



# Improving thermodynamic consistency among vapor pressure, heat of vaporization, and liquid and ideal gas isobaric heat capacities through multi-property optimization



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## ABSTRACT

Vapor pressure, heat of vaporization, liquid isobaric heat capacity, and ideal gas isobaric heat capacity can be measured for pure organic compounds between the triple point and critical point. Additionally, heat of vaporization is proportional to the derivative of vapor pressure with respect to temperature through the Clapeyron equation, and the difference of liquid and ideal gas heat capacities are proportional to the derivative of heat of vaporization with respect to temperature. These relationships and experimental data were compared for several compounds to interpolate and extrapolate available data and increase consistency amongst data sets and optimizing the accepted property values has been developed so that this procedure can be applied to other compounds in the DIPPR 801 database for which there are fewer experimental data available. The process involves critically evaluating available experimental data and the correlations used to fit these temperature-dependent properties. Multi-property optimization includes weighting the various data values based on the accuracy of the data and on the perceived relative importance of the properties in process design. User-defined weighting systems will be established to provide optimization flexibility across these properties for future use of the DIPPR 801 database.

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## 1. Introduction

Many chemical processes run along the saturation curve, including distillation, condensation, and boiling. For this reason, the thermodynamic properties for pure compounds along the saturation curve are especially important to know well. However, even for well-known compounds, there are gaps in experimental data for vapor pressure ( $P_{\text{vap}}$ ), heat of vaporization ( $\Delta H_{\text{vap}}$ ), and liquid and ideal gas isobaric heat capacities ( $C_p^l$  and  $C_p^g$ , respectively), all of which are thermodynamically interrelated properties. From the triple point temperature ( $T_{\text{TP}}$ ) to the critical temperature ( $T_c$ ), experimental data for each of these properties exist in varying frequencies, as represented in Fig. 1, mainly due to ease of measurement. Data for  $P_{\text{vap}}$  are very common around the normal

boiling point ( $T_{\text{NB}}$ ) and to a lesser extent towards the critical point. Data for  $\Delta H_{\text{vap}}$  are usually only available around  $T_{\text{NB}}$ , while  $C_p^l$  data are found from  $T_{\text{TP}}$  to  $T_{\text{NB}}$ .  $C_p^g$  data are not very common, but the temperature dependent curve can be predicted using *ab initio* or reliable group contribution methods. This knowledge can be used to inform the best methods for an optimization that uses experimental data for these properties to find the best values. To determine the best values for these properties in regions without data, thermodynamic relationships amongst these properties can be used.  $P_{\text{vap}}$  is related to  $\Delta H_{\text{vap}}$  through the Clapeyron equation,

$$\frac{dP_{\text{vap}}}{dT} = \frac{\Delta H_{\text{vap}}}{T(V_{\text{vap}} - V_{\text{liq}})} \quad (1)$$

with  $T$  as temperature and  $V_{\text{vap}}$  and  $V_{\text{liq}}$  as vapor and liquid volumes at saturation. All of these properties are related through the temperature slope of  $\Delta H_{\text{vap}}$ .

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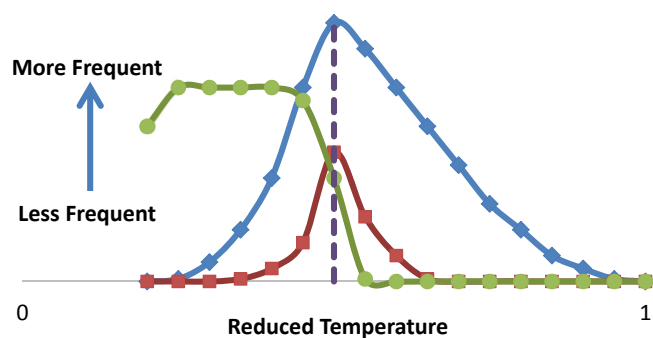


Fig. 1. A qualitative look at the relative frequency of experimental data for (—●—) vapor pressure, (—■—) heat of vaporization, and (—●—) liquid heat capacity around the (—●—) normal boiling point.

$$\frac{d\Delta H_{\text{vap}}}{dT} = C_p^{\text{ig}} - T \int_0^{P_{\text{vap}}} \left( \frac{\partial^2 V_{\text{vap}}}{\partial T^2} \right) dP - C_p^{\text{l}} + \left\{ \left[ V_{\text{vap}} - T \left( \frac{\partial V_{\text{vap}}}{\partial T} \right)_P \right] - \left[ V_{\text{liq}} - T \left( \frac{\partial V_{\text{liq}}}{\partial T} \right)_P \right] \right\} \frac{dP_{\text{vap}}}{dT} \quad (2)$$

This relationship has been used by DIPPR to predict  $C_p^{\text{l}}$  at high temperatures, but a multi-property optimization can be used to increase thermodynamic consistency among these properties along the whole saturation curve. In order to gain insight into this optimization process, well-known compounds have been picked, and their data thoroughly vetted, to develop procedures and good practices for this optimization. The compounds picked for this process are: propylene, propane, pentane, hexafluoroethane, and ammonia. Even these compounds have gaps in data along the saturation curve, notably at low temperature for  $\Delta H_{\text{vap}}$  and at high temperature for  $C_p^{\text{l}}$ . Others have regressed equations of state to fit experimental data for a wider range of thermodynamic properties with the “short” Helmholtz equations of state with 12 parameters, but this analysis requires data over the whole PVT plane for a number of other properties as well [1], which is uncommon at best for many of the compounds evaluated by DIPPR. Instead, a cubic equation of state will be used and the vapor pressure correlation will be optimized, therefore reducing the number of parameters to be optimized and simplifying the optimization.

## 2. Constants and correlations

In order to use the thermodynamic relationships relating  $P_{\text{vap}}$ ,  $\Delta H_{\text{vap}}$ ,  $C_p^{\text{ig}}$ , and  $C_p^{\text{l}}$ , the best values of  $T_c$ ,  $P_c$ , and  $\omega$  were taken from the DIPPR database for each compound chosen in this project, owing to the rigorous analyses used to pick good values from experiment or prediction. The Soave-Redlich–Kwong cubic equation of state [2] was used to calculate  $V_{\text{vap}}$ , and the Rackett correlation [3] given by DIPPR for each compound was used to calculate  $V_{\text{liq}}$ . The four properties listed at the outset deserve further discussion.

### 2.1. Vapor pressure – $P_{\text{vap}}$

Vapor pressure data are the most readily available of any of the properties given. These data are usually most common around the normal boiling point, with accuracy of measurements decreasing towards the extrema in temperature. Two  $P_{\text{vap}}$  correlations will be examined in this project. The Riedel and the Wagner temperature

dependent  $P_{\text{vap}}$  expressions are

$$P_{\text{vap}} = \exp \left( A + \frac{B}{T} + C \ln(T) + DT^E \right) \quad (3)$$

$$P_{\text{vap}} = P_c \exp \left( \frac{A(1 - T_r) + B(1 - T_r)^{1.5} + C(1 - T_r)^X + D(1 - T_r)^Y}{T_r} \right) \quad (4)$$

where  $A - E$  are fitting coefficients,  $P_c$  is the critical pressure, and  $T_r$  is the reduced temperature. There are several permutations on these correlations that have been used. For the Riedel equation, the  $E$  parameter is usually specified to be 1, 2, or 6 [4–7], and will be referenced as Riedel 1, Riedel 2, and Riedel 6. For the Wagner equation, the two last exponents  $X$  and  $Y$  can be either 2.5 and 5, respectively, or 3 and 6, respectively [8,9], and will be referred to as Wagner 2.5,5 and Wagner 3,6.

Due to the ease of access to  $P_{\text{vap}}$  data, the  $P_{\text{vap}}$  correlation itself will be optimized to become more thermodynamically consistent with the other properties. A similar process has been used before to increase the accuracy of  $P_{\text{vap}}$  at low temperatures using the Virial equation of state for vapor volume [9]. (See page 7.6 of [10] for a more extensive list of references.) Since there are only 4 fitting parameters for each of the  $P_{\text{vap}}$  expressions, the optimization process will be relatively simple to perform and will focus in on the saturation curve for compounds that do not have extensive data. For a full optimization over the whole PVT plane for compounds with extensive data, a many-termed equation of state can be used [11], but that procedure is not the focus of this project.

### 2.2. Heat of vaporization – $\Delta H_{\text{vap}}$

Available heat of vaporization data are mainly in the region near the normal boiling point. The temperature dependent correlation used for  $\Delta H_{\text{vap}}$  does well empirically and lets  $\Delta H_{\text{vap}}(T_c) = 0$  [12]. It is given by

$$\Delta H_{\text{vap}} = A(1 - T_r)^{B+CT_r+DT_r^2+\dots} \quad (5)$$

where  $A - D$  are fitting parameters and  $T_r$  is the reduced temperature. The exponent of this correlation can be expanded if necessary, and is usually fit to a combination of experimental data and derived Clapeyron data points.

### 2.3. Isobaric ideal gas heat capacity – $C_p^{\text{ig}}$

Isobaric ideal gas heat capacity experimental data are relatively rare. When they do exist, they are scattered through different temperature regions. However, because ideal gas properties do not rely on external molecular interactions, the temperature dependent curve for  $C_p^{\text{ig}}$  can be derived from statistical mechanics [13], giving this form for nonlinear compounds

$$C_p^{\text{ig,nonlinear}} = 4R_g + R_g \sum_j^{3m-6} \left( \frac{\Theta_{vj}}{T} \right)^2 \frac{\exp \left( \frac{\Theta_{vj}}{T} \right)}{\left( \exp \left( \frac{\Theta_{vj}}{T} \right) - 1 \right)^2} \quad (6)$$

where  $R_g$  is the universal gas constant,  $m$  is the number of atoms in the molecule, and  $\Theta_{vj}$  is the  $j$ th vibrational temperature as calculated by solving the Schrodinger equation. Group contribution models based on *ab initio* calculations also provide accurate results above 298 K. For ease of use, this theory-derived equation was truncated and the group contribution method and experimental

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