PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

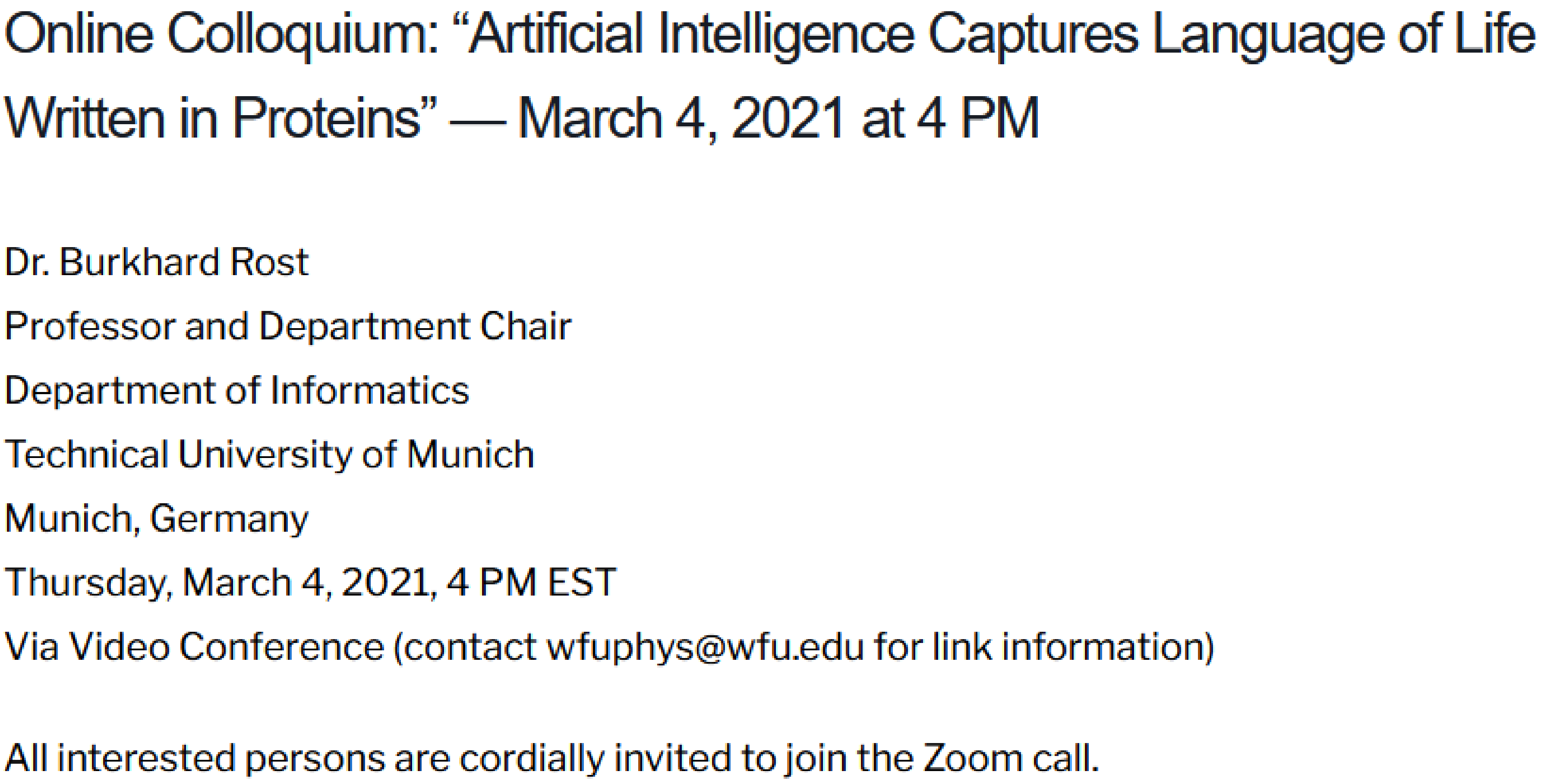
Record!!!

Discussion for Lecture 16:

