

2. What is the enthalpy change when 2 lb of *n*-butane gas is cooled from 320°F and 2 atm to saturated vapor at 6 atm?
3. You are told that 4.3 kg of water at 200 kPa occupies (a) 4.3, (b) 43, (c) 430, (d) 4300, and (e) 43,000 liters. State for each case whether the water is in the solid, liquid, liquid-vapor, or vapor regions.
4. Two hundred pounds of a 35° API distillate is heated from 130°F to 275°F. Estimate the enthalpy change (in Btu). See Appendix K.
5. Water at 400 kPa and 500 K is cooled to 200 kPa and 400 K. What is the enthalpy change? Use the steam tables.

4.4 ENTHALPY CHANGES FOR PHASE TRANSITIONS

Your objectives in studying this section are to be able to:

1. Estimate the heat of fusion or heat of vaporization from empirical formulas, or look up the value in a reference table.
2. Estimate the heat of vaporization from the Clausius–Clapeyron equation or the Othmer plot.
3. Calculate an enthalpy change of a substance including the phase transitions.

In making enthalpy calculations, we noted in Fig. 4.5 that the heat capacity data are discontinuous at the points of a phase transition. The name usually given to the enthalpy changes for these phase transitions is *latent heat* changes, latent meaning “hidden” in the sense that the substance (e.g., water) can absorb a large amount of heat without any noticeable increase in temperature. Unfortunately, the word *heat* is still associated with these enthalpy changes for historical reasons, although they have nothing directly to do with heat as defined in Sec. 4.1. Ice at 0°C can absorb energy amounting to 334 J/g without undergoing a temperature rise or a pressure change, and similarly, liquid water at 1 atmosphere can absorb 2256.1 J/g before the temperature and pressure will change. Figure 4.10 shows, by the vertical lines at constant temperature, the enthalpies for the phase changes for water at 1 atmosphere pressure. The various enthalpy changes are termed:

Enthalpy change	Phase change
Heat of fusion	Solid to liquid
Heat of vaporization	Liquid to vapor
Heat of condensation	Vapor to liquid
Heat of sublimation	Solid to vapor

You can see from the chart for *n*-butane (Fig. 4.9) that the heats of vaporization (and

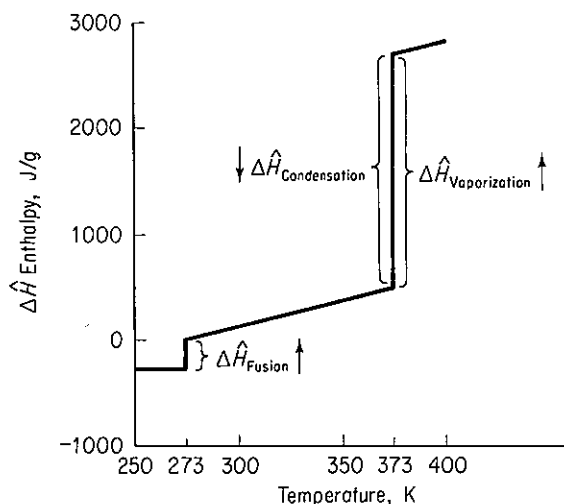


Figure 4.10 Enthalpy change for water at 1 atmosphere showing the phase transitions.

accordingly condensation) changes with temperature all the way up to the critical point, where it vanishes. Calculation of the *quality* of a liquid–vapor mixture was illustrated by Example 3.18.

You can find experimental values of latent heats in the references in Table 4.5, and a brief tabulation is listed in Appendix D. The symbols used for latent heat changes vary, but you usually find one or more of the following employed: $\Delta\hat{H}$, L , λ , Λ . Keep in mind that the enthalpy changes for vaporization given in the steam tables are for water under its vapor pressure at the indicated temperature.

In the absence of experimental values for the latent heats of transition, the following approximate methods will provide a rough *estimate of the molar latent heats*. Reid, Prausnitz and Poling, *The Properties of Gases and Liquids*, give many more methods.¹²

4.4-1 Heat of Fusion

No accurate, simple way to estimate ΔH_f exists. The heat of fusion for many elements and compounds can be roughly approximated by

$$\frac{\Delta\hat{H}_f}{T_f} = \text{constant} = \begin{cases} 2-3 & \text{for elements} \\ 5-7 & \text{for inorganic compounds} \\ 9-11 & \text{for organic compounds} \end{cases} \quad (4.11)$$

where $\Delta\hat{H}_f$ = molar heat of fusion, cal/g mol
 T_f = melting point, K

4.4-2 Heat of Vaporization

Because the heat of vaporization is so large, it is important to estimate ΔH_v accurately. Three techniques are discussed below.

¹² See the supplementary references in Chap. 3.

Clausius–Clapeyron equation. The Clapeyron equation itself is an exact thermodynamic relationship between the slope of the vapor-pressure curve and the molar heat of vaporization and the other variables listed below:

$$\frac{dp^*}{dT} = \frac{\Delta\hat{H}_v}{T(\hat{V}_g - \hat{V}_l)} \quad (4.12)$$

where p^* = vapor pressure

T = absolute temperature

$\Delta\hat{H}_v$ = molar heat of vaporization at T

\hat{V}_i = molar volume of gas or liquid as indicated by the subscript g or l

Any consistent set of units may be used.

If experimental vapor-pressure data are available for a span of temperatures, or a correlation is available, dp^*/dT can be evaluated in the vicinity of T . Furthermore, $(\hat{V}_g - \hat{V}_l)$ can be estimated solely from \hat{V}_g if we neglect \hat{V}_l ; hence for a nonideal gas

$$\frac{dp^*}{dT} = -\frac{\Delta\hat{H}_v}{z(RT^2/p^*)} \quad (4.13)$$

Eq. (4.13) can be solved for $\Delta\hat{H}_v$.

Another variation of Eq. (4.12) is as follows. Assume that:

(a) \hat{V}_l is negligible in comparison with \hat{V}_g .

(b) The ideal gas law is applicable for the vapor:

$$\hat{V}_g = RT/p^*$$

Then

$$\frac{dp^*}{p^*} = \frac{\Delta\hat{H}_v}{RT^2} dT \quad (4.14)$$

Rearrange to

$$\frac{d \ln p^*}{d(1/T)} = 2.303 \frac{d \log_{10} p^*}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R} \quad (4.15)$$

You can plot the $\log_{10} p^*$ vs. $1/T$ and obtain the slope $-(\Delta\hat{H}_v/2.303R)$.

If we further assume that $\Delta\hat{H}_v$ is constant over the temperature range of interest, integration of Eq. (4.15) yields an indefinite integral

$$\log_{10} p^* = -\frac{\Delta\hat{H}_v}{2.303RT} + B \quad (4.16)$$

The indefinite integral, Eq. (4.16), is known as the Clausius–Clapeyron equation. Unfortunately, a plot of $\ln p^*$ versus $1/T$ over a significant range of $1/T$ does not give a straight line. Consequently, Eq. (4.16) often is modified; one result is the Antoine equation discussed in Sec. 3.3. A definite integral of Eq. (4.15) is

$$\log_{10} \frac{p_1^*}{p_2^*} = \frac{\Delta\hat{H}_v}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (4.17)$$

Either of these equations can be used graphically or analytically to obtain $\Delta\hat{H}_v$ for a short temperature interval.

EXAMPLE 4.15 Heat of Vaporization from the Clausius–Clapeyron Equation

Estimate the heat of vaporization of isobutyric acid at 200°C.

Solution

The vapor-pressure data for isobutyric acid (from Perry's *Handbook*) are

Pressure (mm Hg)	Temp. (°C)	Pressure (atm)	Temp. (°C)
100	98.0	1	154.5
200	115.8	2	179.8
400	134.5	5	217.0
760	154.5	10	250.0

Basis: 1 g mol of isobutyric acid

Since $\Delta\hat{H}_v$ remains essentially constant for short temperature intervals, the heat of vaporization can be estimated from Eq. (4.17) and the vapor-pressure data at 179.8°C and 217.0°C.

$$179.8^\circ\text{C} \approx 453.0\text{ K} \quad 217^\circ\text{C} \approx 490.2\text{ K}$$

$$\log_{10} \frac{2}{5} = \frac{\Delta\hat{H}_v}{(2.303)(8.314)} \left(\frac{1}{490.2} - \frac{1}{453.0} \right)$$

$$\Delta\hat{H}_v = 45,483 \text{ J/g mol at } 200^\circ\text{C}$$

The experimental value of $\Delta\hat{H}_v$ is not known at 200°C. At the normal boiling point (154.5°C), $\Delta\hat{H}_v = 41,300 \text{ J/g mol}$, hence the value calculated is high. It should be lower than 41,300.

