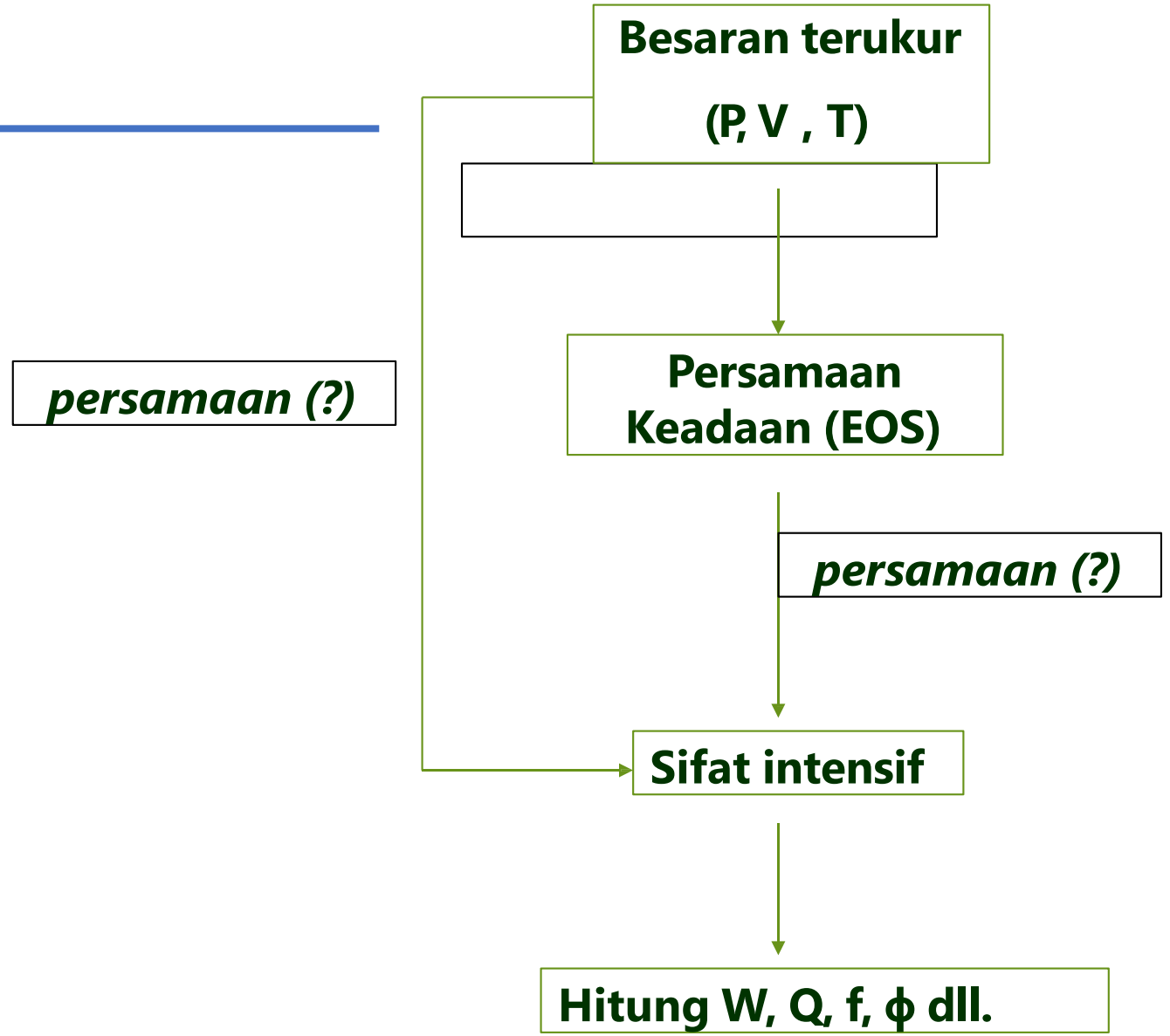
Thermodynamic Properties of Fluids

Termodinamika Teknik Kimia I

Pendahuluan

- **Kaidah Fase Gibbs**: jika sejumlah sifat intensif telah ditetapkan, maka sifat-sifat intensif yang lain akan tertentu pula.
- Nilai numerik suatu sifat termodinamika penting untuk menghitung a.l. : **kerja dan panas dalam suatu proses, kesetimbangan fase/ reaksi kimia.**
- ***Perlu adanya persamaan hubungan antar sifat intensif, juga hubungan sifat intensif dengan persamaan keadaan (EOS) atau besaran-besaran yang mudah terukur (P, V atau T)***


Besaran terukur
(P, V , T)
Persamaan
Keadaan (EOS)
persamaan (?)
persamaan (?)
Sifat intensif
Hitung W, Q, f, ϕ dll.

Hubungan antar Sifat untuk Fase-fase Homogen

Hukum I untuk sistem tertutup:

$$d(nU) = dQ + dW$$

↓ khusus proses reversibel

$$d(nU) = dQ_{rev} + dW_{rev}$$

$dW_{rev} = -Pd(nV)$ | $dQ_{rev} = Td(nS)$ — Hukum II

$$d(nU) = Td(nS) - Pd(nV)$$

- Persamaan tersebut hanya mengandung sifat-sifat sistem.
- Dapat diterapkan pada sistem tertutup dengan massa konstan, baik pada proses reversible atau irreversible.
- Perubahan sifat (properties change) di antara keadaan-keadaan yang setimbang.
- Sistem bisa berupa fase homogen atau heterogen, inert atau terlibat reaksi kimia.

Persamaan *) mengandung sifat-sifat termodinamika yg utama, yaitu:

$$d(nU) = Td(nS) - Pd(nV) \quad *)$$

$$P, V, T, U, and\ S$$

Entalpi:

$$H \equiv U + PV$$

Energi (bebas) Helmholtz:

$$A \equiv U - TS$$

Energi (bebas) Gibbs:

$$G \equiv H - TS$$

Untuk satu mol fluida homogen dengan komposisi konstan:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -PdV - SdT$$

$$dG = VdP - SdT$$

PD eksak

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

Maxwell's equations

Perubahan Entalpi *f (P,T)*

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

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

$$dH = C_P dT + \left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right] dP$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

Perubahan Entropi *f (P,T)*

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \qquad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

Perubahan Energi Dalam *f (P,T)*

$$H \equiv U + PV$$

Pers. 6.19 →

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V$$

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$$

Perubahan Entalpi & Entropi Gas Ideal

$$PV^{ig} = RT$$

$$\left(\frac{\partial V^{ig}}{\partial T}\right)_P = \frac{R}{P}$$

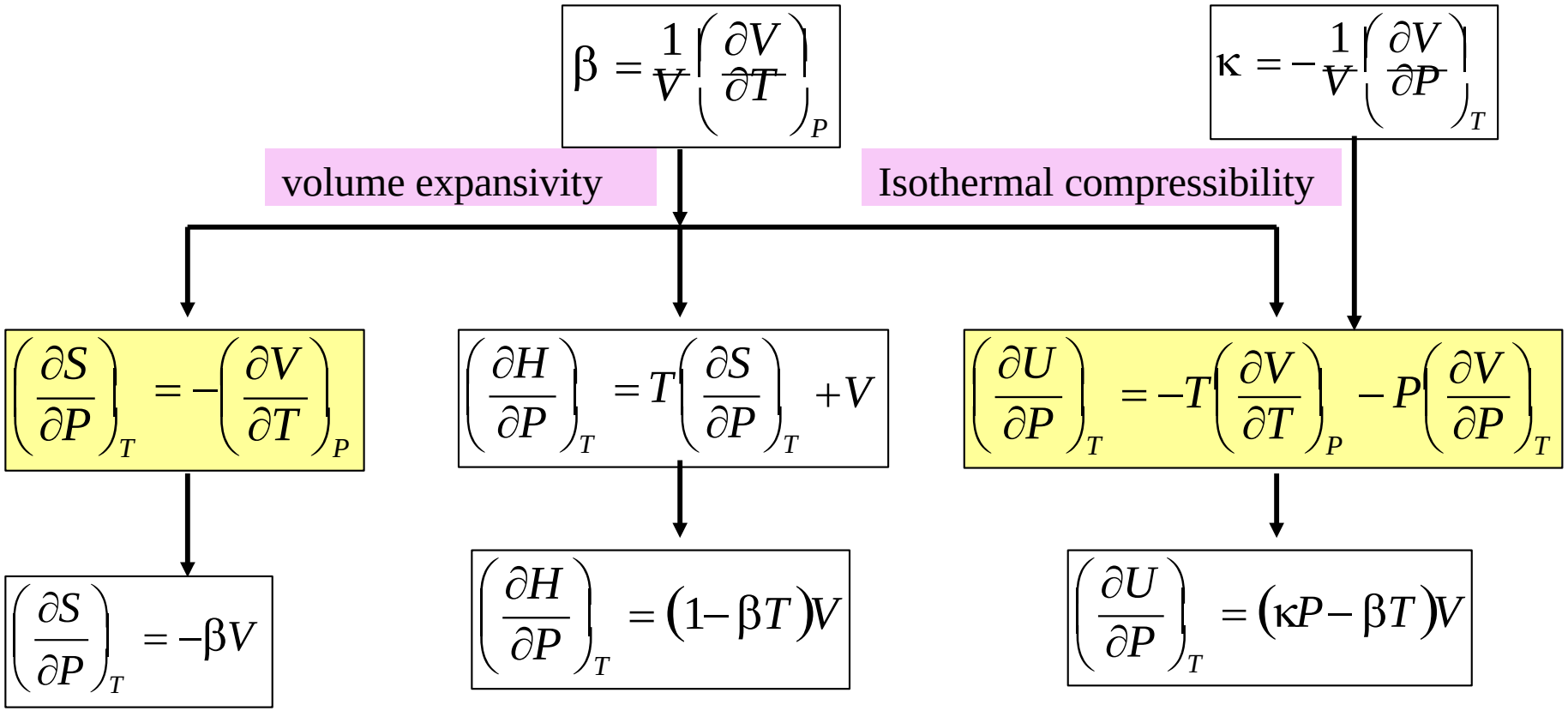
$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

$$dH^{ig} = C_P{}^{ig} dT$$

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$dS^{ig} = C_P^{ig} \frac{dT}{T} - R\frac{dP}{P}$$

Bentuk Alternatif untuk Cairan



Bentuk Alternatif untuk Cairan (lanjutan)

$$\left(\frac{\partial V}{\partial T}\right)_P = \beta V$$

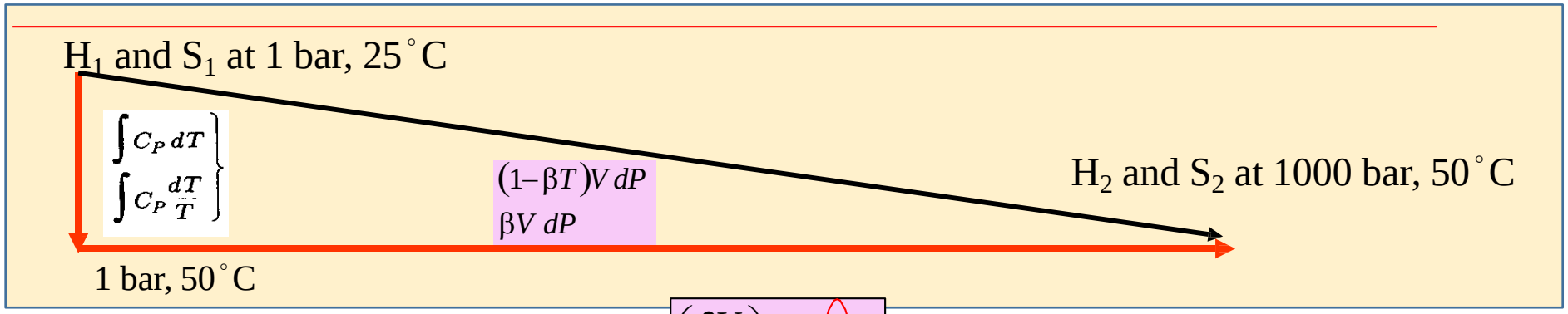
$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

$$dH = C_P dT + (1 - \beta T) V dP$$

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$dS = C_P \frac{dT}{T} - \beta V dP$$

Determine the enthalpy and entropy changes of liquid water for a change of state from 1 bar and 25 °C to 1000 bar and 50 °C. The data for water are given.



$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \beta V$$

volume expansivity

$$dH = C_P dT + (1-\beta T) V dP$$

$$\Delta H = \langle C_P \rangle (T_2 - T_1) + (1 - \langle \beta \rangle T_2) \langle V \rangle (P_2 - P_1)$$

$$\Delta H = 75.310(323.15 - 298.15) + \frac{(1-(513\times10^{-6})(323.15))(18.204)(1000-1)}{10} = 3400\, J/mol$$

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\Delta S = \langle C_P \rangle \ln \frac{T_2}{T_1} - \langle \beta \rangle \langle V \rangle (P_2 - P_1)$$

$$\Delta S = 75.310 \ln \frac{323.15}{298.15} - \frac{(513\times10^{-6})(18.204)(1000-1)}{10} = 5.13\, J/mol$$

Energi Dalam & Entropi f (V,T)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$dU = C_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right] dV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

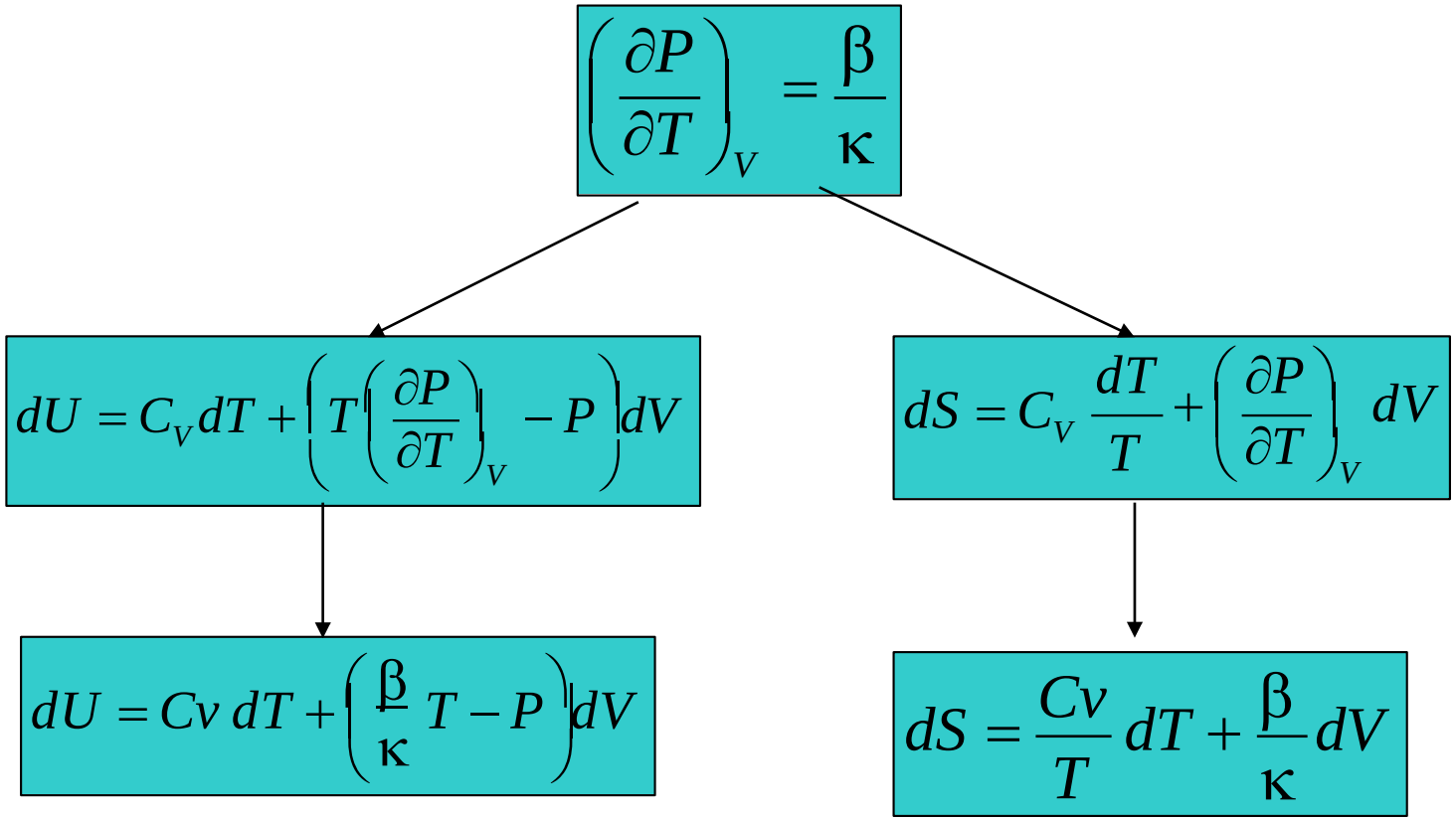
$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$dS = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV$$

Bentuk alternatif



Gibbs energy G = G (P,T)

$$dG = VdP - SdT$$

Thermodynamic property of great potential utility

$$d\left(\frac{G}{RT}\right) \equiv \frac{1}{RT}dG - \frac{G}{RT^2}dT$$

$G \equiv H - TS$ $\quad$ $dG = VdP - SdT$

$$d\left(\frac{G}{RT}\right) \equiv \frac{V}{RT}dP - \frac{H}{RT^2}dT$$

$$d\left(\frac{G}{RT}\right) = \left(\frac{\partial(G/RT)}{\partial P}\right)_T dP + \left(\frac{\partial(G/RT)}{\partial T}\right)_P dT$$

$$\frac{V}{RT} = \left(\frac{\partial(G/RT)}{\partial P}\right)_T$$

$$\frac{H}{RT} = -T\left(\frac{\partial(G/RT)}{\partial T}\right)_P$$

$G/RT = g$
(P,T)

The Gibbs energy serves as a generating function for the other thermodynamic properties.

Residual properties

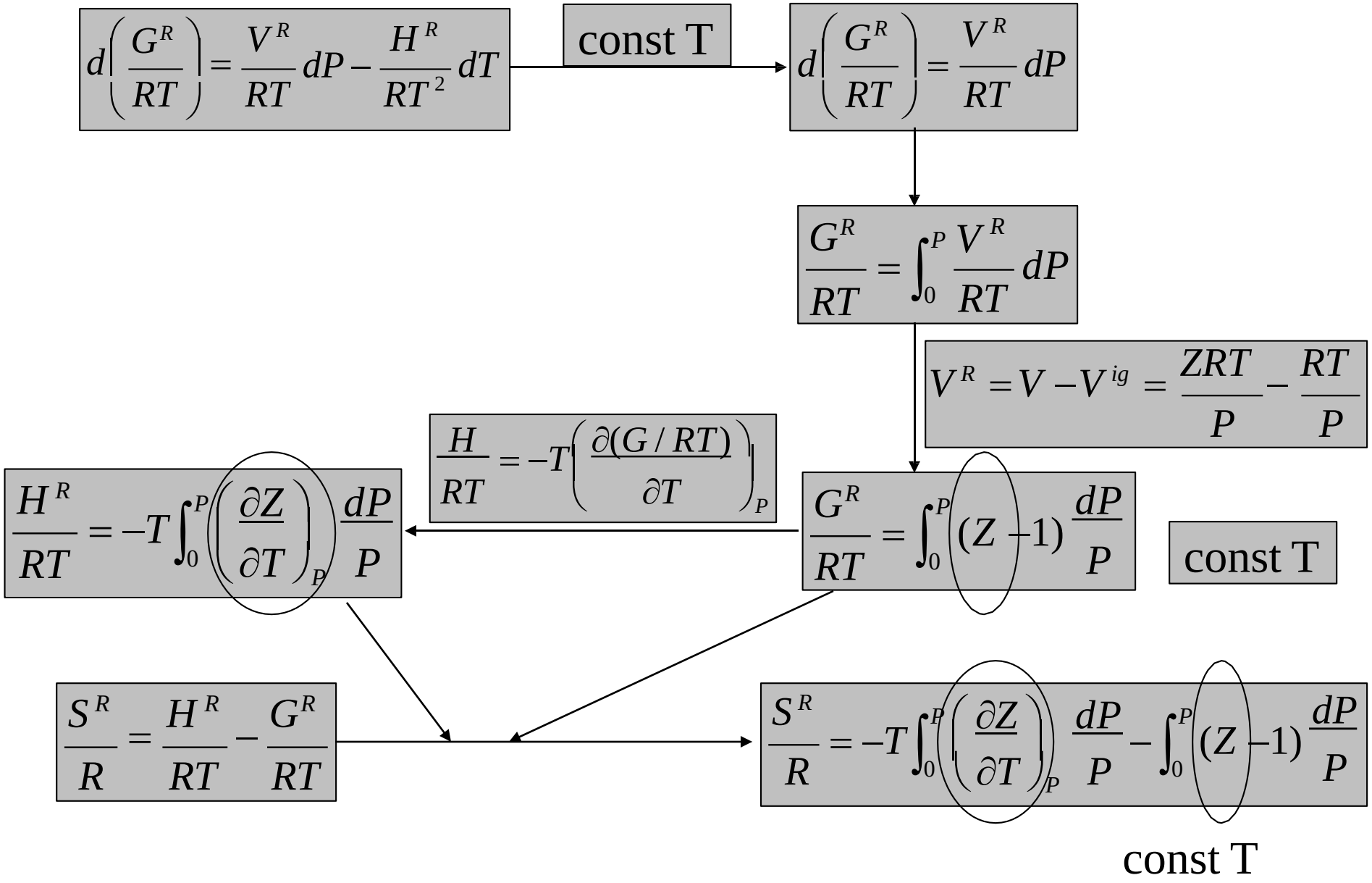
- The definition for the generic residual property:

$$M^R \equiv M - M^{ig}$$

- M and M^{ig} are the actual and ideal-gas properties,
- respectively.
- M is the molar value of any extensive thermodynamic properties e.g., V, U, H, S, or G.

- The residual Gibbs energy serves as a generating function for the other residua properties:

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP - \frac{H^R}{RT^2}dT$$



Z = PV/RT: experimental measurement .Given PVT data or an appropriate equation of state, we can evaluate H^R and S^R and hence all other residual properties.

$$H = H^{ig} + H^{R} = \left\{H_0^{ig} + \int_{T_0}^{T} C_P^{ig}\, dT\right\} + \left\{-RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}\right\}$$

$$= \left\{H_0^{ig} + R \times ICPH(T_0, T; A, B, C, D)\right\} + \left\{-RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}\right\}$$

$$= \left\{H_0^{ig} + \left\langle C_P^{ig} \right\rangle_H (T - T_0)\right\} + \left\{-RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}\right\}$$

$$= \left\{H_0^{ig} + R \times MCPH(T_0, T; A, B, C, D)(T - T_0)\right\} + \left\{-RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}\right\}$$

$$S = S^{ig} + S^{R} = \left\{S_0^{ig} + \int_{T_0}^{T} C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0}\right\} + R\left\{-T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z - 1) \frac{dP}{P}\right\}$$

$$= \left\{S_0^{ig} + R \times ICPS(T_0, T; A, B, C, D) - R \ln \frac{P}{P_0}\right\} + R\left\{-T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z - 1) \frac{dP}{P}\right\}$$

$$= \left\{S_0^{ig} + \left\langle C_P^{ig} \right\rangle_S \ln \frac{T}{T_0} - R \ln \frac{P}{P_0}\right\} + R\left\{-T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z - 1) \frac{dP}{P}\right\}$$

$$= \left\{S_0^{ig} + R \times MCPS(T_0, T; A, B, C, D) \ln \frac{T}{T_0} - R \ln \frac{P}{P_0}\right\} + R\left\{-T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z - 1) \frac{dP}{P}\right\}$$

Calculate the enthalpy and entropy of saturated isobutane vapor at 360 K from the following information: (1) compressibility-factor for isobutane vapor; (2) the vapor pressure of isobutane at 360 K is 15.41 bar; (3) at 300K and 1 bar,
(4) the ideal-gas heat capacity of isobutane vapor:

$$H_0^{ig} = 18115\ J/mol \quad S_0^{ig} = 295.976\ J/mol\cdot K$$

$$C_P^{ig}/R = 1.7765 + 33.037\times10^{-3}T$$

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad \frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P}$$

Graphical integration requires plots of $\left(\frac{\partial Z}{\partial T}\right)_P / P$ and (Z-1)/P vs. P.

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} = -(360)(26.37\times10^{-4}) = -0.9493 \longrightarrow H^R = -2841.3\,J/mol$$

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} = -0.9493 - (-0.02596) = -0.6897 \longrightarrow S^R = -5.734\,J/mol\cdot K$$

$$H = \left\{H_0^{ig} + R\times ICPH\,(300,360;1.7765,33.037E-3,0.0,0.0)\right\} + H^R = 21598.5\ \frac{J}{mol}$$

$$S = \left\{S_0^{ig} + R\times ICPS\,(300,360;1.7765,33.037E-3,0.0,0.0)\right\} - R\ln\frac{15.41}{1} + H^R = 286.676\ \frac{J}{mol\cdot K}$$

Residual properties by equations of state

- If Z = f (P,T):

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P}$$

- The calculation of residual properties for gases and vapors through use of the virial equations and cubic equation of state.

Use of the virial equation of state

two-term virial equation

$$\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P} \qquad Z-1 = \frac{BP}{RT} \qquad \frac{G^R}{RT} = \frac{BP}{RT}$$

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad Z-1 = \frac{BP}{RT}$$

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial}{\partial T}\left(1+\frac{BP}{RT}\right)\right)_P \frac{dP}{P}$$

$$\frac{H^R}{RT} = -T\int_0^P \left(\left(\frac{P}{R}\right)\left(\frac{1}{T}\frac{dB}{dT} - \frac{B}{T^2}\right)\right)_P \frac{dP}{P}$$

$$\frac{H^R}{RT} = \frac{P}{R}\left(\frac{B}{T} - \frac{dB}{dT}\right)$$

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT} \qquad \frac{S^R}{RT} = -\frac{P}{R}\frac{dB}{dT}$$

Three-term virial equation

$$Z - 1 = B\rho + C\rho^2 \qquad P = Z\rho RT$$

$$\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P} \longrightarrow \frac{G^R}{RT} = 2B\rho + \frac{3}{2}C\rho^2 - \ln Z$$

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \longrightarrow \frac{H^R}{RT} = T\left[\left(\frac{B}{T} - \frac{dB}{dT}\right)\rho + \left(\frac{C}{T} - \frac{1}{2}\frac{dC}{dT}\right)\rho^2\right]$$

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT}$$

Application up to moderate pressure

USE OF THE CUBIC EQUATION OF STATE

- The generic cubic equation of state:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)}$$

$$q \equiv \frac{a(T)}{bRT}$$

$$Z = \frac{1}{1-\rho b} - q\frac{\rho b}{(1+\varepsilon\rho b)(1+\sigma\rho b)}$$

$$\beta \equiv \frac{bP}{RT}$$

$$\int_0^{\rho} (Z-1)\frac{d\rho}{\rho} = -\ln(1-\rho b) - qI$$

$$\int_0^{\rho} \left(\frac{\partial Z}{\partial T}\right)_{\rho} \frac{d\rho}{\rho} = -\frac{dq}{dT} I$$

$$I \equiv \int_0^{\rho} \frac{d(\rho b)}{(1+\varepsilon\rho b)(1+\sigma\rho b)} \quad const\ T$$

$$\frac{H^R}{RT} = Z - 1 + \left[\frac{d\ln\alpha(T_r)}{d\ln T_r} - 1\right] qI$$

$$\frac{S^R}{R} = \ln(Z-\beta) + \left[\frac{d\ln\alpha(T_r)}{d\ln T_r}\right] qI$$

Find values for the residual enthalpy H^R and the residual entropy S^R for n-butane gas at 500 K and 50 bar as given by Redlich/Kwong equation.

$$T_r = \frac{500}{425.1} = 1.176 \qquad P_r = \frac{50}{37.96} = 1.317 \qquad \beta = \Omega \frac{P_r}{T_r} = 0.09703 \qquad q = \frac{\Psi \alpha(T_r)}{\Omega T_r} = 3.8689$$

$$Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \varepsilon\beta)(Z + \sigma\beta)} \qquad \varepsilon = 0 \quad \sigma = 1 \quad \rightarrow \quad Z = 0.685$$

$$I \equiv \int_0^{\rho} \frac{d(\rho b)}{(1 + \varepsilon\rho b)(1 + \sigma\rho b)} \quad const\ T \quad \rightarrow \quad I = \frac{1}{\sigma - \varepsilon} \ln\left(\frac{Z + \sigma\beta}{Z + \varepsilon\beta}\right) = 0.13247$$

$$\frac{H^R}{RT} = Z - 1 + \left[\frac{d \ln \alpha(T_r)}{d \ln T_r} - 1\right] qI \quad \rightarrow \quad H^R = -4505 \frac{J}{mol}$$

$$\frac{S^R}{R} = \ln(Z - \beta) + \left[\frac{d \ln \alpha(T_r)}{d \ln T_r}\right] qI \quad \rightarrow \quad S^R = -6.546 \frac{J}{mol \cdot K}$$

Two-phase systems

- Whenever a phase transition at constant temperature and pressure occurs,
  - The molar or specific volume, internal energy, enthalpy, and entropy changes abruptly. The exception is the molar or specific Gibbs energy, which for a pure species does not change during a phase transition.
  - For two phases α and β of a pure species coexisting at equilibrium:

$$G^{\alpha} = G^{\beta}$$

where G^{α} and G^{β} are the molar or specific Gibbs energies of the individual phases

$$G^{\alpha} = G^{\beta} \rightarrow dG^{\alpha} = dG^{\beta}$$

$$dG = VdP - SdT$$

$$V^{\alpha} dP^{sat} - S^{\alpha} dT = V^{\beta} dP^{sat} - S^{\beta} dT \rightarrow \frac{dP^{sat}}{dT} = \frac{S^{\alpha} - S^{\beta}}{V^{\alpha} - V^{\beta}} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

$$dH = TdS + VdP \rightarrow \Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta}$$

The latent heat of phase transition

The Clapeyron equation $\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$

$$\Delta V^{\alpha\beta} = V^{v} = \frac{RT}{P^{sat}}$$

Ideal gas, and $V^{l} << V^{g}$

$$\Delta H^{lv} = -R \frac{d \ln P^{sat}}{d(1/T)}$$

The Clausius/Clapeyron equation

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$$

The Clapeyron equation: a vital connection between the properties of different phases.

$$\longrightarrow \quad P = f(T)$$

$$\Delta H^{lv} = -R\frac{d\ln P^{sat}}{d(1/T)}$$

The Clausius/Clapeyron equation; ln P vs 1/T → linier

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

For the entire temperature range from the triple point to the critical point

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

The Antoine equation, for a specific temperature range

$$\ln P_r^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^{3} + D\tau^{6}}{1-\tau}$$

$$\tau = 1 - T_r$$

The Wagner equation, over a wide temperature range.

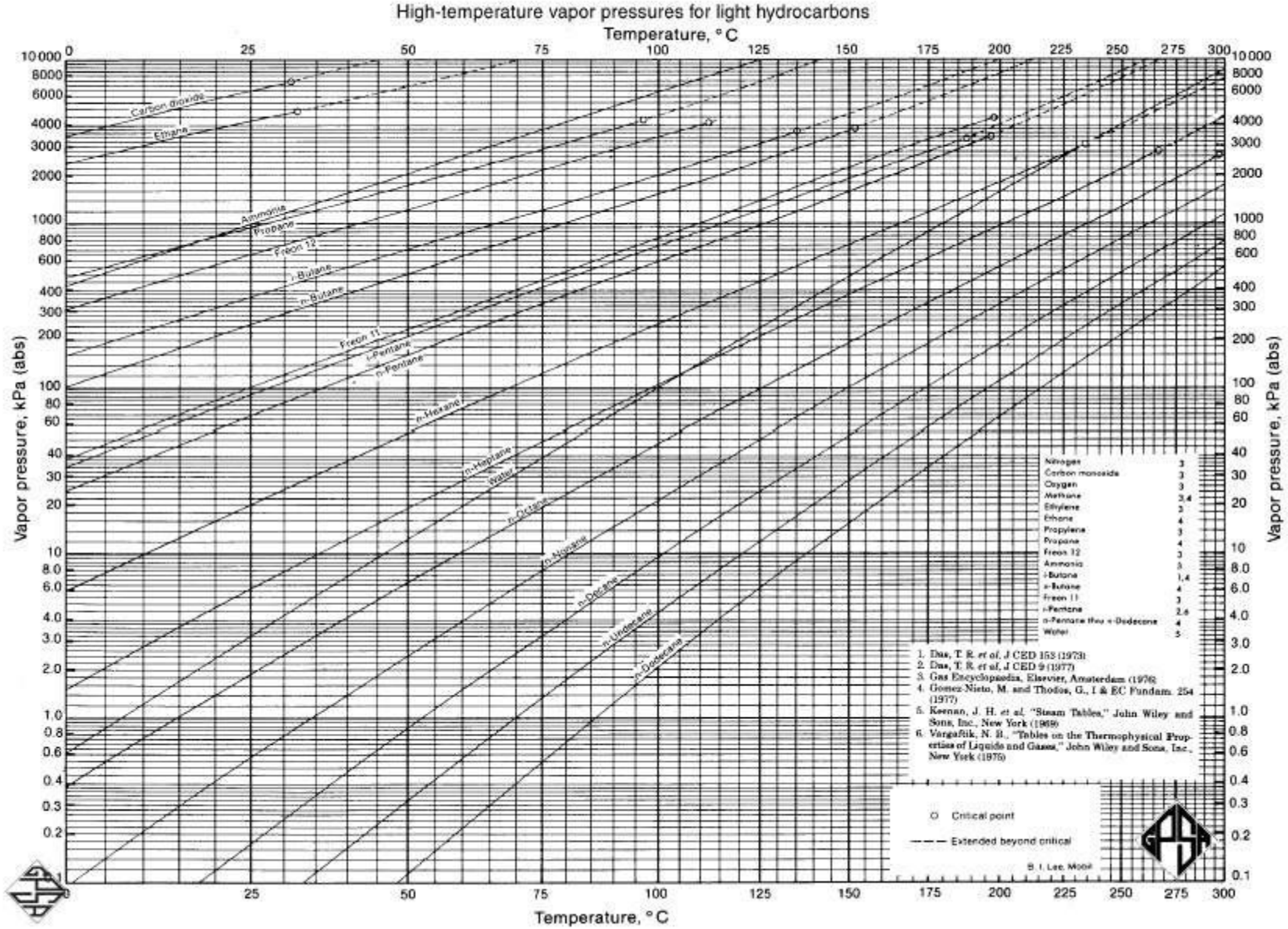


FIG. 23-20
High-Temperature Vapor Pressures for Light Hydrocarbons

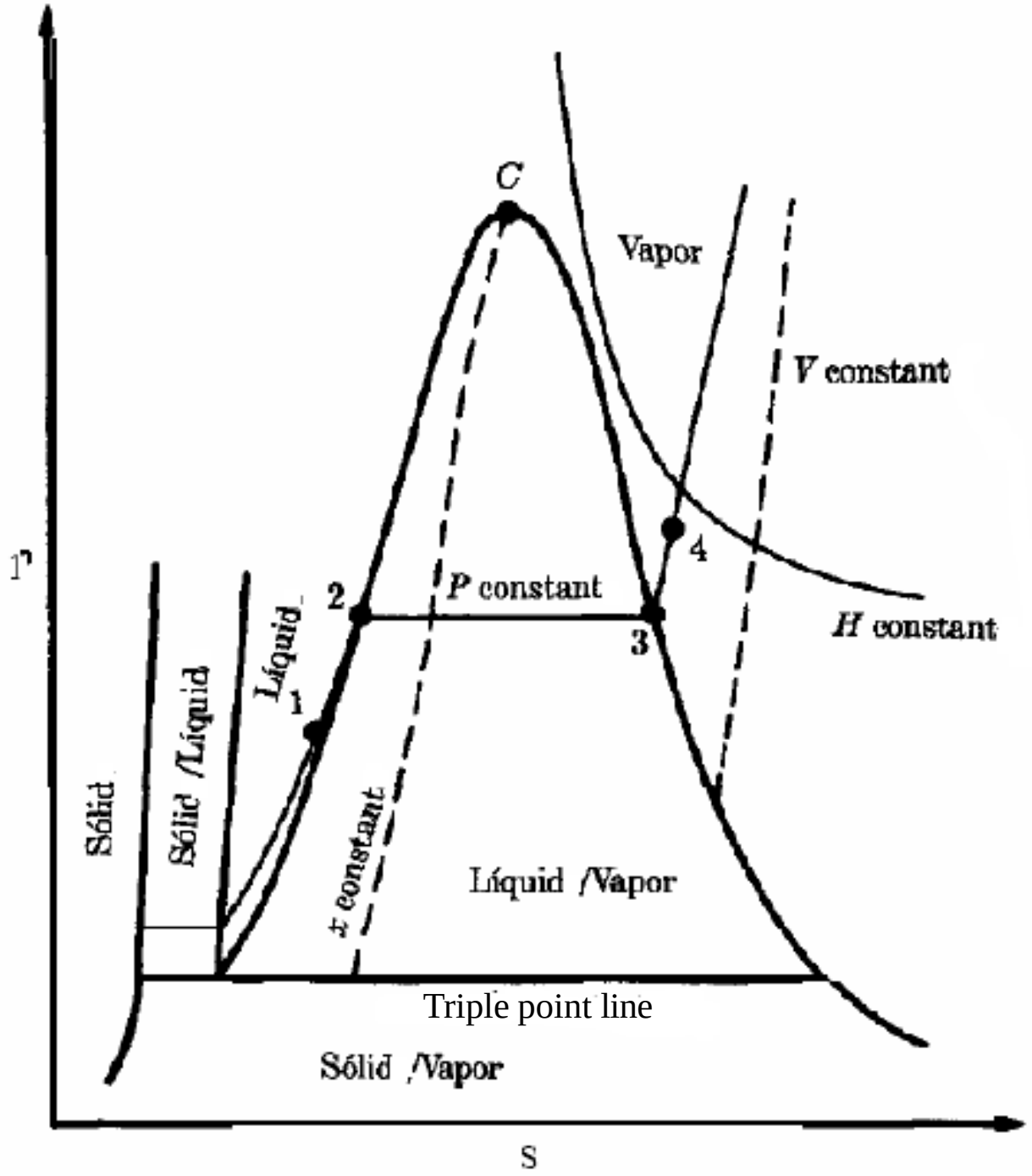
Two-phase liquid/ vapor systems

- When a system consists of saturated-liquid and saturated-vapor phases coexisting in equilibrium, the total value of any extensive property of the two-phase system is the sum of the total properties of the phases:
  - M represents V, U, H, S, etc. $M = (1 - x^v)M^l + x^v M^v$
  - e.g.,

$$V = (1 - x^v)V^l + x^v V^v$$

Thermodynamic diagrams and tables

- A thermodynamic diagram represents the temperature, pressure, volume, enthalpy, and entropy of a substance on a single plot. Common diagrams are:
  - TS diagram
  - PH diagram (ln P vs. H)
  - HS diagram (Mollier diagram)
- In many instances, thermodynamic properties are reported in tables. The steam tables are the most thorough compilation of properties for a single material.


C
Vapor
V constant
4
P constant
2
3
H constant
Líquid
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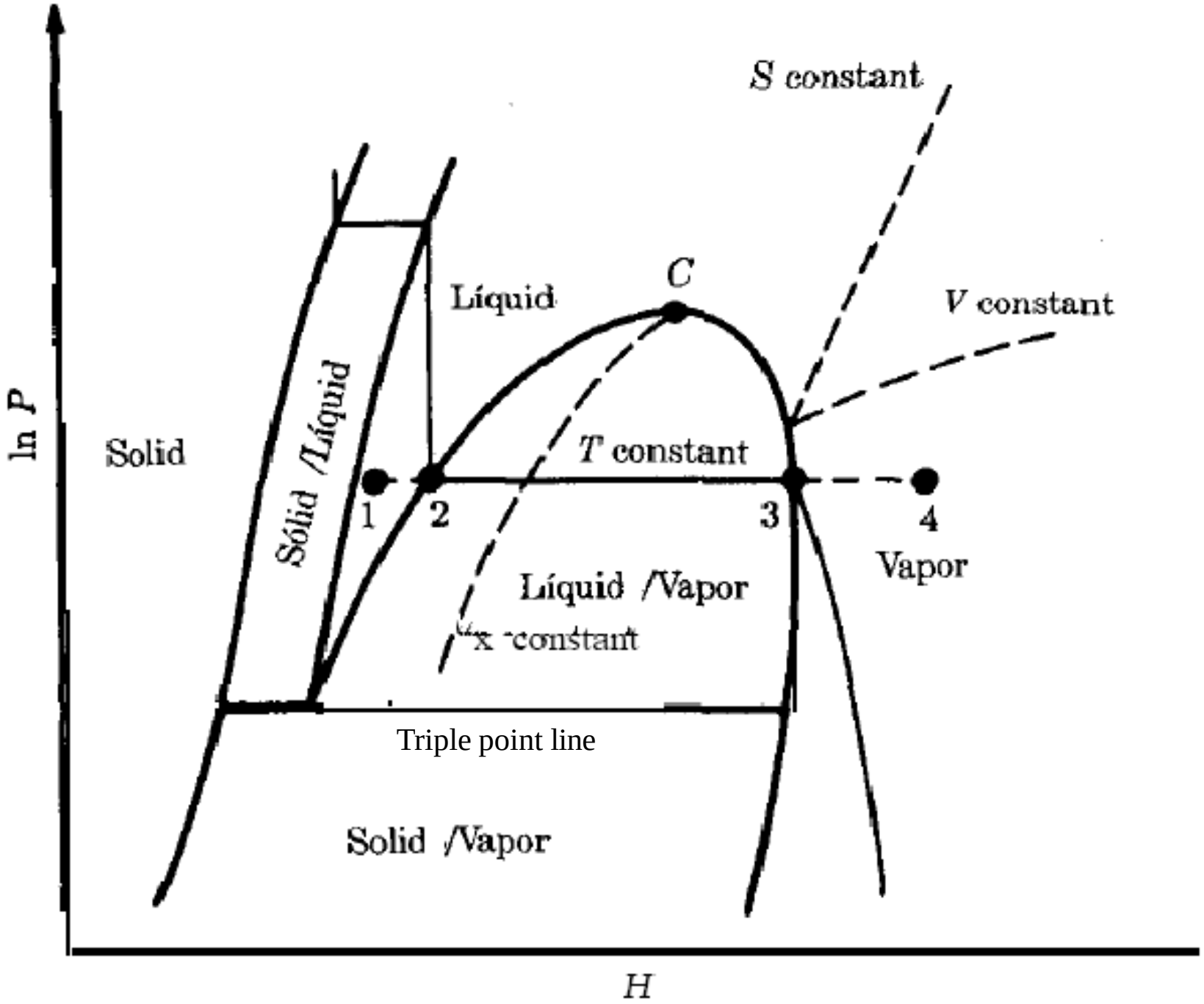
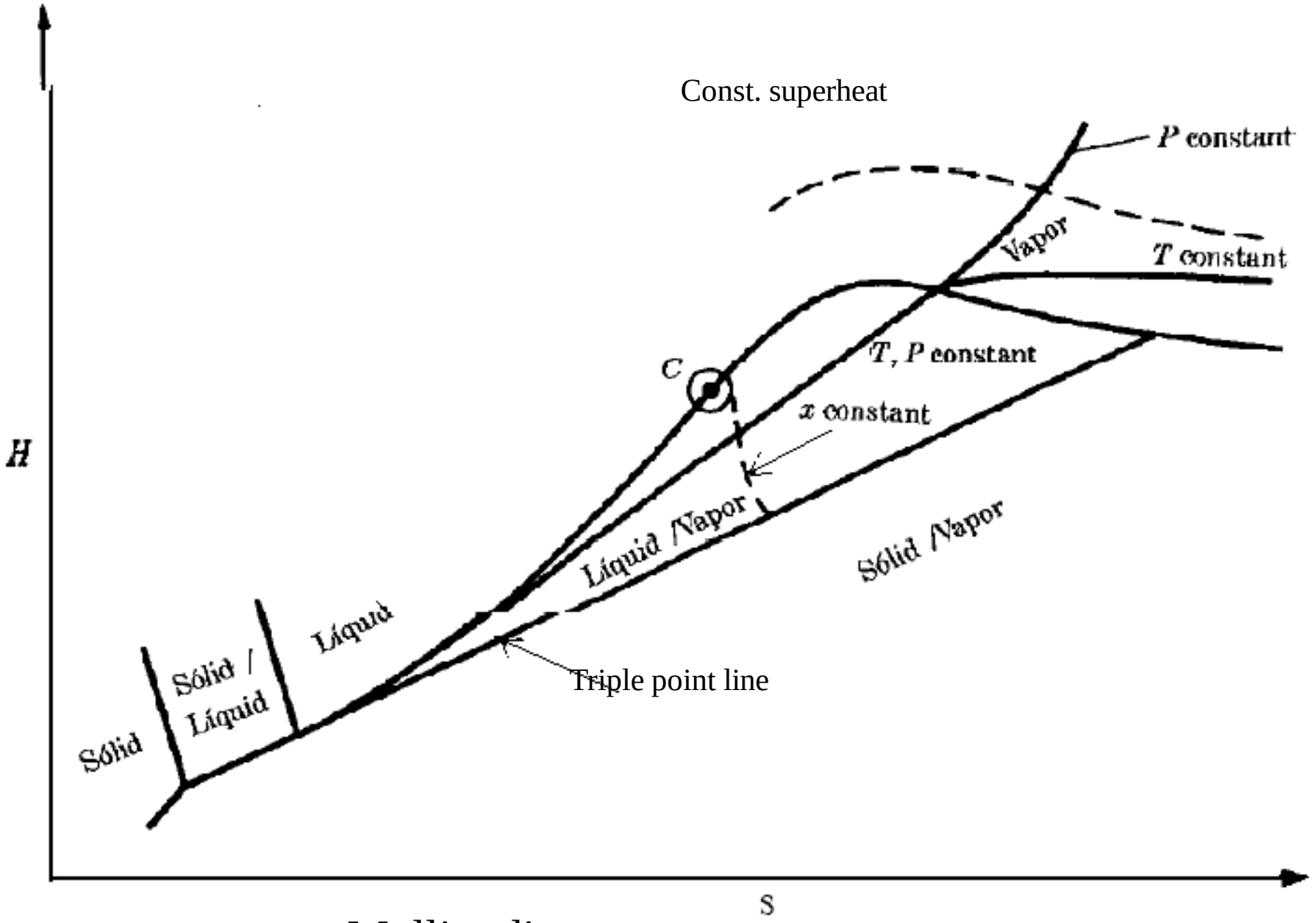
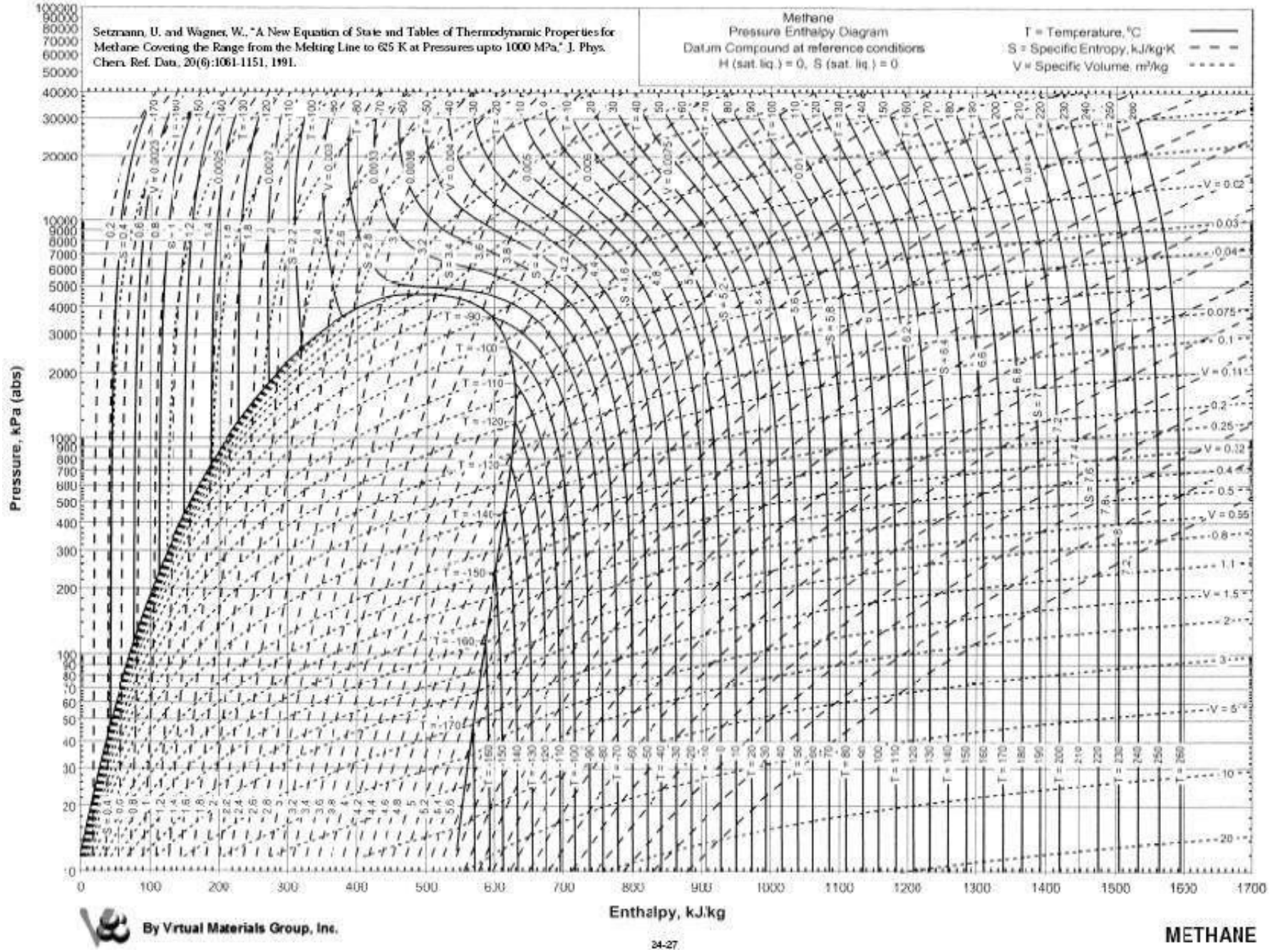
Sólid
x constant
Líquid /Vapor
Triple point line
Sólid /Vapor
S


S constant
C
Líquid
V constant
ln P
Solid
Sólid /Líquid
T constant
1
2
3
4
Vapor
Líquid /Vapor
x constant
Triple point line
Solid /Vapor
H



Mollier diagram


Setzmann, U. and Wagner, W., "A New Equation of State and Tables of Thermodynamic Properties for Methane Covering the Range from the Melting Line to 625 K at Pressures upto 1000 MPa," J. Phys. Chem. Ref. Data, 20(6):1061-1151, 1991.
Methane
Pressure Enthalpy Diagram
Datum Compound at reference conditions
H (sat. liq.) = 0, S (sat. liq.) = 0
T = Temperature, °C
S = Specific Entropy, kJ/kg·K
V = Specific Volume, m³/kg
Pressure, kPa (abs)
Enthalpy, kJ/kg
By Virtual Materials Group, Inc.
METHANE

