutions: one on the liquid side of the critical point and one on the vapor side. For $Z < 1$ and large values of T_r all solutions are either imaginary or negative and thus not physically significant. For $Z > 1$ there is one physically significant solution and one negative solution. The chart clearly maps the areas in which the ideal gas law meets a given accuracy requirement. The $Z = 0.999$ and $Z = 1.001$ curves show the limits of $\pm 0.1\%$ accuracy, the $Z = 0.99$ and $Z = 1.01$ curves show the limits of $\pm 1\%$ accuracy, etc.

The chart shows a small but finite region of $Z \approx 1$ which extends into the area of $P > P_c$ and $T < T_c$, where the ideal gas law is known to be highly inaccurate. Ideal gas behavior indicates a lack of molecular interaction, either attractive or repulsive. The anomalous $Z \approx 1$ region is one in which attractive and repulsive forces balance to produce pseudo-ideal behavior. The small size of the region and the rapidity with which Z changes in its vicinity make the ideal gas law useless there.

The iso-compressibility chart may be used as a tool for quick checking of whether a state or process is adequately described by the ideal gas law. It must, of course, be used with caution when $T < T_c$, since it does not predict condensaton. Its most important use, however, is as an educational tool, helping students visualize the range for which the ideal gas law is accurate.

ASYMPTOTIC ERROR EXPRESSIONS

Examination of Fig. 1 shows that the curves of constant Z approach asymptotes at low and high values of T_r. The expressions for these asymptotes may be expected to give simple, approximate expressions for the accuracy limits of the ideal gas law.

For $Z \approx 1$, $T_r \ll 1$, and $P_r \ll 1$, (3) becomes

$$P_r \approx \frac{Z - Z^2}{\alpha} T_r^{5/2} \qquad (4)$$

For $Z \approx 1$ and $T_r \gg 1$, (3) becomes

$$P_r \approx \frac{Z^2 - Z}{\beta} T_r \qquad (5)$$

If ε is a small fractional deviation from the ideal gas law then $Z = 1 - \varepsilon$ in (4), $Z = 1 + \varepsilon$ in (5), and ε^2 is negligible. Small errors in the ideal gas law can thus be approximated as the greater of

$$\varepsilon = 0.4275\,\frac{P_r}{T_r^{5/2}} \text{ and } \varepsilon = 0.08664\,\frac{P_r}{T_r} \qquad (6)$$

Figure 2 compares the asymptotes given by (6) for $\pm 1\%$ error with the iso-compressibility curves for $Z = 0.99$ and $Z = 1.01$. The asymptotes always fall below the respective curves, so that (6) gives a conservative value for the errors in the ideal gas law for given conditions.

As with the iso-compressibility chart itself, these expressions must be used with caution when there is a possibility of condensation.

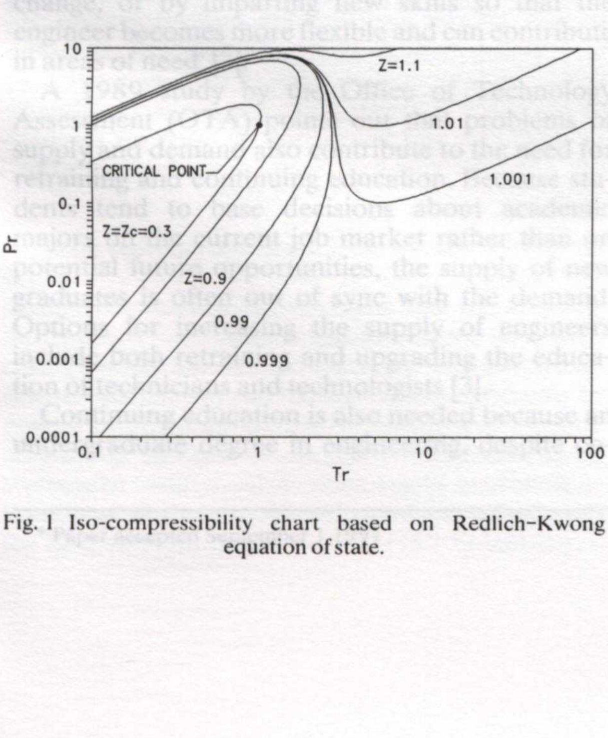

Fig. 1 Iso-compressibility chart based on Redlich–Kwong equation of state.