Reduced form of the Clapeyron equation. This is an equation in terms of the reduced pressure and temperature which gives good results:

$$d \ln p^* = - \frac{\Delta\hat{H}_v}{zRT_c} d\left(\frac{1}{T_r}\right)$$

or

$$\frac{\Delta\hat{H}_v}{zRT_c} = - \frac{d \ln p^*}{d(1/T_r)}$$

If we compute the right-hand side, say, from the Antoine equation (see Appendix G), we get

$$\frac{\Delta\hat{H}_v}{zRT_c} = \frac{B}{T_c} \left[\frac{T_r}{T_r + (C/T_c)} \right]^2 \quad (4.18)$$

Chen's equation. An equation that yields values of $\Delta\hat{H}_v$ (in kJ/g mol) to within 2% is *Chen's equation*:

$$\Delta\hat{H}_v = \frac{T_b[0.0331(T_b/T_c) + 0.0297 \log_{10} p_c - 0.0327]}{1.07 - T_b/T_c}$$

where T_b is the normal boiling point of the liquid in K, and p_c is the critical pressure in atmospheres.

Prediction using enthalpy of vaporization at the normal boiling point. As an example, Watson¹³ found empirically that

$$\frac{\Delta\hat{H}_{v_2}}{\Delta\hat{H}_{v_1}} = \left(\frac{1 - T_{r_2}}{1 - T_{r_1}} \right)^{0.38}$$

where $\Delta\hat{H}_{v_2}$ = heat of vaporization of a pure liquid at T_2

$\Delta\hat{H}_{v_1}$ = heat of vaporization of the same liquid at T_1

Yaws¹⁴ lists various other values of the exponent for various substances.

4.4-3 Reference Substance Plots

A number of graphical techniques have been proposed to estimate the molal heat of vaporization of a liquid at any temperature by comparing the $\Delta\hat{H}_v$ for the unknown liquid with that of a known liquid such as water. Two of these methods are described below.

Duhring plot. The temperature of the wanted compound A is plotted against the temperature of the known (reference) liquid at *equal vapor pressure*. For example, if the temperature of A (isobutyric acid) and the reference substance (water) are determined at 760, 400, and 200 mm Hg pressure, then a plot of the temperatures of A vs. the temperatures of the reference substance will be approximately a straight line over a wide temperature range, and have a slope of $(\Delta\hat{H}_{v_A}/\Delta\hat{H}_{v_{H_2O}})(T_{H_2O}/T_A)^2$.

Othmer plot. The Othmer plot¹⁵ is based on the same concepts as the Duhring plot except that the *logarithms* of vapor pressures are plotted against each other at *equal temperatures*. As illustrated in Fig. 4.11, a plot of the $\log_{10} (p_A^*)$ against $\log_{10} (p_{ref}^*)$ chosen at the same temperature yields a straight line over a very wide temperature range.

To indicate how to apply the Othmer plot to estimate the heat of vaporization of compound A, we apply the Clapeyron equation to each substance and take the

¹³ K. M. Watson, *Ind. Eng. Chem.*, v. 23, p. 360 (1931); v. 35, p. 398 (1943).

¹⁴ C. L. Yaws, *Physical Properties*, McGraw-Hill, New York, 1977.

¹⁵ D. F. Othmer, *Ind. Eng. Chem.*, v. 32, p. 841 (1940). For a complete review of the technique and a comparative statistical analysis among various predictive methods, refer to D. F. Othmer and H. N. Huang, *Ind. Eng. Chem.*, v. 57, p. 40 (1965); D. F. Othmer and E. S. Yu, *Ind. Eng. Chem.*, v. 60, no. 1, p. 22 (1968); and D. F. Othmer and H. T. Chem, *Ind. Eng. Chem.*, v. 60, no. 4, p. 39 (1968).