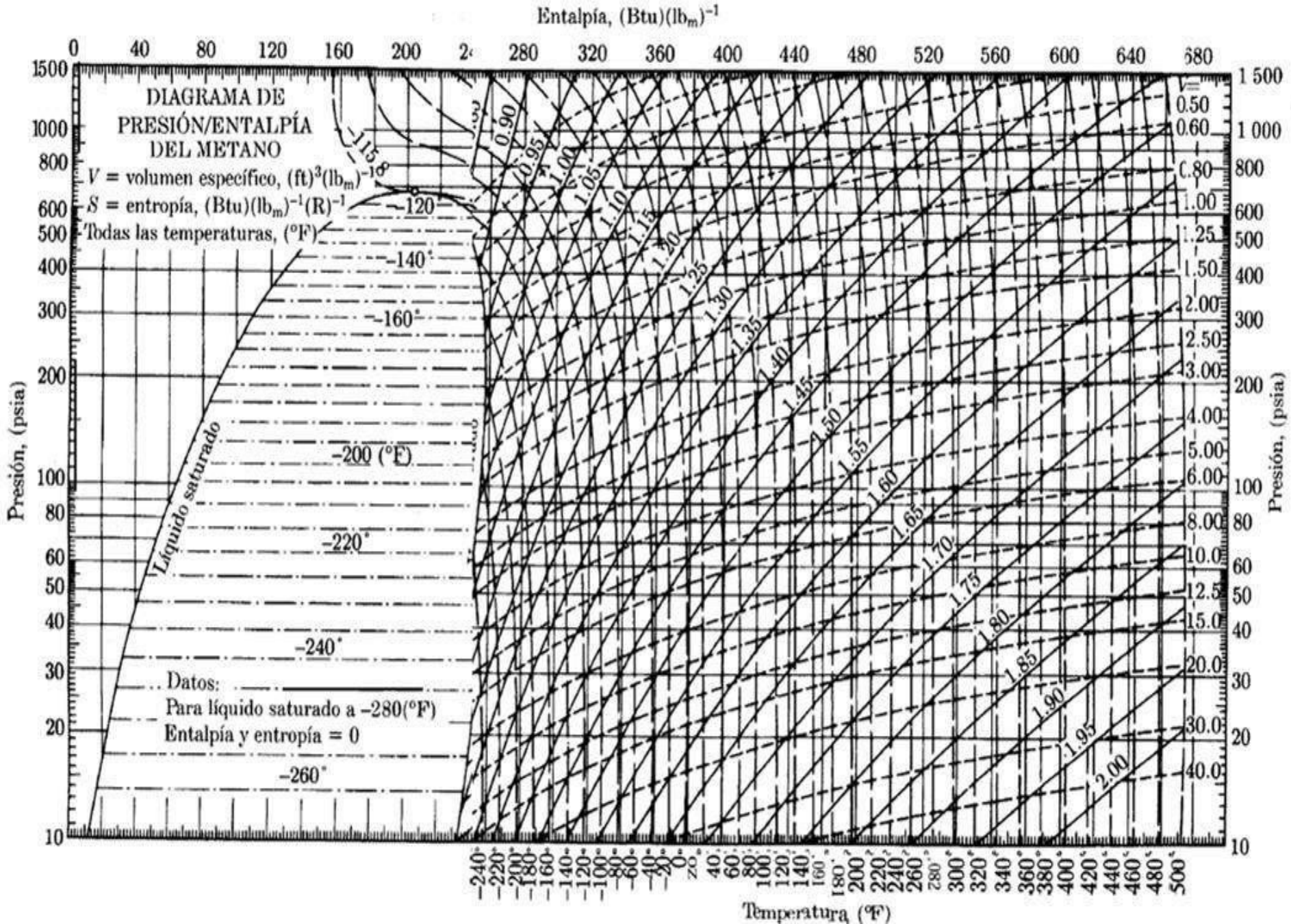


DIAGRAMA DE
PRESIÓN/ENTALPÍA
DEL METANO
V = volumen específico, (ft)³(lbm)⁻¹
S = entropía, (Btu)(lbm)⁻¹(R)⁻¹
Todas las temperaturas, (°F)
Líquido saturado
Datos:
Para líquido saturado a –280(°F)
Entalpía y entropía = 0
Entalpía, (Btu)(lbm)⁻¹
Presión, (psia)
Temperatura (°F)

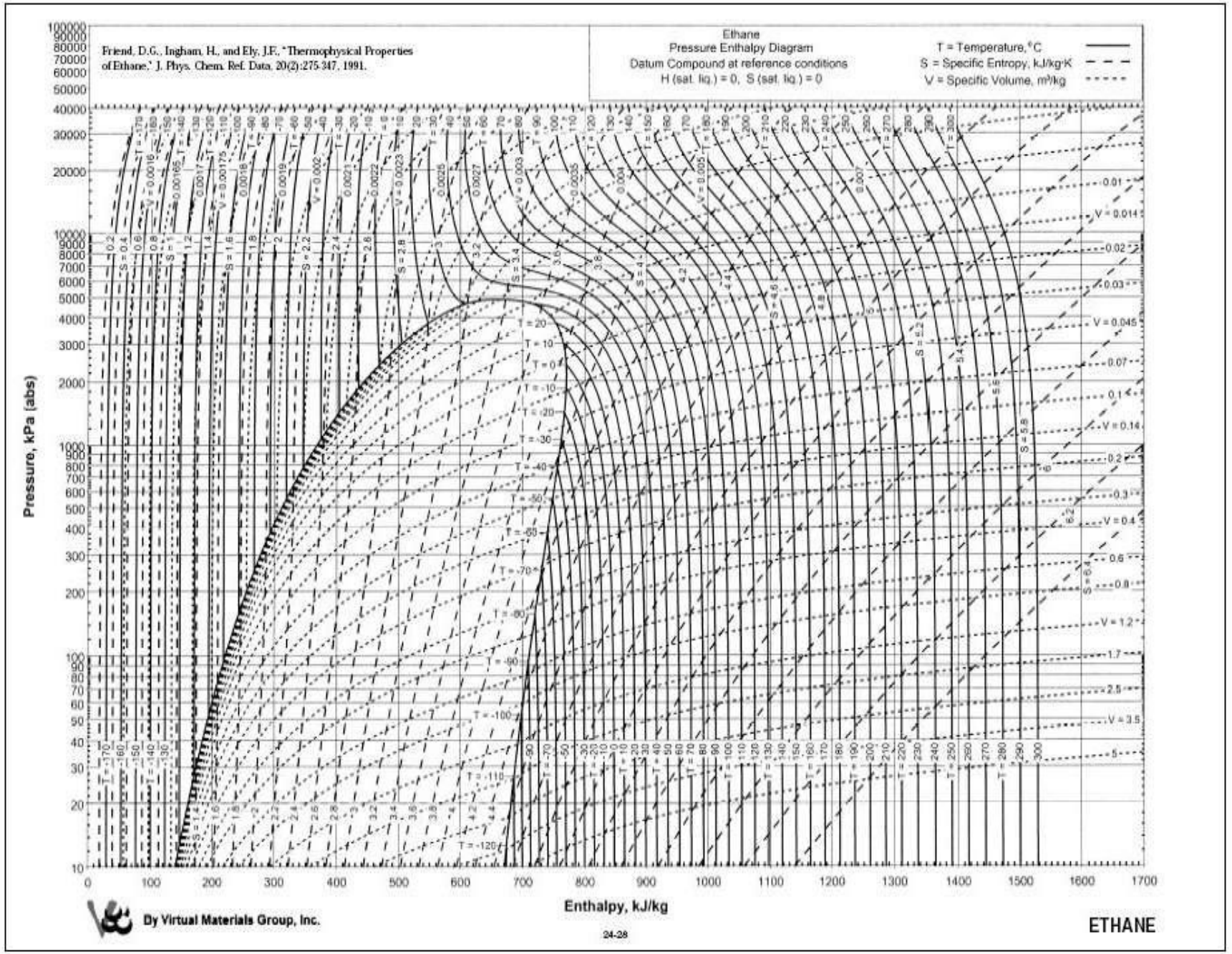
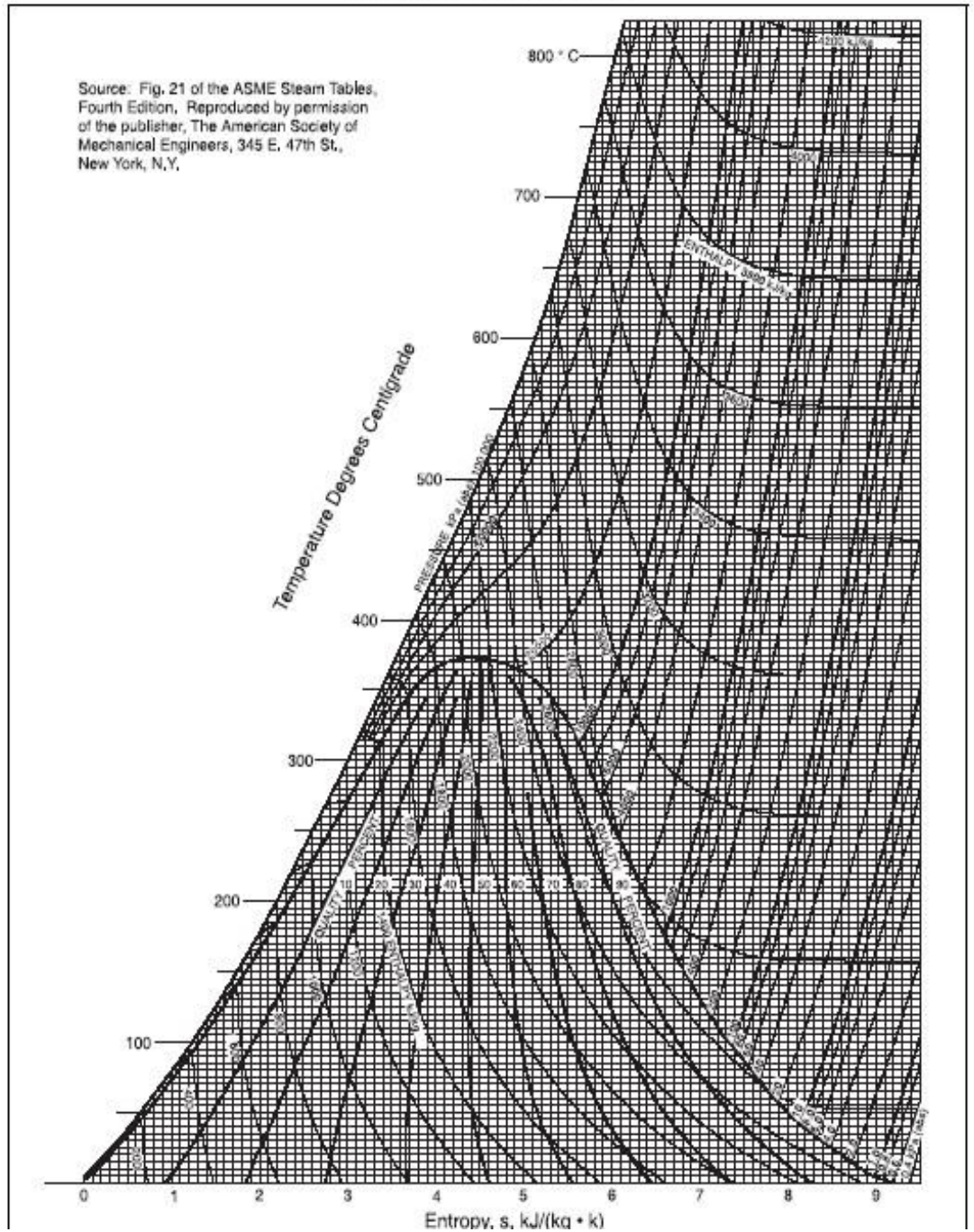

Friend, D.G., Ingham, H., and Ely, J.F., "Thermophysical Properties of Ethane," J. Phys. Chem. Ref. Data, 20(2):275-347, 1991.
Ethane
Pressure Enthalpy Diagram
Datum Compound at reference conditions
H (sat. liq.) = 0, S (sat. liq.) = 0
T = Temperature, °C
S = Specific Entropy, kJ/kg·K
V = Specific Volume, m³/kg
Pressure, kPa (abs)
Enthalpy, kJ/kg
Dy Virtual Materials Group, Inc.
24-28
ETHANE

FIG. 24-34

Thermodynamic Properties of Water



Superheated steam originally at P_1 and T_1 expands through a nozzle to an exhaust pressure P_2. Assuming the process is reversible and adiabatic, determine the downstream state of the steam and ΔH for the following conditions:

(a) P_1 = 1000 kPa, T_1 = 250 °C, and P_2 = 200 kPa.

(b) P_1 = 150 psia, T_1 = 500 °F, and P_2 = 50 psia.

Since the process is both reversible and adiabatic, the entropy change of the steam is zero.

