ASTM INTERNATIONAL

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Standard Practice for
Calculating Heat of Vaporization or Sublimation from Vapor Pressure Data[1]

1. Scope

1.1 This practice describes the calculation of the heat of vaporization of a liquid or the heat of sublimation of a solid from measured vapor pressure data. It is applicable to pure liquids, azeotropes, pure solids, and homogenous solid solutions over the temperature range for which the vapor pressure equation fitted to the measured data is applicable.

NOTE 1—This practice is generally not applicable to liquid mixtures. For a pure liquid or azeotrope, composition does not change upon vaporization so that the integral heat of vaporization is identical to the differential heat of vaporization. Non-azeotropic liquid mixtures change composition upon vaporizing. Heat of vaporization data computed from this practice for a liquid mixture are valid only as an approximation to the mixture differential heat of vaporization; it is not a valid approximation to the mixture integral heat of vaporization.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2879 Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope

E1142 Terminology Relating to Thermophysical Properties

E1194 Test Method for Vapor Pressure

E1719 Test Method for Vapor Pressure of Liquids by Ebulliometry

E1782 Test Method for Determining Vapor Pressure by Thermal Analysis

3. Terminology

3.1 *Symbols:*

3.1.1 *A, B, C*—Antoine vapor pressure equation constants ($\log_{10}$, kPa, K), Antoine vapor pressure equation:

$$\log_{10} P = A - B/(T + C) \tag{1}$$

3.1.2 *P*—vapor pressure, kPa.

3.1.3 P_c—critical pressure, kPa.

3.1.4 P_r—reduced pressure = P/P_c.

3.1.5 *T*—absolute temperature, K.

3.1.6 T_c—critical temperature, K.

3.1.7 T_r—reduced temperature = T/T_c.

3.1.8 *V*—molar volume, cm^3/mol.

3.1.9 *R*—gas constant, 8.31433 J/mol-K; 8314330 kPa-cm^3/mol-K.

3.1.10 ΔH_V—heat of vaporization, J/mol.

3.1.11 ΔZ_V—difference in compressibility factor ($Z = PV/RT$) upon vaporization. Clapeyron equation:

$$\Delta H_V = -R \Delta Z_V \left[d(\ln P)/d(1/T) \right] \tag{2}$$

3.1.11.1 *Discussion*—The subscript "V" will be used throughout this practice to designate the vaporization of a liquid. If the vapor pressure data were measured for a solid, substitute the subscript "S" for the sublimation of a solid.

3.2 *Definitions*—Specialized terms used in this practice are defined in Terminology E1142.

3.2.1 *sublimation*—transition from a solid phase to a gaseous phase.

3.2.2 *vaporization*—transition from a liquid phase to a gaseous phase.

4. Summary of Practice

4.1 Vapor pressure data are measured by other referenced ASTM standards and then correlated with the Antoine equation. The heat of vaporization or sublimation is computed at the desired temperature from the vapor-pressure temperature derivative from the fitted Antoine equation by use of the Clapeyron equation (1).[3] In the Clapeyron equation, ΔZ_V is determined by either the Clausius-Clapeyron (1) or the Haggenmacher (2) approximations.

4.2 An example calculation is given in Annex A1.

5. Significance and Use

5.1 If the heat of vaporization or sublimation is absorbed or liberated in a process at constant pressure, it is called enthalpy of vaporization or sublimation. Enthalpy of vaporization or sublimation is a fundamental thermodynamic property of a liquid or solid. It is an important quantity in the design of heat exchangers and other chemical process units. Enthalpy of vaporization is also used to calculate solubility parameters (3).

5.2 This practice may be used in research, regulatory compliance, and quality assurance applications.

6. Experimental Vapor Pressure Data

6.1 Vapor pressure data are measured by Test Methods D2879, E1194, E1719, or E1782. Note the safety precautions contained in the test method used.

6.1.1 Vapor pressure data from other reliable sources, for example, peer-review technical journals, may be used. The source of the vapor pressure data must be noted.

6.2 The measured vapor pressure data are fitted to an Antoine vapor pressure equation. See 10.3 in Test Method E1719 for details on least-squares regression of vapor pressure data.

7. Calculation

7.1 At each temperature of interest, calculate the vapor pressure from the Antoine equation and calculate the vapor-pressure temperature derivative from the fitted Antoine equation constants from:

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[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

$$[d(\ln P)/d(1/T)] = -2.3025851[BT^2/(T+C)^2] \qquad (3)$$

7.2 Calculate an approximation to ΔZ_V at each temperature.

7.2.1 The Clausius-Clapeyron approximation to ΔZ_V is:

$$\Delta Z_V \equiv 1.0 \qquad (4)$$

7.2.2 The Haggenmacher approximation to ΔZ_V is:

$$\Delta Z_V = \left\{ 1 - [P_r/(T_r)^3] \right\}^{\frac{1}{2}} \qquad (5)$$

NOTE 2—The Clausius-Clapeyron approximation is generally used for solids and for liquids at low T_r. The Haggenmacher approximation is generally used for liquids up to $T_r \approx 0.75$.

7.2.3 If equation of state (Z) data are available for both the condensed and gaseous phases, ΔZ_V may be calculated directly from the equation of state data.

7.3 Calculate the heat of vaporization or heat of sublimation at each temperature from the Clapeyron equation:

$$\Delta H_V = -R\Delta Z_V [d(\ln P)/d(1/T)] \qquad (6)$$

8. Report

8.1 Report the following information:

8.1.1 The test method and source of the vapor pressure data used in the heat of vaporization or heat of sublimation calculation. A vapor pressure data table shall also be reported.