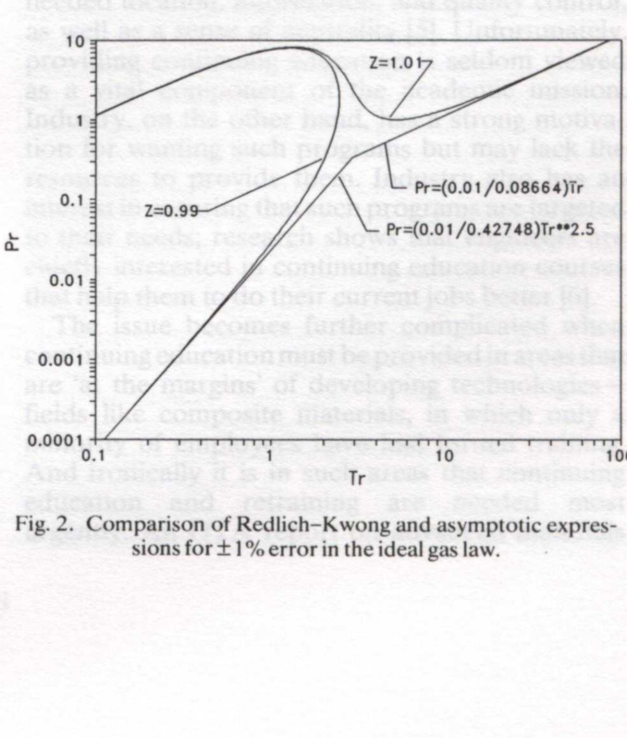

Fig. 2. Comparison of Redlich–Kwong and asymptotic expressions for $\pm 1\%$ error in the ideal gas law.

COMPARISON WITH TABULATED PROPERTIES

The Redlich–Kwong equation of state is not exact. In order to assure ourselves that the ideal gas law limitations given above are realistic, we may compare the iso-compressibility curves given by (3) with tabulated data for various gases.

Figure 3 shows the $Z = 0.99$ and $Z = 1.01$ curves together with points for the same values of Z for argon, hydrogen, nitrogen, and carbon dioxide. The points are taken from Helsenrath *et al.* [3]. Each gas is seen to follow the same trends as the equation of state, but with curves slightly displaced. This displacement demonstrates the limitation of the law of corresponding states and is primarily due to variation in Z_c among the gases listed. The variation is greatest in the anomalous $Z \approx 1$ region. Over most of the curve the variation is small.

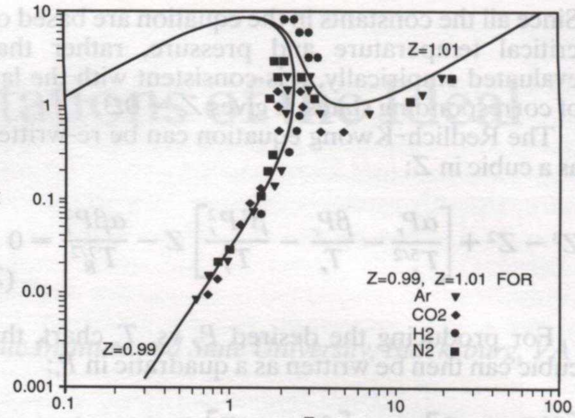

Fig. 3. Comparison of Redlich–Kwong expression and tabulated data [3] for ±1% error in the ideal gas law.

CONCLUSION

The iso-compressibility chart generated with the Redlich-Kwong equation of state provides a clear visual demonstration of the limitations of the ideal gas law.

Asymptotic approximations to the curves of constant compressibility (6) provide simple approximations for small errors in the ideal gas law.

The iso-compressibility curves generated from the Redlich-Kwong equation compare well with tabulated compressibility data.

The iso-compressibility chart and associated asymptotic expressions may prove useful in introductory thermodynamics curricula.

REFERENCES

1. L. C. Nelson and E. F. Obert, Generalized *p-v-T* Properties of Gases, *Trans. A.S.M.E.*, **76**, 1057–1066 (1954).
2. O. Redlich and J. N. S. Kwong, On the Thermodynamics of Solutions, *Chemical Reviews*, **44**, 233–244 (1949).
3. J. Hilsenrath *et al.*, *Tables of Thermal Properties of Gases*, Circular 564, U.S. National Bureau of Standards, Washington (1955).