(a) From the steam stable and the use of interpolation,

At P_1 = 1000 kPa, T_1 = 250 °C:

H_1 = 2942.9 kJ/kg, S_1 = 6.9252 kJ/kg.K

At P_2 = 200 kPa,

$S_2 = S_1 = 6.9252$ kJ/kg.K < $S_{\text{saturated vapor}}$,

the final state is in the two-phase liquid-vapor region:

$$S_2 = (1-x_2^v)S_2^l + x_2^v S_2^v \rightarrow 6.9252 = 1.5301(1-x_2^v) + 7.1268x_2^v$$

$$x_2^v = 0.9640$$

$$H_2 = (1-0.964)(504.7) + (0.964)(2706.3) = 2627.0$$

$$\Delta H = H_2 - H_1 = -315.9\ \frac{kJ}{kg}$$

(a) From the steam stable and the use of interpolation,

At P_1 = 150 psia, T_1 = 500°F:

H_1 = 1274.3 Btu/lbm, S_1 = 1.6602 Btu/lbm.R

At P_2 = 50 psia,

$S_2 = S_1 = 1.6602$ Btu/lbm.K > $S_{\text{saturated vapor}}$,

the final state is in the superheat region:

$$T_2 = 283.28^{\circ}F \qquad H_2 = 1175.3\ Btu/lbm$$

$$\boxed{\Delta H = H_2 - H_1 = -99.0\ \frac{Btu}{lbm}}$$

A 1.5 m^3 tank contains 500 kg of liquid water in equilibrium with pure water vapor, which fills the remainder of the tank. The temperature and pressure are 100 °C, and 101.33 kPa. From a water line at a constant temperature of 70 °C and a constant pressure somewhat above 101.33 kPa, 750 kg of liquid is bled into the tank. If the temperature and pressure in the tank are not to change as a result of the process, how much energy as heat must be transferred to the tank?

Energy balance: $\frac{d(mU)_{cv}}{dt} = \dot{Q} + H\dot{m}''$ → $\frac{d(mU)_{cv}}{dt} = \dot{Q} + H'\frac{dm_{cv}}{dt}$

$$Q = \Delta(mU)_{cv} - H'\Delta m_{cv}$$

$$H = U + PV$$

$$Q = \Delta(mH)_{cv} - \Delta(PmV)_{cv} - H'\Delta m_{cv}$$

$$Q = (m_2H_2)_{cv} - (m_1H_1)_{cv} - H'\Delta m_{cv}$$

At the end of the process, the tank still contains saturated liquid and saturated vapor in equilibrium at 100 °C and 101.33 kPa.

$$Q = (m_2 H_2)_{cv} - (m_1 H_1)_{cv} - H'\Delta m_{cv}$$

$$H' = 293.0\frac{kJ}{kg} \quad saturated liquid @ 70^\circ C$$

$$H_{cv}^{l} = 419.1\frac{kJ}{kg} \quad saturated liquid @ 100^\circ C$$

$$H_{cv}^{v} = 2676.0\frac{kJ}{kg} \quad saturated\ vapor @ 100^\circ C$$

From the steam table, the specific volumes of saturated liquid and saturated vapor at 100 ˚C are 0.001044 and 1.673 m^3/kg , respectively.

$$(m_1 H_1)_{cv} = m_1^l H_1^l + m_1^v H_1^v = 500(419.1) + \frac{1.5 - (500)(0.001044)}{1.673}(2676.0) = 211616kJ$$

$$m_2 = 500 + \frac{1.5 - (500)(0.001044)}{1.673} + 750 = m_2^l + m_2^v$$

$$1.5 = 1.673 m_2^v + 0.001044 m_2^l$$

$$(m_2 H_2)_{cv} = m_2^l H_2^l + m_2^v H_2^v = 524458kJ$$

$$Q = (m_2 H_2)_{cv} - (m_1 H_1)_{cv} - H'\Delta m_{cv} = 524458 - 211616 - (750)(293.0) = 93092kJ$$

Generalized Property Correlations for Gases (Korelasi Umum untuk Sifat- sifat Gas)

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$P = P_c P_r$ $\quad$ $T = T_c T_r$

$$\frac{H^R}{RT_c} = -T_r^2\int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}$$

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P}$$

$$\frac{S^R}{R} = -T_r\int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z-1)\frac{dP_r}{P_r}$$

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \qquad \frac{S^R}{R} = -T_r \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z-1)\frac{dP_r}{P_r}$$

$$Z = Z^0 + \omega Z^1$$

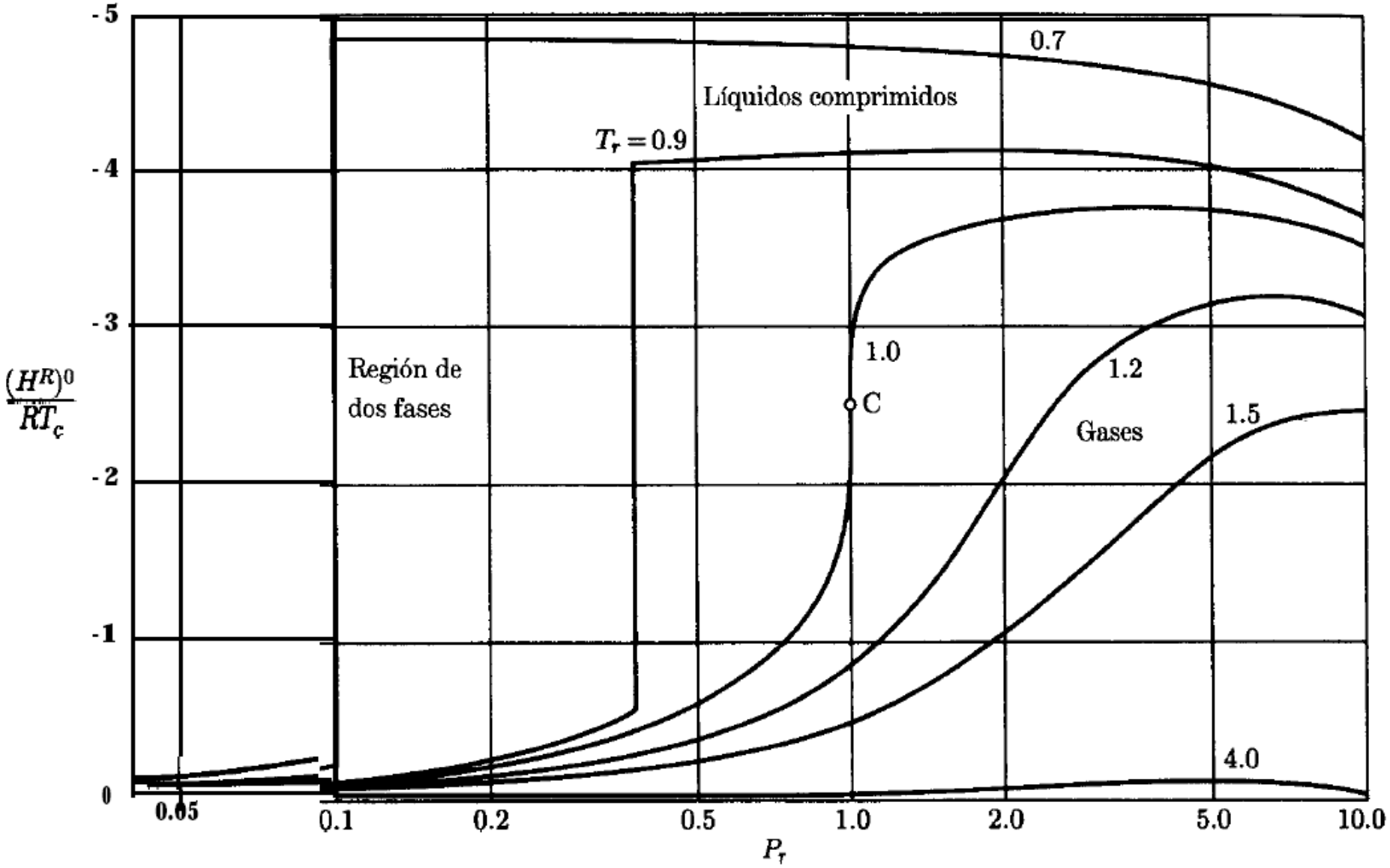
$$\frac{H^R}{RT_c} = \left[-T_r^2 \int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}\right] - \omega \left[-T_r^2 \int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}\right]$$

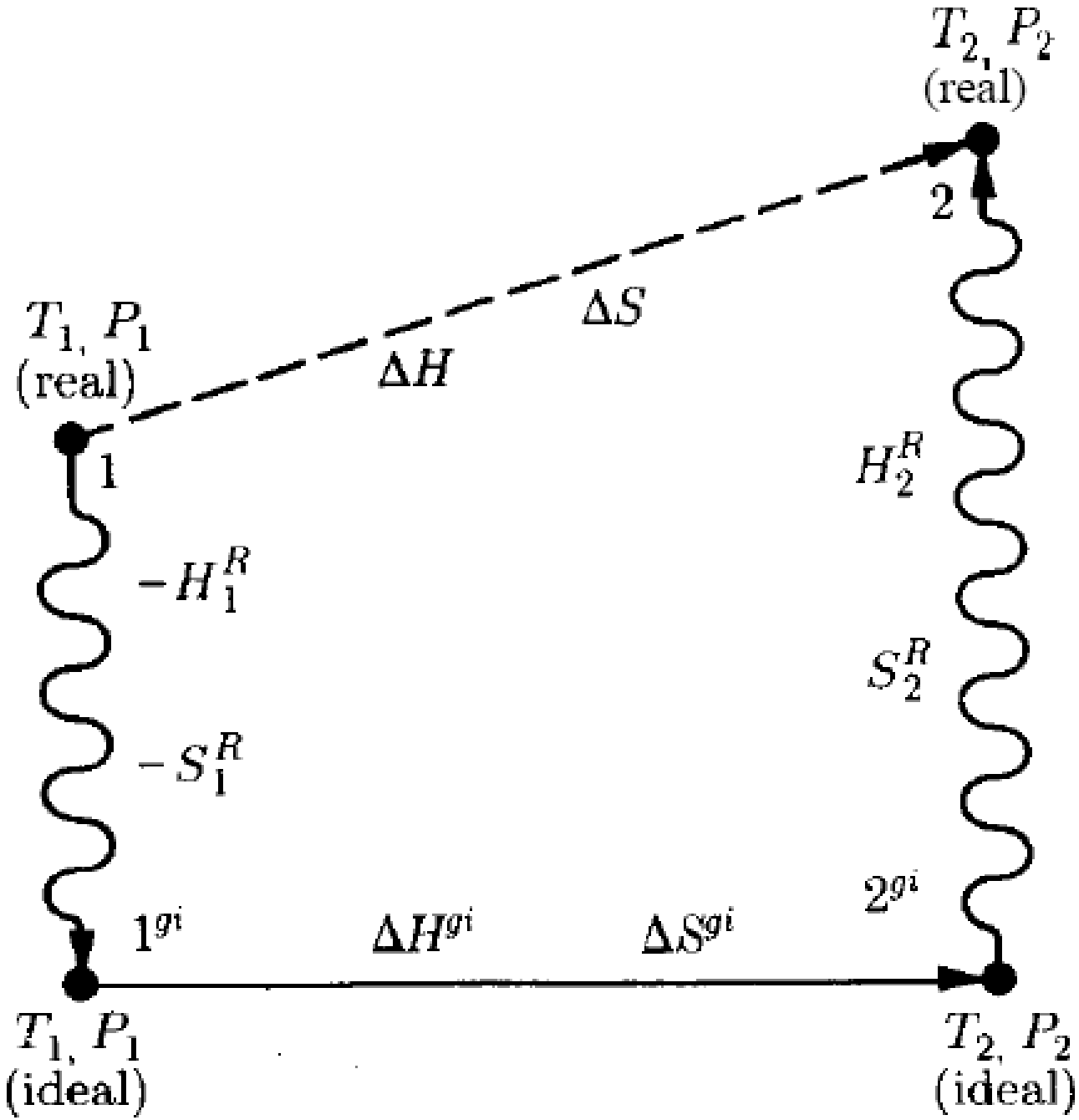
$$\frac{S^R}{R} = \left[-T_r \int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} \frac{dP}{P_r} - \int_0^{P_r} (Z^0-1)\frac{dP_r}{P_r}\right] - \omega \left[-T_r \int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z^1-1)\frac{dP_r}{P_r}\right]$$

$$\frac{H^R}{RT_c} = \left[\frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c}\right] = HRB(TR, PR, OMEGA)$$

$$\frac{S^R}{R} = \left[\frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R}\right] = SRB(TR, PR, OMEGA)$$

Table E5 ~ E12


-5
-4
-3
-2
-1
0
$\frac{(H^R)^0}{RT_c}$
0.7
Líquidos comprimidos
$T_r = 0.9$
Región de
dos fases
1.0
C
1.2
Gases
1.5
4.0
0.05
0.1
0.2
0.5
1.0
2.0
5.0
10.0
P_r


T_2, P_2
(real)
2
ΔS
T_1, P_1
(real)
ΔH
1
H_2^R
$-H_1^R$
S_2^R
$-S_1^R$
2^{gi}
1^{gi}
ΔH^{gi}
ΔS^{gi}
T_1, P_1
(ideal)
T_2, P_2
(ideal)

$$H_2 = H_0^{ig} + \int_{T_0}^{T_2} C_P^{ig}\, dT + H_2^R$$

$$H_1 = H_0^{ig} + \int_{T_0}^{T_1} C_P^{ig}\, dT + H_1^R$$

$$\Delta H = \int_{T_1}^{T_2} C_P^{ig}\, dT + H_2^R - H_1^R$$

$$\Delta H = \left\langle C_P^{ig} \right\rangle_H (T_2 - T_1) + H_2^R - H_1^R$$

$$S_2 = S_0^{ig} + \int_{T_0}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_0} + S_2^R$$

$$S_1 = S_0^{ig} + \int_{T_0}^{T_1} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_1}{P_0} + S_1^R$$

$$\Delta S = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R$$

$$\Delta S = \left\langle C_P^{ig} \right\rangle_S \ln \frac{P_2}{P_1} + S_2^R - S_1^R$$

Use of diagram for residual property calculation (Lee-Kesler Method)

- Generalized Correlation for Compressibility factor
- Generalized Correlation for Residual Enthalpy
- Generalized Correlation for Residual Entropy

Estimate V, U, H, and S for 1-butene vapor at 200°C and 70 bar if H and S are set equal to zero for saturated liquid at 0°C. Assume that only data available are:

$$T_c = 420K \qquad P_c = 40.43\,bar \qquad \omega = 0.191 \qquad T_n = 266.9K\ (nomalboiling\ pt.)$$

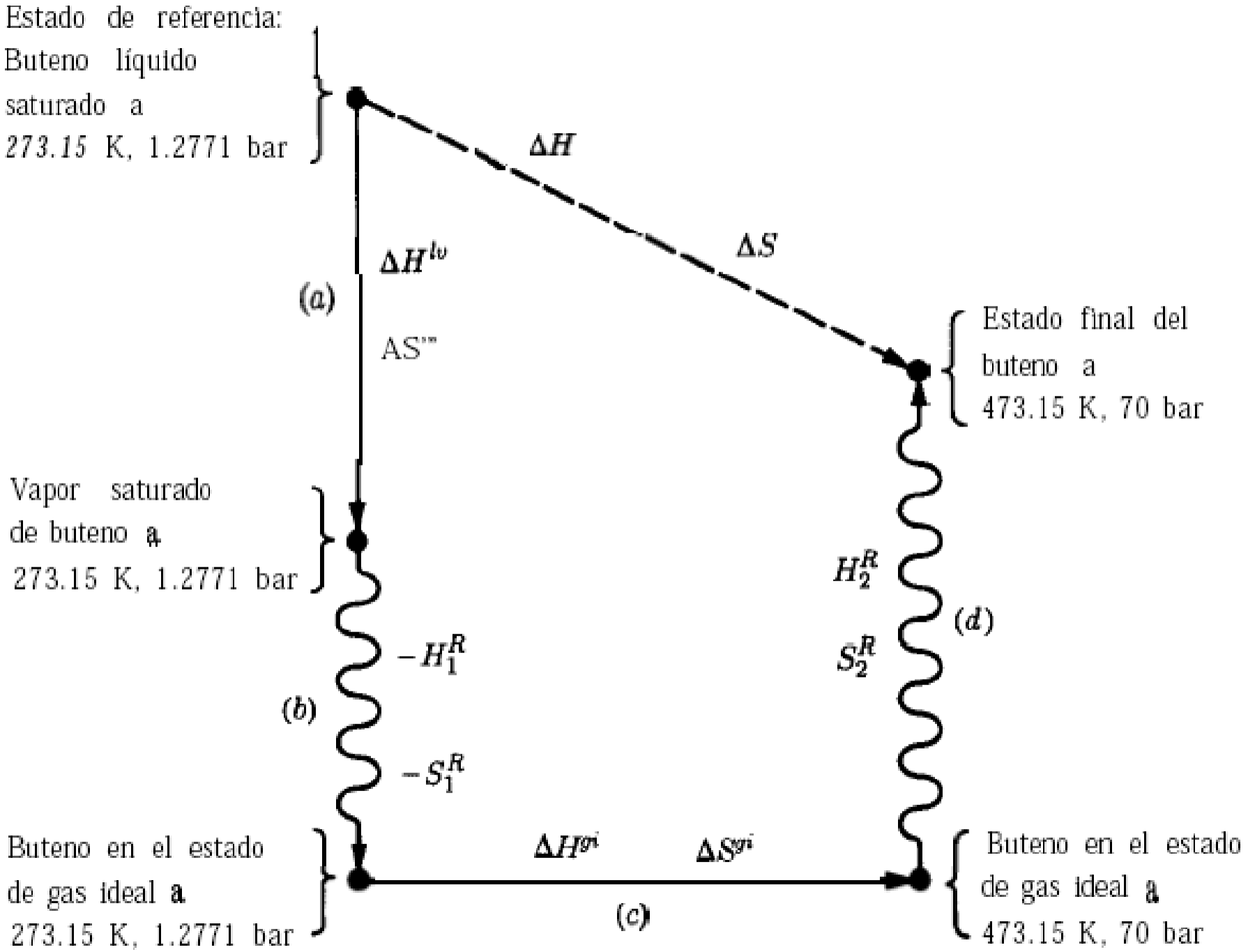
$$C_P^{ig} / R = 1.967 + 31.630\times10^{-3}T - 9.837\times10^{-6}T^2$$

$$T_r = 1.127 \qquad P_r = 1.731$$

$$Z = Z^0 + \omega Z^1$$
$$= 0.485 + (0.191)(0.142)$$
$$= 0.512$$

$$V = \frac{ZRT}{P} = 287.8\,\frac{cm^3}{mol}$$

Assuming four steps:
(a) Vaporization at T_1 and $P_1 = P^{sat}$
(b) Transition to the ideal-gas state at (T_1, P_1)
(c) Change to (T_2, P_2) in the ideal-gas state
(d) Transition to the actual final state at (T_2, P_2)


Estado de referencia:
Buteno líquido
saturado a
273.15 K, 1.2771 bar
ΔH
ΔS
ΔH^lv
(a)
AS'"
Estado final del
buteno a
473.15 K, 70 bar
Vapor saturado
de buteno a
273.15 K, 1.2771 bar
H_2^R
(d)
S_2^R
−H_1^R
(b)
−S_1^R
Buteno en el estado
de gas ideal a
273.15 K, 1.2771 bar
ΔH^gi
ΔS^gi
(c)
Buteno en el estado
de gas ideal a
473.15 K, 70 bar

Step (a)

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

$$\ln 1.0133 = A - \frac{B}{266.9}$$

$$\ln 40.43 = A - \frac{B}{420}$$

For = 273.15K,
P^{sat} = 1.2771 bar

The latent heat at normal boiling point:

$$\frac{\Delta H_n^{lv}}{RT_n} = \frac{1.092(\ln P_c - 1.013)}{0.930 - T_{r_n}} = 9.979$$

The latent heat at 273.15 K:

$$\frac{\Delta H^{lv}}{\Delta H_n^{lv}} = \left(\frac{1 - T_r}{1 - T_{r_n}}\right)^{0.38}$$

$$\Delta H^{lv} = 21810 \frac{J}{mol}$$

$$\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta}$$

$$\Delta S^{lv} = 79.84 \frac{J}{mol \cdot K}$$

Step (b)

$$T_r = 0.650 \qquad P_r = 0.0316$$

$$\frac{H^R}{RT_c} = \left[\frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c}\right] = HRB(TR, PR, OMEGA) = -0.0985$$

$$-H_1^R = 344 \frac{J}{mol}$$

$$\frac{S^R}{R} = \left[\frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R}\right] = SRB(TR, PR, OMEGA) = -0.1063$$

$$-S_1^R = 0.88 \frac{J}{mol \cdot K}$$

Step (c)

$$\Delta H^{ig} = 8.314 \times ICPH(273.15,473.15;1.967,31.630E-3,-9.837E-6,0.0) = 20564 \ \frac{J}{mol}$$

$$\Delta S^{ig} = 8.314 \times ICPS(273.15,473.15;1.967,31.630E-3,-9.837E-6,0.0) - 8.314 \ln \frac{70}{1.2771}$$

$$= 22.18 \ \frac{J}{mol \cdot K}$$

Step (d)

$$T_r = 1.127 \qquad P_r = 1.731$$

$$\frac{H^R}{RT_c} = \left[\frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} \right] = -2.430$$

$$H_2^R = -8485 \ \frac{J}{mol}$$

$$\frac{S^R}{R} = \left[\frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} \right] = -1.705$$

$$S_2^R = -14.18 \ \frac{J}{mol \cdot K}$$

Total

$$H = \Delta H = 21810 - (-344) + 20564 - 8485 = 34233 \ \frac{J}{mol}$$

$$S = \Delta S = 79.84 - (-0.88) + 22.18 - 14.18 = 88.72 \ \frac{J}{mol \cdot K}$$

$$U = H - PV = 34233 - (70)(287.8)/10 = 32218 \ \frac{J}{mol}$$

TERIMA KASIH

FOR YOUR ATTENTION