8.1.2 The Antoine equation constants fitted to the vapor pressure data.

8.1.3 The approximation to ΔZ_V used in the calculation.

8.1.4 The values and source of the critical temperature and critical pressure data if the Haggenmacher approximation was used for ΔZ.

8.1.5 A table that contains temperature, vapor pressure, the vapor pressure temperature derivative [$d(\ln P)/d(1/T)$], difference in compressibility factor (ΔZ_V), and ΔH_V, the heat of vaporization or heat of sublimation.

8.1.6 The specific dated version of this practice used.

8.2 See the sample calculations and report in Annex A1.

9. Keywords

9.1 Antoine equation; Clausius-Clapeyron equation; enthalpy of sublimation; enthalpy of vaporization; Haggenmacher equation; heat of sublimation; heat of vaporization; vapor pressure

ANNEX

(Mandatory Information)

A1. SAMPLE CALCULATIONS AND REPORT

A1.1 Source of Sample Vapor Pressure Data

A1.1.1 This sample calculation is performed on the sample vapor pressure data given for a toluene specimen in Annex A3 of Test Method E1719. Heat of vaporization is calculated in 10 K increments between 290 K and 400 K. Calculations for both the Clausius-Clapeyron and Haggenmacher approximations to ΔZ_V are listed.

A1.2 Sample Experimental Data

A1.2.1 These controlled pressure-boiling temperature data pairs were measured by Test Method E1719 on a 75 mL specimen charged to a vapor-lift pump ebulliometer:

P (kPa)	T (K)
10.0	318.4
20.0	335.4
30.0	345.8
50.0	360.7
70.0	371.2
85.0	377.9
100.0	383.3

A1.2.2 A non-linear least-squares fit of the Antoine equation, $\log_{10}P = A - B/(T + C)$, produced these constants:

A (fit) = 6.168057
B (fit) = 1397.23
C (fit) = −48.10

A1.3 Sample Calculation

A1.3.1 The critical temperature and pressure for toluene (**4**) are:

T_c = 591.75 K
P_c = 4108.69 kPa

At 290 K:

T_r = 0.490071821
P_r = 0.000600191

Vapor pressure = $10^{\wedge}[6.168057 - 1397.23/(290 - 48.10)]$

$= 2.465997$ kPa

$[d(\ln P)/d(1/T)] = -2.3025851[1397.23 * 290^2/(290 - 48.10)^2] = -4623.8938$ K

A1.3.2 Haggenmacher approximation to ΔZ_V:

$\Delta Z_v = \{1 - [0.000600191/(0.4900718121)^3]\}^{\frac{1}{2}} = 0.997447$

A1.3.3 ΔH_V from Clausius-Clapeyron approximation:

$\Delta H_v = (-8.31433)*1.00*(-4623.8938) = 38444.6$ J/mol

A1.3.4 ΔH_V from Haggenmacher approximation:

$\Delta H_v = (-8.31433)*0.997447*(-4623.8938) = 38346.4$ J/mol

A1.4 Sample Heat of Vaporization Report

A1.4.1 *Clausius-Clapeyron Approximation Report:*

A1.4.1.1 Data are for a toluene specimen and are listed in Annex A3 of Test Method E1719. These controlled pressure-boiling temperature data pairs were measured by Test Method E1719 on a 75 mL specimen charged to a vapor-lift pump ebulliometer:

P (kPa)	T (K)
10.0	318.4
20.0	335.4
30.0	345.8
50.0	360.7
70.0	371.2
85.0	377.9
100.0	383.3

A1.4.1.2 A non-linear least-squares fit of the Antoine equation:

$$\log_{10} P = A - B/(T + C)$$

produced these constants:

A (fit) = 6.168057
B (fit) = 1397.23
C (fit) = −48.10

A1.4.1.3 The Clausius Clapeyron approximation for ΔZ_V was used.

Temperature K	Pressure kPa	$[d(\ln P)/d(1/T)]$ K	ΔZ_V	ΔH_V J/mol
290	2.4659968	−4623.8938	1.00000000	38444.6
300	4.1811179	−4563.2028	1.00000000	37940.0
310	6.8089762	−4507.5026	1.00000000	37476.9
320	10.697757	−4456.2047	1.00000000	37050.4
330	16.277326	−4408.8094	1.00000000	36656.3
340	24.064868	−4364.8893	1.00000000	36291.1
350	34.668504	−4324.0774	1.00000000	35951.8
360	48.788774	−4286.0560	1.00000000	35635.7
370	67.217970	−4250.5496	1.00000000	35340.5
380	90.837442	−4217.3173	1.00000000	35064.2
390	120.61303	−4186.1482	1.00000000	34805.0
400	157.58889	−4156.8566	1.00000000	34561.5

A1.4.2 *Haggenmacher Approximation Report:*

A1.4.2.1 Data are for a toluene specimen and are listed in Annex A3 of Test Method E1719. These controlled pressure-boiling temperature data pairs were measured by Test Method E1719 on a 75 mL specimen charged to a vapor-lift pump ebulliometer:

P (kPa)	T (K)
10.0	318.4
20.0	335.4
30.0	345.8
50.0	360.7
70.0	371.2
85.0	377.9
100.0	383.3

A1.4.2.2 A non-linear least-squares fit of the Antoine equation: