CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)

02. EQUILIBRIUM IN PURE COMPONENT SYSTEMS

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Outline

- The Chemical Potential
- Phase Diagrams: *P*-*T* Projection
- Equilibrium Curves’ Meaning (*P*-*T* Projection)
- Slopes of Equilibrium Curves
- Clapeyron Equation
- Clausius-Clapeyron Equation
- Vapor Pressure Models
- Latent Heat of Vaporization Estimation.

Types of Equilibria and Equilibrium

- Three types of equilibria must be satisfied to have equilibrium established under all constraints
  - Thermal equilibrium

$$T^{I} = T^{II} = \cdots = T^{N}$$

  - Mechanical equilibrium

$$P^{I} = P^{II} = \cdots = P^{N}$$

  - Chemical equilibrium

$$g^{I} = g^{II} = \cdots = g^{N}$$

The Chemical Potential

- The molar Gibbs free energy of pure component is also known as *chemical potential* (symbol μ).
    - because it is the thermodynamic potential of the chemical species at constant T, and P:
    - If the chemical potential in one phase is higher than in another phase, the species will migrate into the phase with the lowest chemical potential
    - If the chemical potential is the same in two or more phases, then the species can exist with equal probability in any of these phases.
- For a pure species, “chemical potential” and “molar Gibbs free energy” are synonymous.
- For mixtures, there is a distinction as each component in the mixture has its own chemical potential (μ_i).

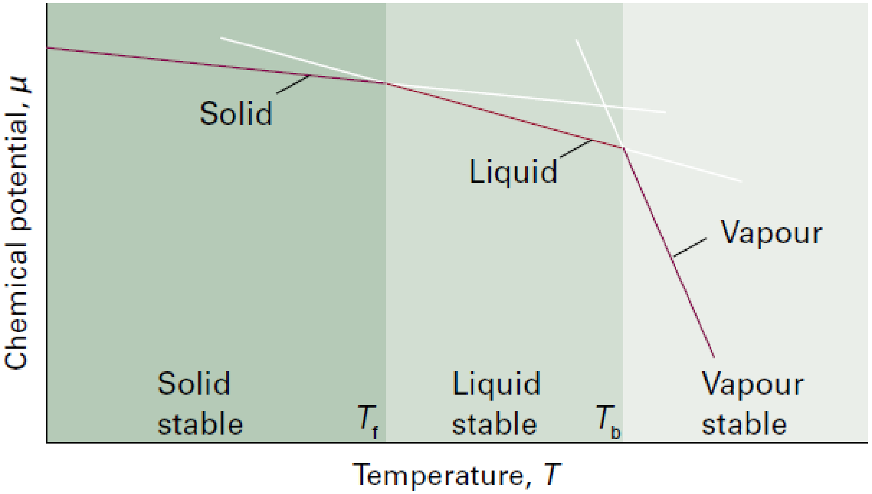
Mathematics of the Chemical Potential

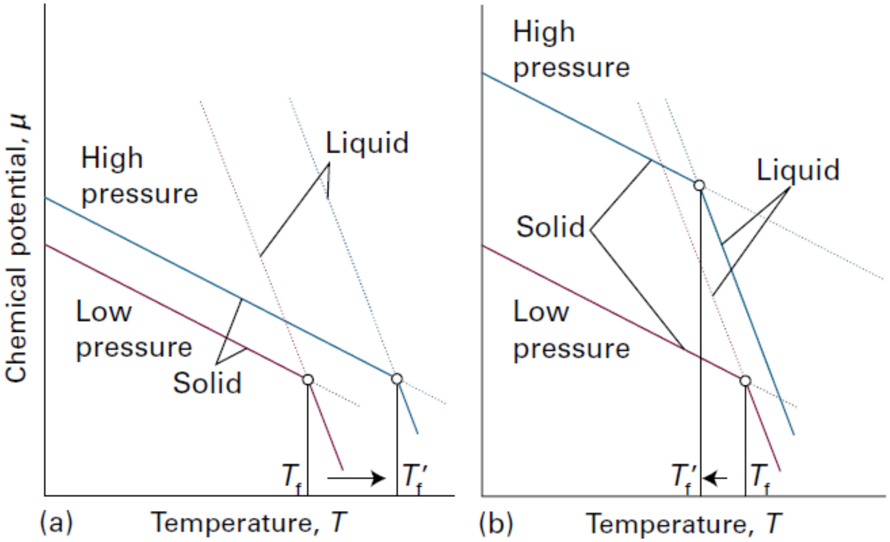
- The chemical potential for a pure substance is given as:

$$dG = d\mu = -SdT + VdP$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V$$





(a) In this case the molar volume of the solid is smaller than that of the liquid and μ(s) increases less than μ(l). As a result, the freezing temperature rises. (b) Here the molar volume is greater for the solid than the liquid (as for water), μ(s) increases more strongly than μ(l), and the freezing temperature is lowered.

Brief illustration 4B.1

Atkins, Physical Chemistry

The standard molar entropy of liquid water at 100 °C is 86.8 J K⁻¹ mol⁻¹ and that of water vapour at the same temperature is 195.98 J K⁻¹ mol⁻¹. It follows that when the temperature is raised by 1.0 K the changes in chemical potential are

$$\Delta\mu(\mathrm{l}) \approx -S_{\mathrm{m}}(\mathrm{l})\Delta T = -87\,\mathrm{J\,mol^{-1}}$$
$$\Delta\mu(\mathrm{g}) \approx -S_{\mathrm{m}}(\mathrm{g})\Delta T = -196\,\mathrm{J\,mol^{-1}}$$

At 100 °C the two phases are in equilibrium with equal chemical potentials. At 101 °C the chemical potential of both vapour and liquid are lower than at 100 °C, but the chemical potential of the vapour has decreased by a greater amount. It follows that the vapour is the stable phase at the higher temperature, so vaporization will be spontaneous.

Example 4B.1 Assessing the effect of pressure on the chemical potential

Calculate the effect on the chemical potentials of ice and water of increasing the pressure from 1.00 bar to 2.00 bar at 0 °C. The mass density of ice is $0.917\,\mathrm{g\,cm^{-3}}$ and that of liquid water is $0.999\,\mathrm{g\,cm^{-3}}$ under these conditions.

Collect your thoughts From $\mathrm{d}\mu = V_\mathrm{m}\mathrm{d}p$, you can infer that the change in chemical potential of an incompressible substance when the pressure is changed by Δp is $\Delta\mu = V_\mathrm{m}\Delta p$. Therefore, you need to know the molar volumes of the two phases of water. These values are obtained from the mass density, ρ, and the molar mass, M, by using $V_\mathrm{m} = M/\rho$. Then $\Delta\mu = M\Delta p/\rho$. To keep the units straight, you will need to express the mass densities in kilograms per cubic metre ($\mathrm{kg\,m^{-3}}$) and the molar mass in kilograms per mole ($\mathrm{kg\,mol^{-1}}$), and use $1\,\mathrm{Pa\,m^3} = 1\,\mathrm{J}$.

The solution The molar mass of water is $18.02\,\mathrm{g\,mol^{-1}}$ (i.e. $1.802\times10^{-2}\,\mathrm{kg\,mol^{-1}}$); therefore, when the pressure is increased by 1.00 bar ($1.00\times10^{5}\,\mathrm{Pa}$)

$$\Delta\mu(\text{ice}) = \frac{(1.802\times10^{-2}\,\mathrm{kg\,mol^{-1}})\times(1.00\times10^{5}\,\mathrm{Pa})}{917\,\mathrm{kg\,m^{-3}}} = +1.97\,\mathrm{J\,mol^{-1}}$$

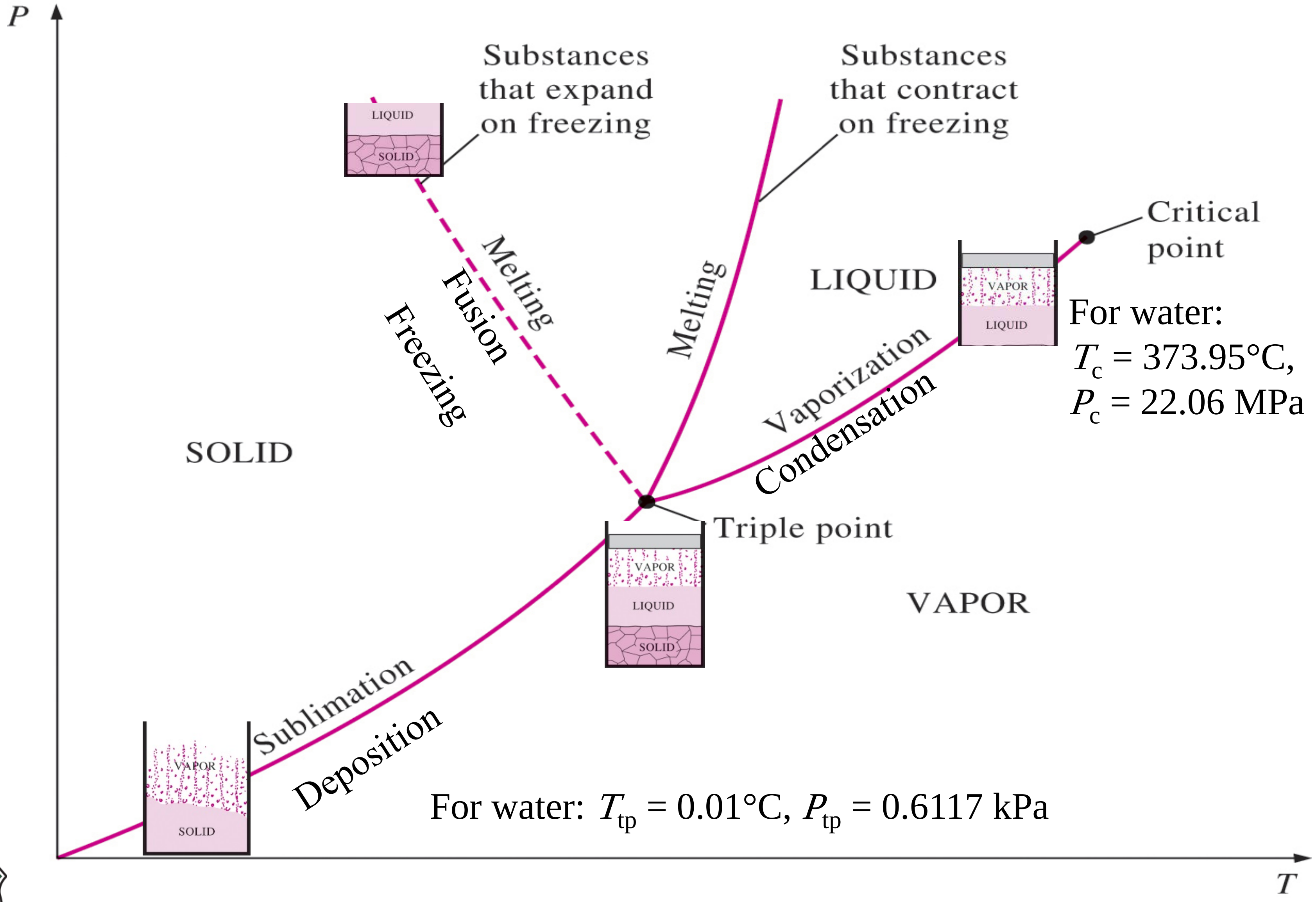
$$\Delta\mu(\text{water}) = \frac{(1.802\times10^{-2}\,\mathrm{kg\,mol^{-1}})\times(1.00\times10^{5}\,\mathrm{Pa})}{999\,\mathrm{kg\,m^{-3}}}$$

$$= +1.80\,\mathrm{J\,mol^{-1}}$$

Comment. The chemical potential of ice rises by more than that of water, so if they are initially in equilibrium at 1 bar, then there is a tendency for the ice to melt at 2 bar.

Atkins, Physical Chemistry

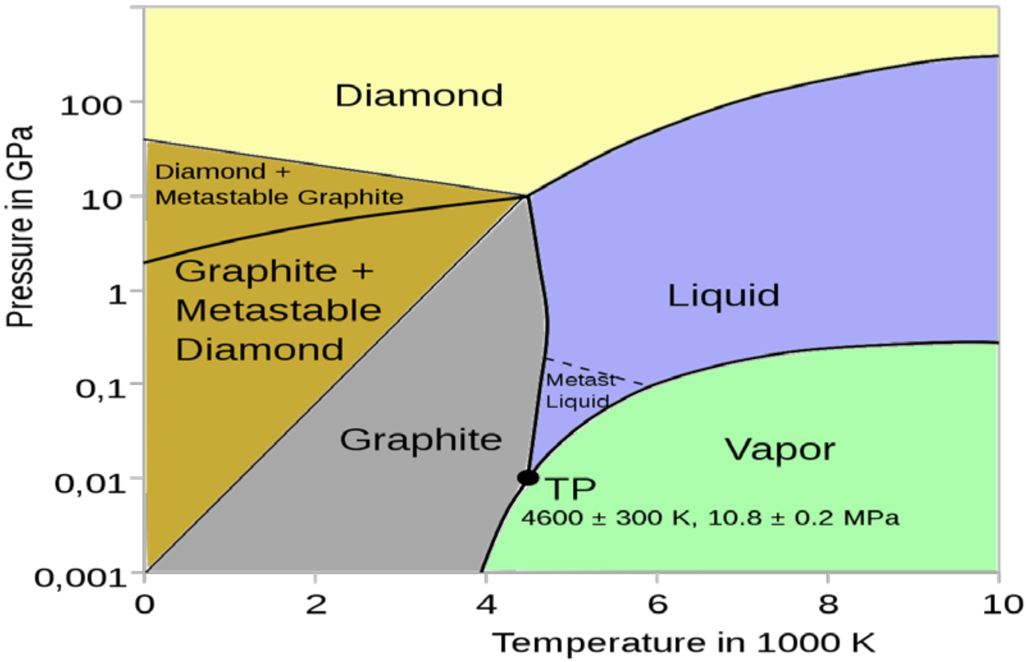
Phase Diagrams: *P*-*T* Projection

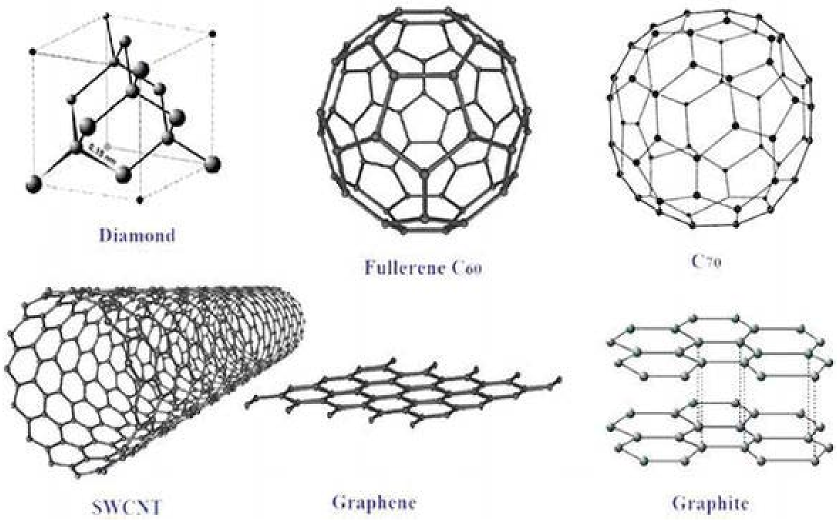


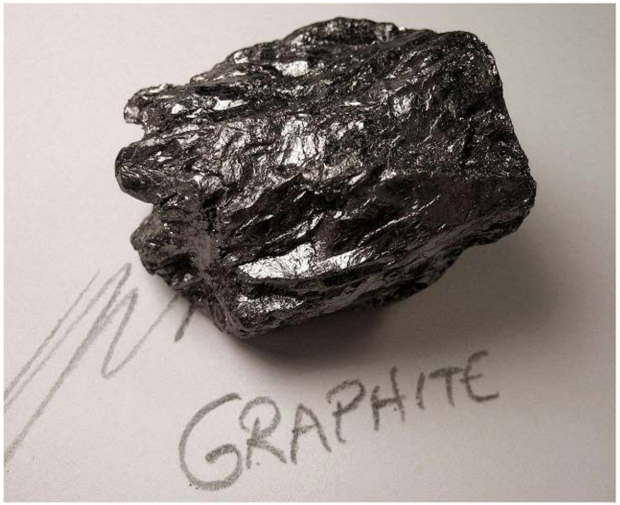
For water:
T_c = 373.95°C,
P_c = 22.06 MPa

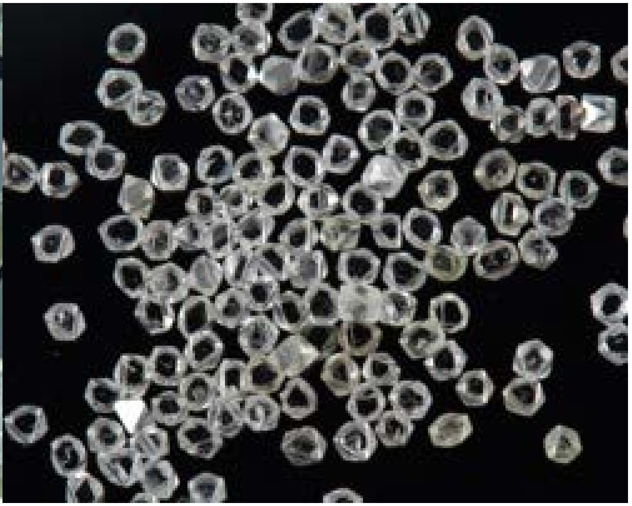
For water: T_{tp} = 0.01°C, P_{tp} = 0.6117 kPa

Carbon phase diagram









Graphite

Natural diamond

Industrial diamond

Equilibrium Curves’ Meaning (P-T Projection)

- The slope of the **vapor-liquid equilibrium** (VLE) curve gives the rate of change of the **vapor pressure** of the liquid with temperature.
- The slope of the **vapor-solid** coexistence curve is equal to the change of the vapor pressure of the solid (**sublimation pressure**) with temperature.
- The inverse of the slope of the **liquid-solid** coexistence line gives the **change of the melting temperature** of the solid with pressure.

Slopes of Equilibrium Curves

- The slopes of all coexistence curves can be found from the equality of the Gibbs free energy (chemical potential) at equilibrium.

$$G^{I}(T,P)=G^{II}(T,P) \quad \Rightarrow \quad dG^{I}=dG^{II}$$

- *G* is related to (*P*, *T*) which are equal, at equilibrium, in both phases.

$$V^{I}dP-S^{I}dT=V^{II}dP-S^{II}dT$$

$$\left(\frac{dP^{\mathrm{sat}}}{dT}\right)_{G^{I}=G^{II}}=\left(\frac{S^{I}-S^{II}}{V^{I}-V^{II}}\right)=\frac{\Delta S^{\mathrm{sat}}}{\Delta V^{\mathrm{sat}}}$$

The Clapeyron Equation

- G is related also to the enthalpy and entropy at saturation by:

$$G^{I} = H^{I} - TS^{I} = G^{II} = H^{II} - TS^{II}$$

$$S^{I} - S^{II} = \frac{H^{I} - H^{II}}{T} \quad \Rightarrow \Delta S^{\text{sat}} = \frac{\Delta H^{\text{sat}}}{T}$$

- Substitute to get the **Clapeyron equation** which relates the enthalpy and volume changes to the slope of the coexistence curve.

$$\left(\frac{dP^{\text{sat}}}{dT}\right)_{G^{I}=G^{II}} = \frac{\Delta S^{\text{sat}}}{\Delta V^{\text{sat}}} = \frac{\Delta H^{\text{sat}}}{T\,\Delta V^{\text{sat}}}$$

- This is an **exact** equation derived from thermodynamics.

Interpreting the Clapeyron Equation

- ΔH, ΔV, and ΔS are all nonzero away from the fluid critical point, and approach zero as the critical point is approached.
- **None** of the coexistence curves has a **zero slope**.
  - Due to the non-zero value of both the entropy and enthalpy changes accompanying phase transitions.
  - Due to ΔV being non-zero.
- Generally, the heat of fusion and volume change on melting are positive.
  - Leads to the positive slope of the S-L curves.
  - Water is an exception to this.

Brief illustration 4B.3

Atkins, Physical Chemistry

For water at 0 °C, the standard volume of transition of ice to liquid is $-1.6\,\mathrm{cm^3\,mol^{-1}}$, and the corresponding standard entropy of transition is $+22\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The slope of the solid–liquid phase boundary at that temperature is therefore

$$\frac{\mathrm{d}T}{\mathrm{d}p}=\frac{-1.6\times10^{-6}\,\mathrm{m^3\,mol^{-1}}}{22\,\mathrm{J\,K^{-1}\,mol^{-1}}}=-7.3\times10^{-8}\,\frac{\mathrm{K}}{\mathrm{J\,m^{-3}}}$$

$$=-7.3\times10^{-8}\,\mathrm{K\,Pa^{-1}}$$

which corresponds to $-7.3\,\mathrm{mK\,bar^{-1}}$. An increase of 100 bar therefore results in a lowering of the freezing point of water by 0.73 K.

Clausius-Clapeyron Equation

- Applies to vapor-liquid and vapor-solid equilibria.
  - At temperatures for which the saturation pressure is not very high:

$$V^V \gg V^L \Rightarrow \Delta V^{\text{sat}} \approx V^V$$

  - Assumes the vapor phase is an ideal gas:

$$\Delta V^{\text{sat}} \approx V^V = RT / P$$

  - Substitute in the Clapeyron equation

$$\frac{dP^{\text{sat}}}{dT} = \frac{P^{\text{sat}} \Delta H^{\text{sat}}}{RT^2} \Rightarrow \frac{d \ln P^{\text{sat}}}{dT} = \frac{\Delta H^{\text{sat}}}{RT^2}$$

- This equation is referred to as the **Clausius-Clapeyron** equation.

Simplifications in the Clausius-Clapeyron Equation

- The latent heat of vaporization is a function of temperature. Assume it is independent of temperature over a narrow temperature range to obtain:

$$\ln \frac{P^{\text{sat}}(T_2)}{P^{\text{sat}}(T_1)} = -\frac{\Delta H^{\text{sat}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- This equation can be used for:
  - Correlation of vapor pressure data in a narrow interval.
  - Interpolation of vapor pressure data.
  - Extrapolation of vapor pressure data (**caution!**).
- The latent heat of vaporization is not constant, it decreases with temperature and vanishes at the critical point.

EXAMPLE 6.3 (Kortesky) Estimation of the Enthalpy of Vaporization from Measured Data

Trimethyl gallium, Ga(CH3)$_3$, can be used as a feed gas to grow films of GaAs. Estimate the enthalpy of vaporization of Ga(CH3)$_3$ from the data of saturation pressure vs. temperature given in Table E6.3.5.

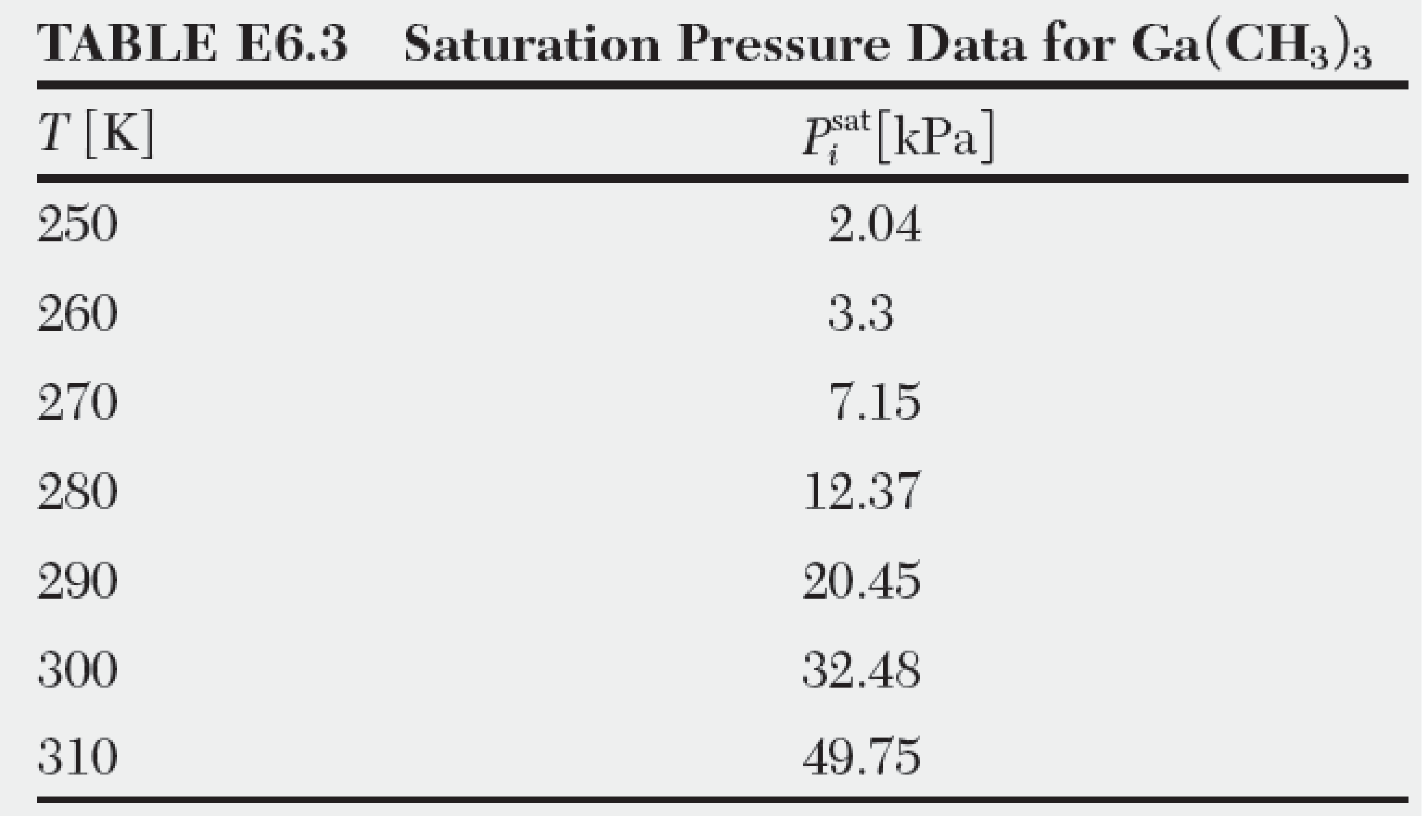


TABLE E6.3 Saturation Pressure Data for $Ga(CH_3)_3$

T [K]	P_i^{sat} [kPa]
250	2.04
260	3.3
270	7.15
280	12.37
290	20.45
300	32.48
310	49.75

SOLUTION Examination of Equation (6.11) suggests that if we plot ln P_i^{sat} vs. T^{-1}, the slope will give $-(\Delta h_{\text{vap, Ga(CH}_3)_3}/R)$. The data in Table E6.3 are plotted in such a manner in Figure E6.3. A least-squares linear regression is also shown in Figure E6.3. The high correlation coefficient implies $\Delta h_{\text{vap, Ga(CH}_3)_3}$ is constant in this temperature range.

Taking the slope of the line, we get:

$$-\frac{\Delta h_{\text{vap,Ga(CH}_3)_3}}{R} = -4222.1[\text{K}]$$

Solving for the enthalpy of vaporization gives:

$$\Delta h_{\text{vap, Ga(CH}_3)_3} = 35.1\ [\text{kJ/mol}]$$

For comparison, a value measured by static bomb combustion calorimetry has been reported as 33.1 kJ/mol, a difference of 6.0%.

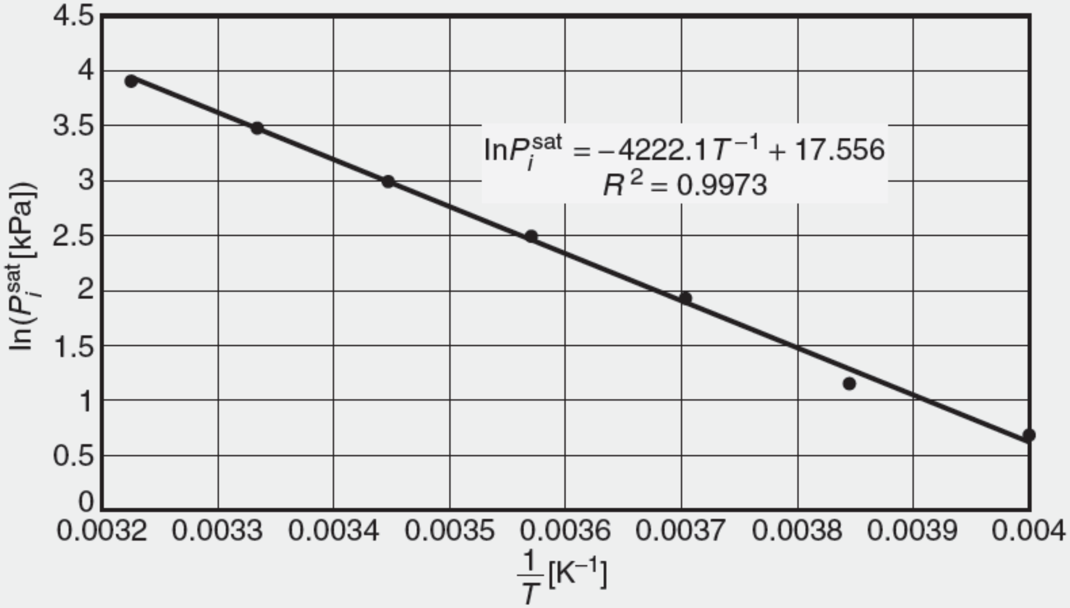


Figure E6.3 Plot of data in Table E6.2 and a least-squares linear fit of the data.

[5] (Via NIST) J. F. Sackman, and L. H. Long, *Trans. Faraday Soc.*, **54**, 1797 (1958).

Vapor Pressure Models

- Clausius-Clapeyron

$$\ln P^{\text{sat}} = A - \frac{B}{T}$$

- Antoine

$$\ln P^{\text{sat}} = A' - \frac{B'}{T + C'}$$

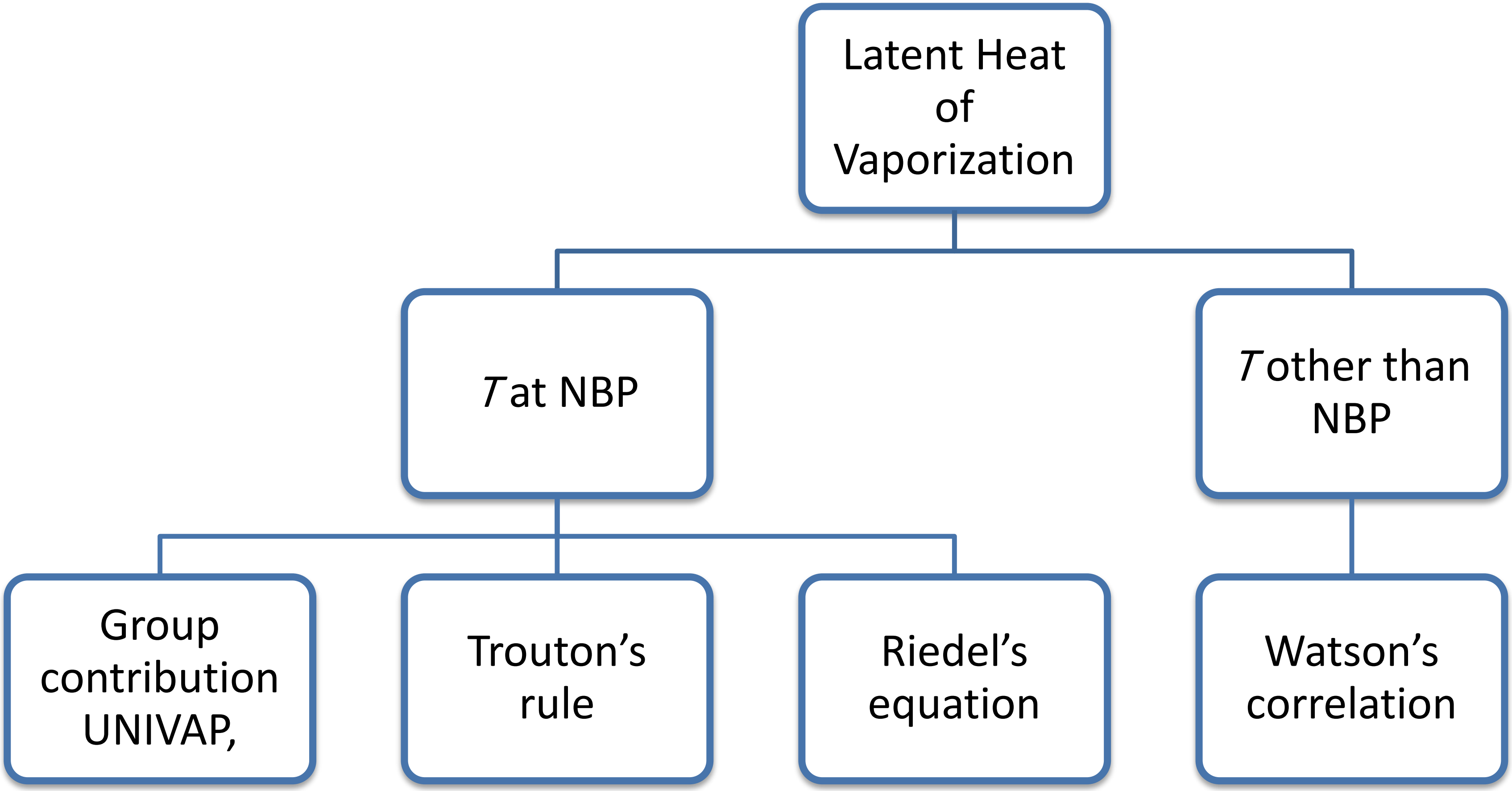
- Riedel

$$\ln P^{\text{sat}} = A'' + \frac{B''}{T} + C'' \ln T + DT^{6}$$

- Harlecher-Braun

$$\ln P^{\text{sat}} = A''' + \frac{B'''}{T} + C''' \ln T + \frac{D' P^{vap}}{T^{2}}$$

Estimation of Latent Heat of Vaporization



Latent Heat of Vaporization

T at NBP

T other than NBP

Group contribution UNIVAP,

Trouton’s rule

Riedel’s equation

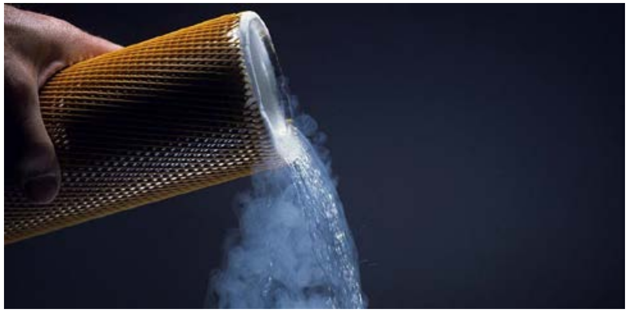
Watson’s correlation

Estimating Δh^{vap} at Normal Boiling Point (NBP)

- Trouton's rule gives a rough estimate:

$$\frac{\Delta h_{NBP}^{\text{vap}}}{RT_{NBP}} \approx 10$$

- Riedel's equation gives estimates to within 5% of the experimental values:



$$\frac{\Delta h_{NBP}^{\text{vap}}}{RT_{NBP}} = \frac{1.092\left[\ln\left(P_c\right) - 1.013\right]}{0.930 - T_{r_{NBP}}}$$

Estimation at $T \neq T_{NBP}$

- The Watson's correlation may be used to estimate the latent heat of vaporization of a liquid from knowledge of a single point.

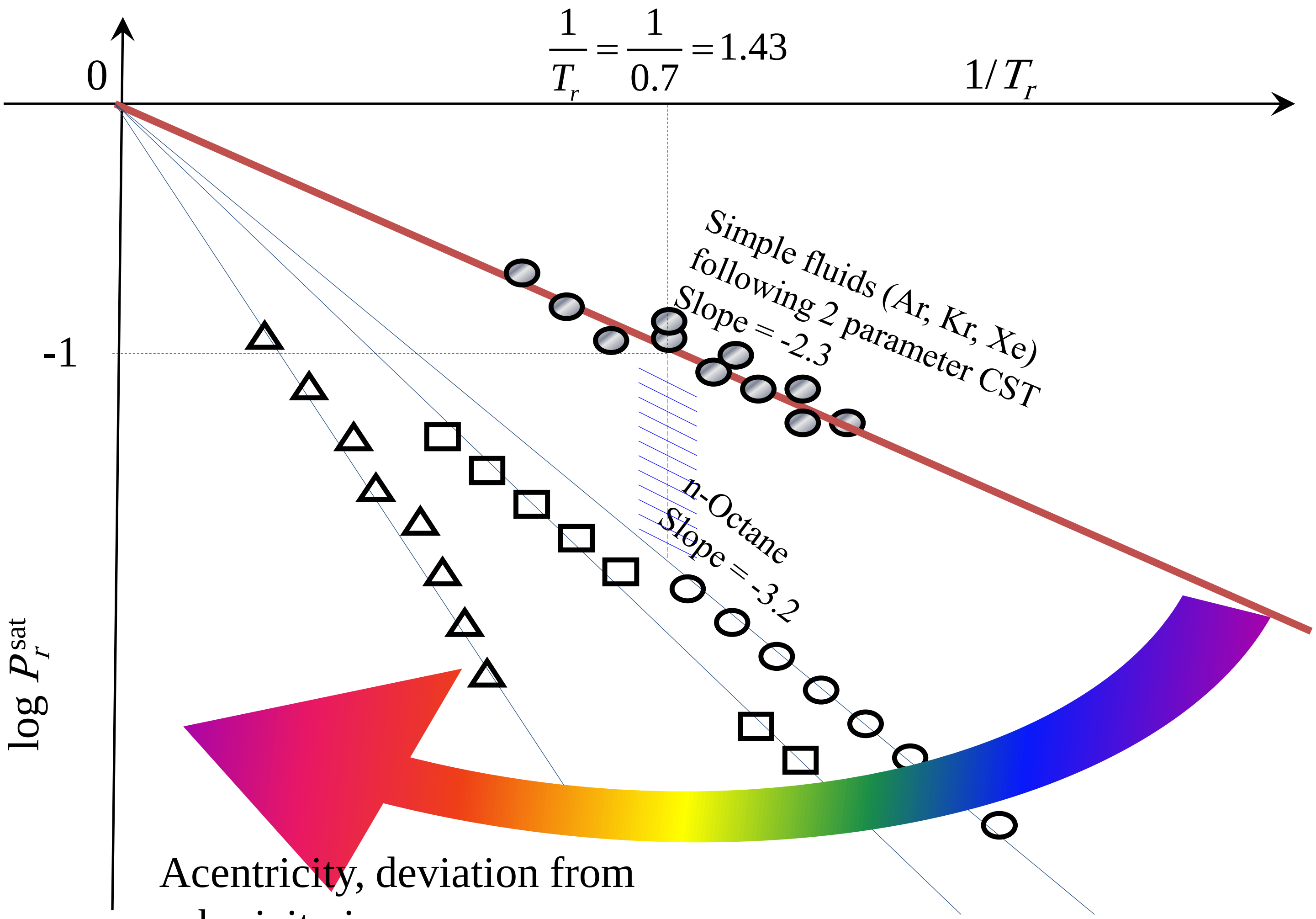
$$\frac{\Delta h_2}{\Delta h_1} = \left(\frac{1 - T_{r_2}}{1 - T_{r_1}} \right)^{0.38}$$

Example:

a) Estimate the latent heat of vaporization water at its NBP using Trouton's rule, and Riedel's equation.
b) Estimate the latent heat of vaporization of water at 300°C.
c) Compare your results with those reported in the steam tables.

Ex. Water

Pitzer’s Acentric Factor



Acentricity, deviation from sphericity increases

Pitzer's Acentric Factor: Definition

- The two parameter Corresponding States Theory (CST) fails to correlate data other than these for simple fluids.
- Development of the acentric factor (to deviate from spherical shape of simple fluids)

$$\omega = -1.0 - \log(P_r^{\text{sat}})_{T_r = 0.7}$$

- The Acentric factor (ω)
  - For **simple fluids** (Ar, Kr, Xe) is ~ zero.
  - **Positive** (greater than zero) for all other fluids.
    - Exception: **Quantum fluids** (H_2, He, Ne) which do not conform to CST unless some effective critical parameters are introduced.

Formula	Name	$MW_{[\mathrm{g/mol}]}$	T_c [K]	P_c [bar]	ω	A	B	C	$T_{\min}$	T_{mix}
CH_2O	Formaldehyde	30.026	408	65.86	0.253	9.8573	2204.13	−30.15	185	271
CH_4	Methane	16.042	190.6	46.00	0.008	8.6041	897.84	−7.16	93	120
CH_4O	Methanol	32.042	512.6	80.96	0.559	11.9673	3626.55	−34.29	257	364
C_2H_4	Acetylene	26.038	308.3	61.40	0.184	9.7279	1637.14	−19.77	194	202
C_2H_3N	Acetonitrile	41.052	548	48.33	0.321	9.6672	2945.47	−49.15	260	390
C_2H_4	Ethylene	28.053	282.4	50.36	0.085	8.9166	1347.01	−18.15	120	182
C_2H_4O	Acetaldehyde	44.053	461	55.73	0.303	9.6279	2465.15	−37.15	210	320
C_2H_4O	Ethylene oxide	44.053	469	71.94	0.200	10.1198	2567.61	−29.01	300	310
$C_2H_4O_2$	Acetic acid	60.052	594.4	57.86	0.454	10.1878	3405.57	−56.34	290	430
C_2H_6	Ethane	30.069	305.4	48.74	0.099	9.0435	1511.42	−17.16	130	199
C_2H_6O	Ethanol	46.068	516.2	63.83	0.635	12.2917	3803.98	−41.68	270	369
C_3H_6	Propylene	42.080	365.0	46.20	0.148	9.0825	1807.53	−26.15	160	240
C_3H_6O	Acetone	58.079	508.1	47.01	0.309	10.0311	2940.46	−35.93	241	350
C_3H_8	Propane	44.096	370.0	42.44	0.152	9.1058	1872.46	−25.16	164	249
C_3H_8O	1-Propanol	60.095	536.7	51.68	0.624	10.9237	3166.38	−80.15	285	400
Ar	Argon	39.948	150.8	48.74	−0.004	8.6128	700.51	−5.84	81	94
BCl_3	Boron trichloride	117.169	451.95	38.71	0.148	9.0985	2242.71	−38.99	182	286
B_2H_6	Diborane	27.670	289.80	40.50	0.138	8.7074	1377.84	−22.18	118	181
Br_2	Bromine	159.808	584	103.35	0.132	9.2239	2582.32	−51.56	259	354
CCl_3F	Trichlorofluoromethane	137.367	471.2	44.08	0.188	9.2314	2401.61	−36.3	240	300
CF_4	Carbon tetrafluoride	88.004	227.6	37.39	0.191	9.4341	1244.55	−13.06	93	148
C_2F_6	Hexafluoroethane	138.012	292.8	30.42	0.255	9.1646	1559.11	−24.51	180	195
$CHCl_3$	Chloroform	119.377	536.4	54.72	0.216	9.3530	2696.79	−46.16	260	370
CO	Carbon monoxide	28.010	132.9	34.96	0.049	7.7484	530.22	−13.15	63	108
CO_2	Carbon dioxide	44.010	304.2	73.76	0.225	15.9696	3103.39	−0.16	154	204
CS_2	Carbon disulfide	76.143	552	79.03	0.115	9.3642	2690.85	−31.62	228	342
Cl_2	Chlorine	70.905	417	77.01	0.073	9.3408	1978.32	−27.01	172	264
F_2	Fluorine	37.997	144.3	52.18	0.048	9.0498	714.10	−6.00	59	91
H_2	Hydrogen	2.016	33.2	12.97	−0.22	7.0131	164.90	3.19	14	25
HBr	Hydrogen bromide	80.912	363.2	85.52	0.063	7.8485	1242.53	−47.86	184	221
HCN	Hydrogen cyanide	27.025	456.8	53.90	0.407	9.8936	2585.80	−37.15	234	330
HCl	Hydrogen chloride	36.461	324.6	83.09	0.12	9.8838	1714.25	−14.45	137	200
H_2O	Water	18.015	647.3	220.48	0.344	11.6834	3816.44	−46.13	284	441
H_2S	Hydrogen sulfide	34.082	373.2	89.37	0.100	9.4838	1768.69	−26.06	190	230

References

- Expanded from §7.2: Matsoukas, Themis. Fundamentals of chemical engineering thermodynamics. Pearson Education, 2013.
- Sandler, Stanley I. *Chemical, biochemical, and engineering thermodynamics*. John Wiley & Sons, 2017.
- Koretsky, Milo D. Engineering and chemical thermodynamics. John Wiley & Sons, 2012.