Thermodynamics of phase change

Reading: Chapter 5.3

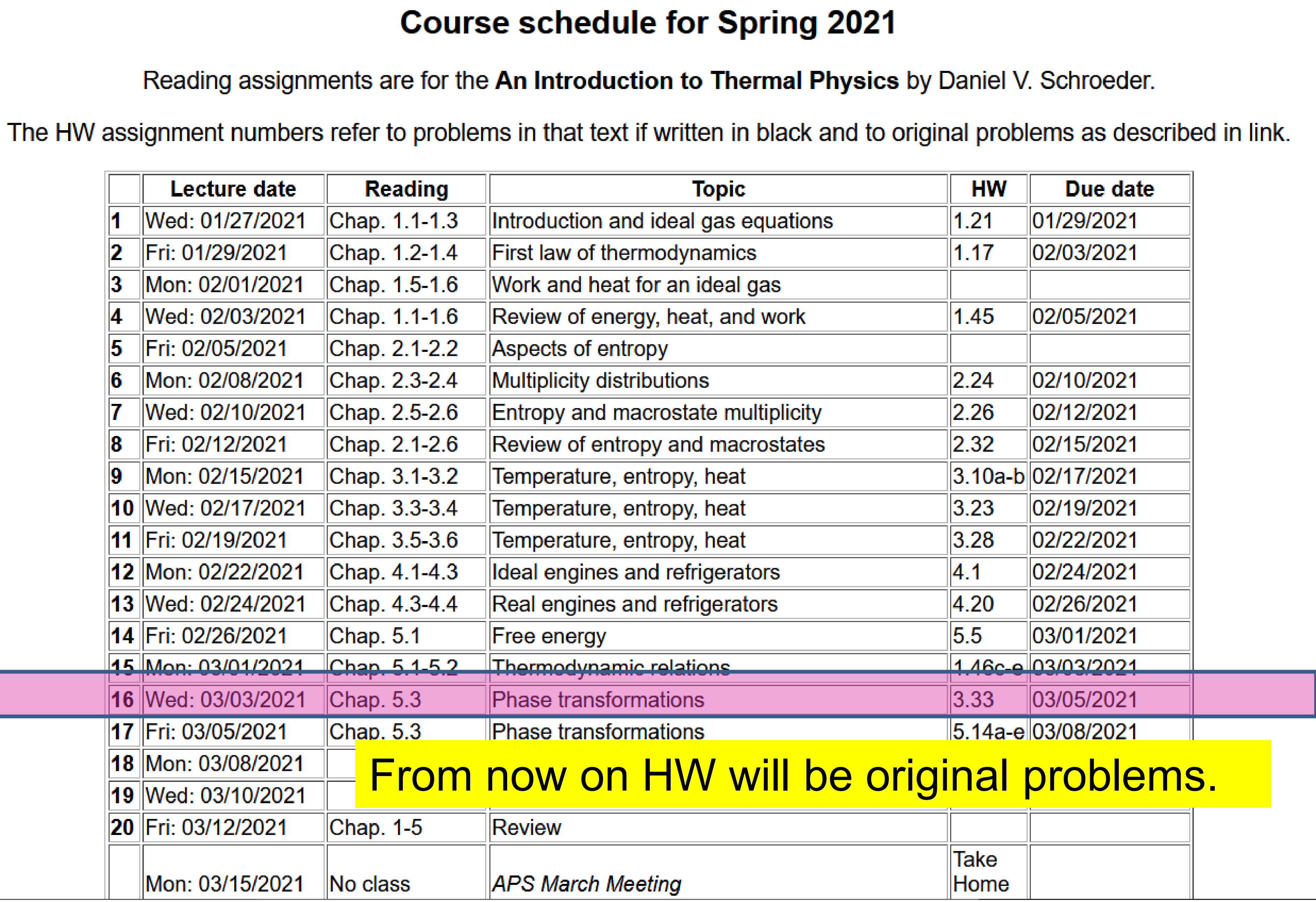
1. Examples of phase transformations
2. Equations related to phase transformations
3. Model equations of state that caption some of the physics of phase transformations



Online Colloquium: “Artificial Intelligence Captures Language of Life Written in Proteins” — March 4, 2021 at 4 PM

Dr. Burkhard Rost
Professor and Department Chair
Department of Informatics
Technical University of Munich
Munich, Germany
Thursday, March 4, 2021, 4 PM EST
Via Video Conference (contact wfuphys@wfu.edu for link information)

All interested persons are cordially invited to join the Zoom call.



Course schedule for Spring 2021

Reading assignments are for the **An Introduction to Thermal Physics** by Daniel V. Schroeder.

The HW assignment numbers refer to problems in that text if written in black and to original problems as described in link.

	Lecture date	Reading	Topic	HW	Due date
1	Wed: 01/27/2021	Chap. 1.1-1.3	Introduction and ideal gas equations	1.21	01/29/2021
2	Fri: 01/29/2021	Chap. 1.2-1.4	First law of thermodynamics	1.17	02/03/2021
3	Mon: 02/01/2021	Chap. 1.5-1.6	Work and heat for an ideal gas		
4	Wed: 02/03/2021	Chap. 1.1-1.6	Review of energy, heat, and work	1.45	02/05/2021
5	Fri: 02/05/2021	Chap. 2.1-2.2	Aspects of entropy		
6	Mon: 02/08/2021	Chap. 2.3-2.4	Multiplicity distributions	2.24	02/10/2021
7	Wed: 02/10/2021	Chap. 2.5-2.6	Entropy and macrostate multiplicity	2.26	02/12/2021
8	Fri: 02/12/2021	Chap. 2.1-2.6	Review of entropy and macrostates	2.32	02/15/2021
9	Mon: 02/15/2021	Chap. 3.1-3.2	Temperature, entropy, heat	3.10a-b	02/17/2021
10	Wed: 02/17/2021	Chap. 3.3-3.4	Temperature, entropy, heat	3.23	02/19/2021
11	Fri: 02/19/2021	Chap. 3.5-3.6	Temperature, entropy, heat	3.28	02/22/2021
12	Mon: 02/22/2021	Chap. 4.1-4.3	Ideal engines and refrigerators	4.1	02/24/2021
13	Wed: 02/24/2021	Chap. 4.3-4.4	Real engines and refrigerators	4.20	02/26/2021
14	Fri: 02/26/2021	Chap. 5.1	Free energy	5.5	03/01/2021
15	Mon: 03/01/2021	Chap. 5.1-5.2	Thermodynamic relations	1.46c-e	03/03/2021
16	Wed: 03/03/2021	Chap. 5.3	Phase transformations	3.33	03/05/2021
17	Fri: 03/05/2021	Chap. 5.3	Phase transformations	5.14a-e	03/08/2021
18	Mon: 03/08/2021				
19	Wed: 03/10/2021				
20	Fri: 03/12/2021	Chap. 1-5	Review		
	Mon: 03/15/2021	No class	*APS March Meeting*	Take Home	

From now on HW will be original problems.

Your questions –

From Kristen – Could you explain the critical point in a bit more detail? 2. Could you explain figure 5.21 in more detail, specifically the references to integrals made in the text (the Maxwell construction)?

From Parker – My question for the week is what is the purpose of using the van der Waals Model instead of the usual ideal gas equation?

From Michael – How are the critical temperature, critical pressure, and critical volume all related to one another. Would they follow the same mathematical expression we would expect using the ideal gas law?

From Rich -- -Does the Van der Waals equation accurately model liquids, and if not, how could it accurately be used to model the phase shift? -For the unattainable conformations in the Gibbs Free energy/phase shift plot, what would these positions look like for the system theoretically?

Your questions –

From Chao -- In the last class we got the formula above. However, since the pressure is constant, why we have two different value of p?

$$\mu = \mu(T,P) = \mu(T_0,P_0) + \left(\mu(T_0,P) - \mu(T_0,P_0)\right)$$
$$= \mu(T_0,P_0) + k_B T_0 \ln\left(\frac{P}{P_0}\right)$$

Comment -- This expression is useful if the constant P is different from the value in the table (for example P_0) and if the system is an ideal gas.

Comment – on another property of the Gibbs free energy and the chemical potential -- Gibbs-Dunham relationship

Recall from Lecture 15 regarding a single component system (with the specific example of the monoatomic ideal gas –

Gibbs G: $$G = -Nk_BT\left(\ln\left(\frac{k_BT}{P}\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}\right)\right) = G(T,P,N)$$

Gibbs μ: $$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = -k_BT\left(\ln\left(\frac{k_BT}{P}\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}\right)\right) = \mu(T,P)$$

Also note that $G(T,P,N) = N\mu(T,P)$

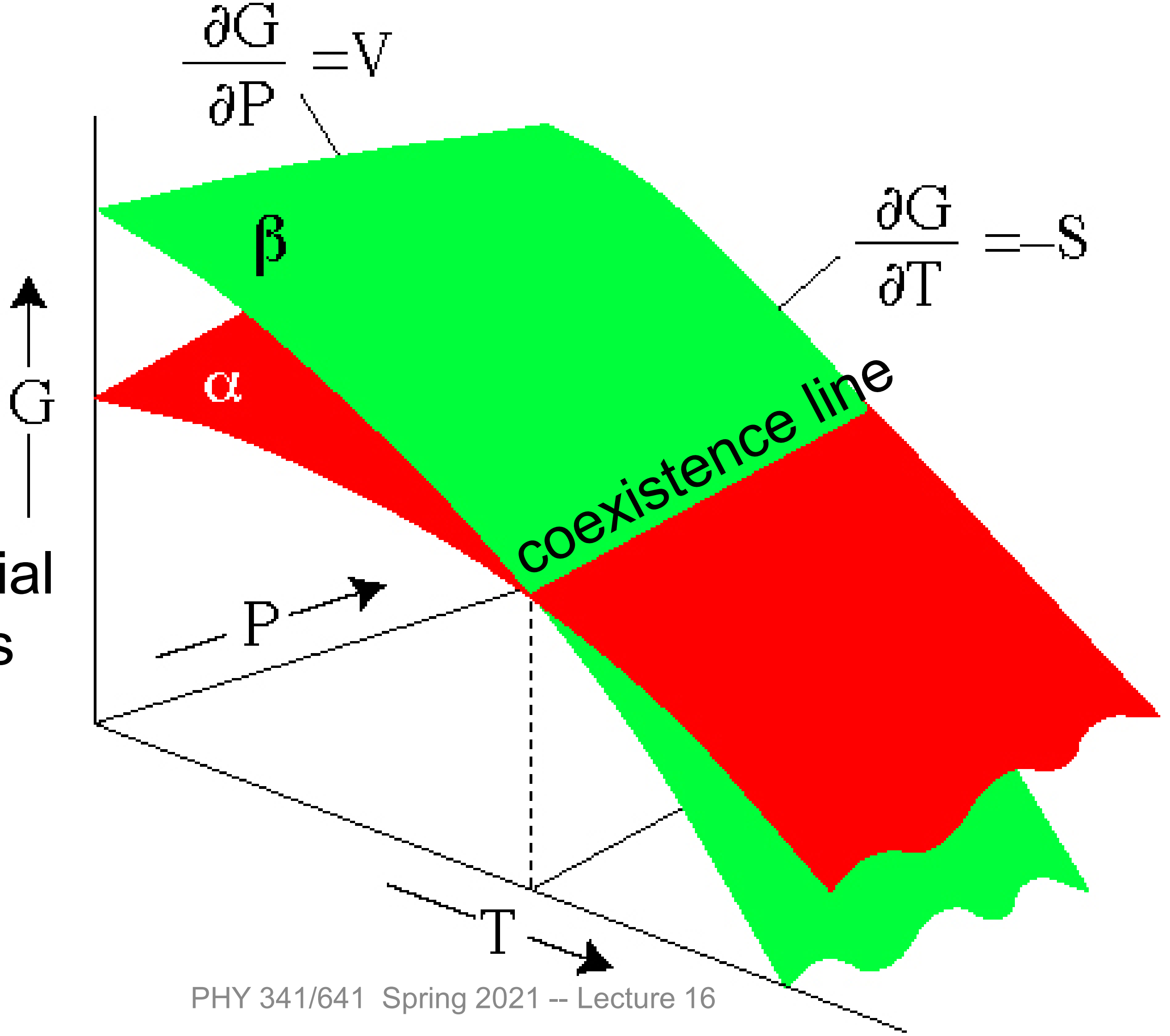
(Expected true for all one component systems)

$$\Rightarrow d\mu = \left(\frac{\partial \mu}{\partial T}\right)_P dT + \left(\frac{\partial \mu}{\partial P}\right)_T dP = -\frac{S}{N}dT + \frac{V}{N}dP$$

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

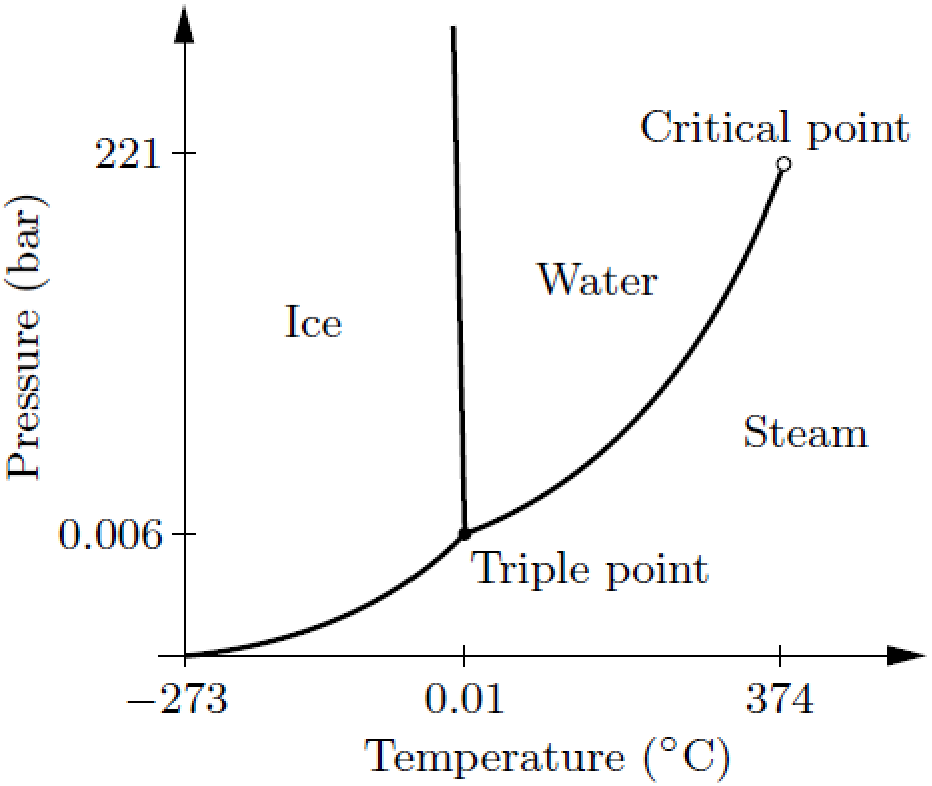
Behavior of Gibbs free energy for a material that changes phase

http://hacker.faculty.geol.ucsb.edu/geo124T/lecture.html



Example material that has phases α and β --

Coexistence lines as a function of T and P for phases of water



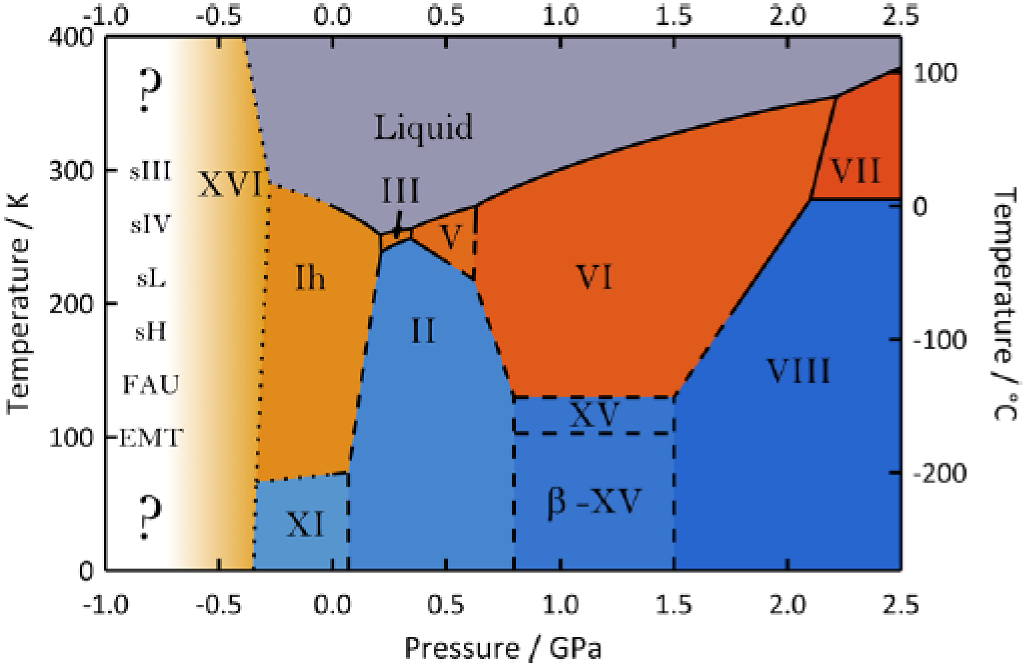
T (°C)	P_v (bar)	L (kJ/mol)
−40	0.00013	51.16
−20	0.00103	51.13
0	0.00611	51.07
0.01	0.00612	45.05
25	0.0317	43.99
50	0.1234	42.92
100	1.013	40.66
150	4.757	38.09
200	15.54	34.96
250	39.74	30.90
300	85.84	25.30
350	165.2	16.09
374	220.6	0.00

Figure 5.11. Phase diagram for H_2O (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994). Copyright ©2000, Addison-Wesley.

Phase transition terminology

- ☐ Triple point: A particular temperature (T_t) and pressure (P_t) at which three phases (solid, liquid, gas) of the system exist together. At the triple point the chemical potentials are all equal – $\mu_{solid} = \mu_{liquid} = \mu_{gas}$.
- ☐ Critical point: A particular temperature (T_c) and pressure (P_c) at which the existence or coexistence of phase change qualitatively. For example, the critical point of water involves the change from the coexistence of liquid and vapor to a single "fluid" phase

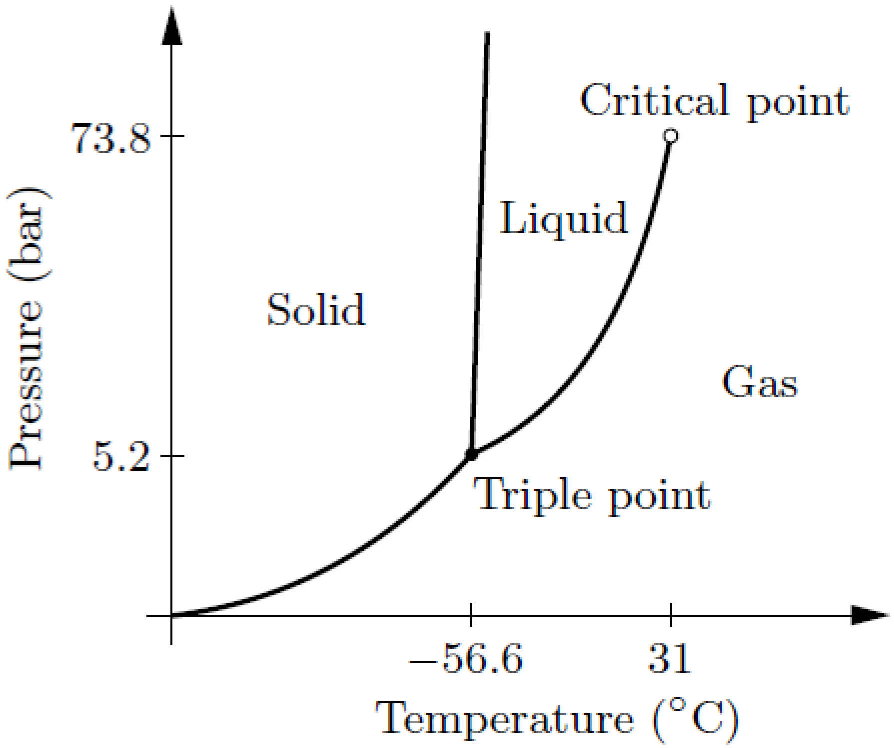
Some details of crystalline phases of ice



Ref: (DOI)
10.1038/s42004-020-00349-2

Fig. 2 Phase diagram at negative to intermediate pressure. Stable phases of ice and liquid water up to 2.5 GPa and 400 K, excluding water vapour and metastable phases. Dashed lines indicate extrapolations based on experiments at higher temperature. Dotted lines at negative pressure are sketched based on simulations by Conde et al. in ref. [9] and shifted to match experimental data at positive pressure. Grey indicates liquid water. Blue indicates H-ordered ices, orange/red indicates H-disordered ices. Shades of colour indicate density. Predicted low-density ice polymorphs as candidates for future experimental discovery derived from clathrate hydrate and zeolite structures are listed at the far negative pressure end.

Coexistence lines as a function of T and P for phases of CO_2



T (°C)	P_v (bar)
−120	0.0124
−100	0.135
−80	0.889
−78.6	1.000
−60	4.11
−56.6	5.18
−40	10.07
−20	19.72
0	34.85
20	57.2
31	73.8

Figure 5.12. Phase diagram for carbon dioxide (not to scale). The table gives the vapor pressure along the solid-gas and liquid-gas equilibrium curves. Data from Lide (1994) and Reynolds (1979).

Gibbs free energy versus pressure at T=298 K for graphite and diamond.

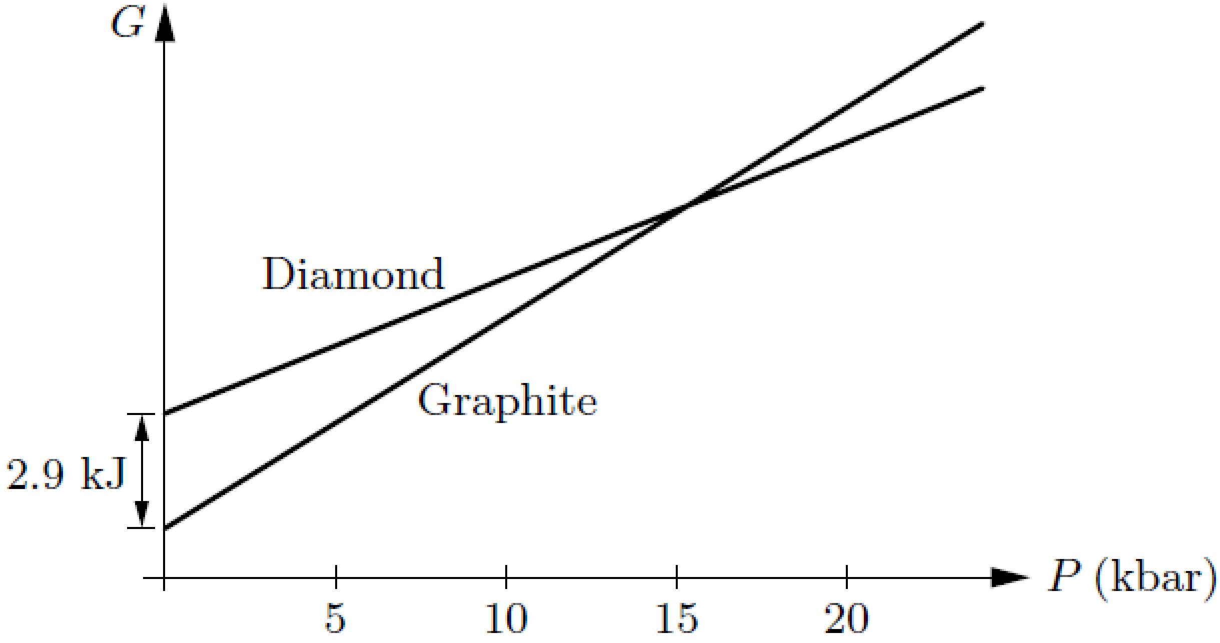
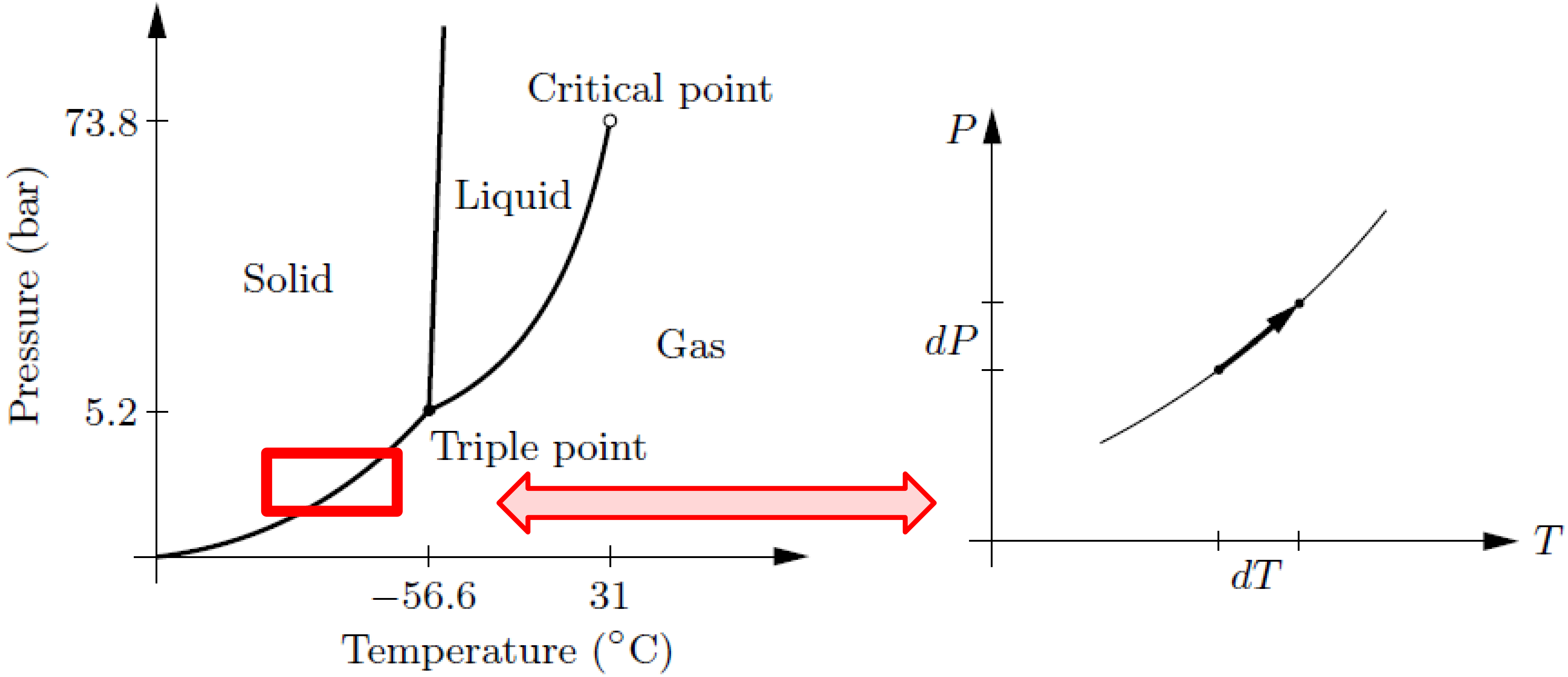


Figure 5.15. Molar Gibbs free energies of diamond and graphite as functions of pressure, at room temperature. These straight-line graphs are extrapolated from low pressures, neglecting the changes in volume as pressure increases. Copyright ©2000, Addison-Wesley.

Analysis of coexistence curve – the Clausius-Clapeyron equation



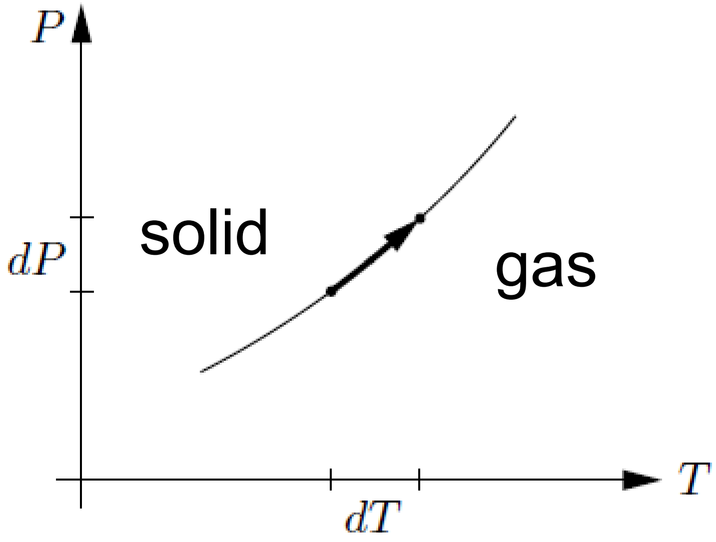
At the phase boundary: $G_{solid} = G_{gas}$

Along the coexistence curve (at fixed number of particles):

$$dG_{solid} = -S_{solid}dT + V_{solid}dP = dG_{gas} = -S_{gas}dT + V_{gas}dP$$

Slope of phase boundary line: $$\frac{dP}{dT} = \frac{S_{gas} - S_{solid}}{V_{gas} - V_{solid}}$$

Analysis of coexistence curve – the Clausius-Clapeyron equation



Slope of phase boundary line:

$$\frac{dP}{dT} = \frac{S_{gas} - S_{solid}}{V_{gas} - V_{solid}}$$

Define latent heat: $L \equiv T\left(S_{gas} - S_{solid}\right)$

$$\frac{dP}{dT} = \frac{L}{T\left(V_{gas} - V_{solid}\right)}$$ Clausius-Clapeyron equation

Example of Clausius-Clapeyron equation -- for diamond and graphite

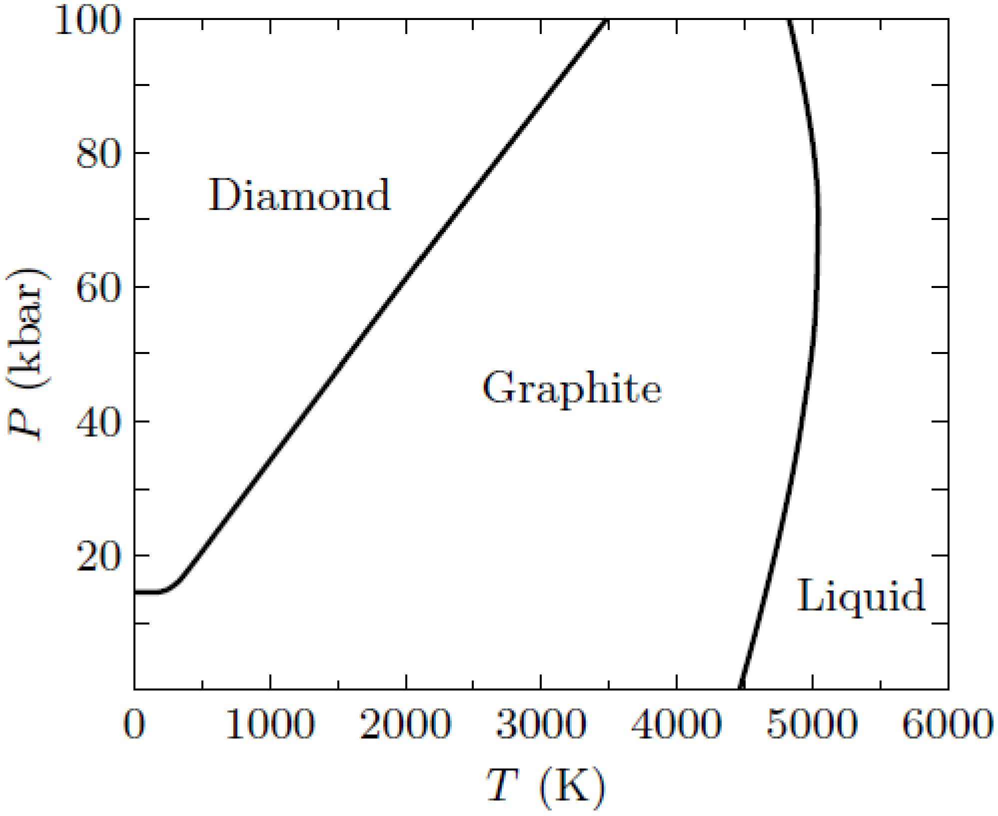
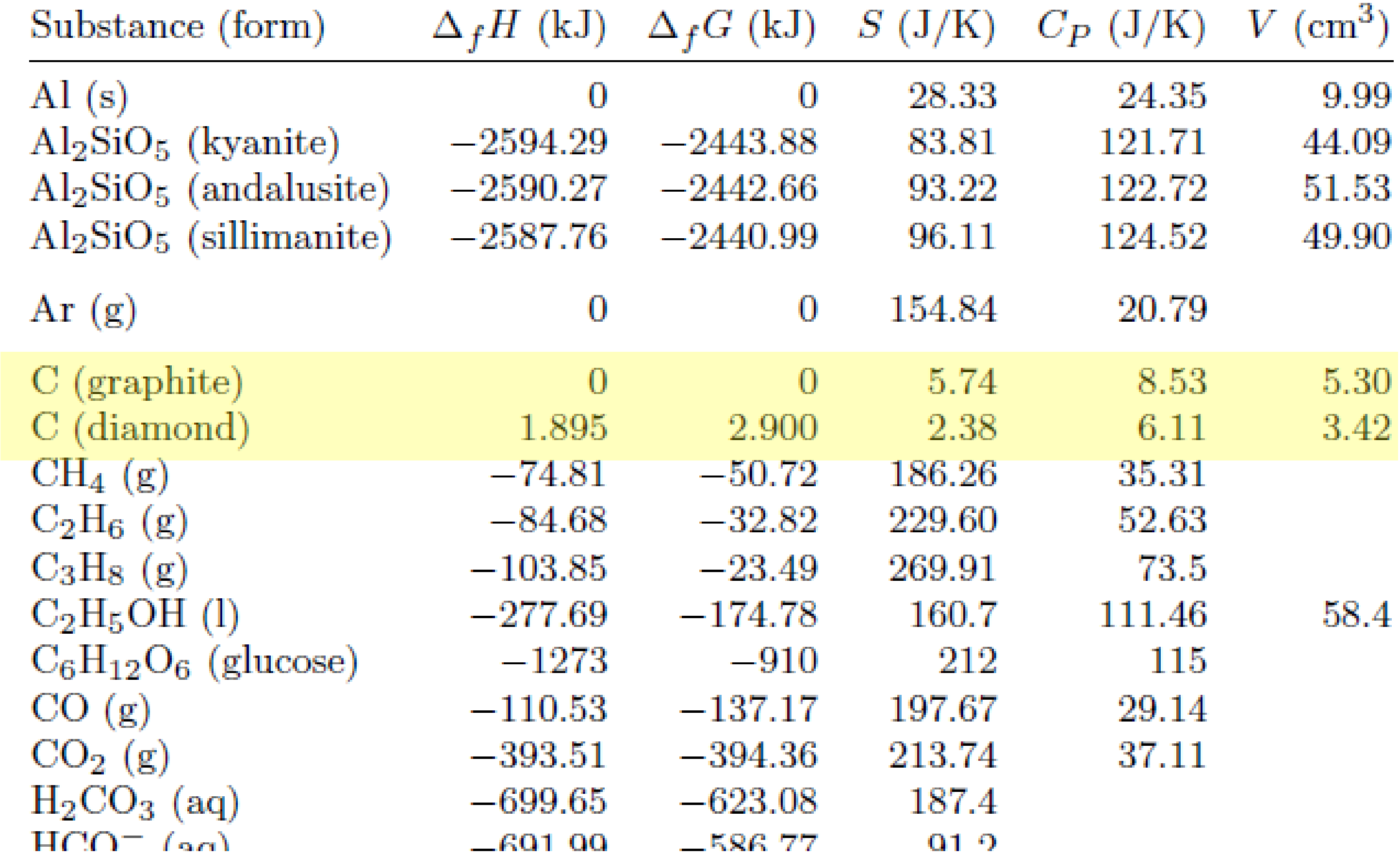


Figure 5.17. The experimental phase diagram of carbon. The stability region of the gas phase is not visible on this scale; the graphite-liquid-gas triple point is at the bottom of the graphite-liquid phase boundary, at 110 bars pressure. From David A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991). Copyright ©2000, Addison-Wesley.

Table from your textbook at T=298 K



Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
Al (s)	0	0	28.33	24.35	9.99
Al_2SiO_5 (kyanite)	−2594.29	−2443.88	83.81	121.71	44.09
Al_2SiO_5 (andalusite)	−2590.27	−2442.66	93.22	122.72	51.53
Al_2SiO_5 (sillimanite)	−2587.76	−2440.99	96.11	124.52	49.90
Ar (g)	0	0	154.84	20.79	
C (graphite)	0	0	5.74	8.53	5.30
C (diamond)	1.895	2.900	2.38	6.11	3.42
CH_4 (g)	−74.81	−50.72	186.26	35.31	
C_2H_6 (g)	−84.68	−32.82	229.60	52.63	
C_3H_8 (g)	−103.85	−23.49	269.91	73.5	
C_2H_5OH (l)	−277.69	−174.78	160.7	111.46	58.4
$C_6H_{12}O_6$ (glucose)	−1273	−910	212	115	
CO (g)	−110.53	−137.17	197.67	29.14	
CO_2 (g)	−393.51	−394.36	213.74	37.11	
H_2CO_3 (aq)	−699.65	−623.08	187.4		
HCO^- (aq)	−691.99	−586.77	91.2		

For one mole:

$$S_{graphite} - S_{diamond} = (5.74 - 2.38)\,J/K = 3.36\,J/K$$

$$V_{graphite} - V_{diamond} = (5.30 - 3.42)\,\text{cm}^3 = 1.88 \times 10^{-6}\ \text{m}^3$$

$$\Rightarrow \frac{dP}{dT} = 1.8 \times 10^6\,Pa/K$$

Example of Clausius-Clapeyron equation -- for water ice and liquid at T=273 K

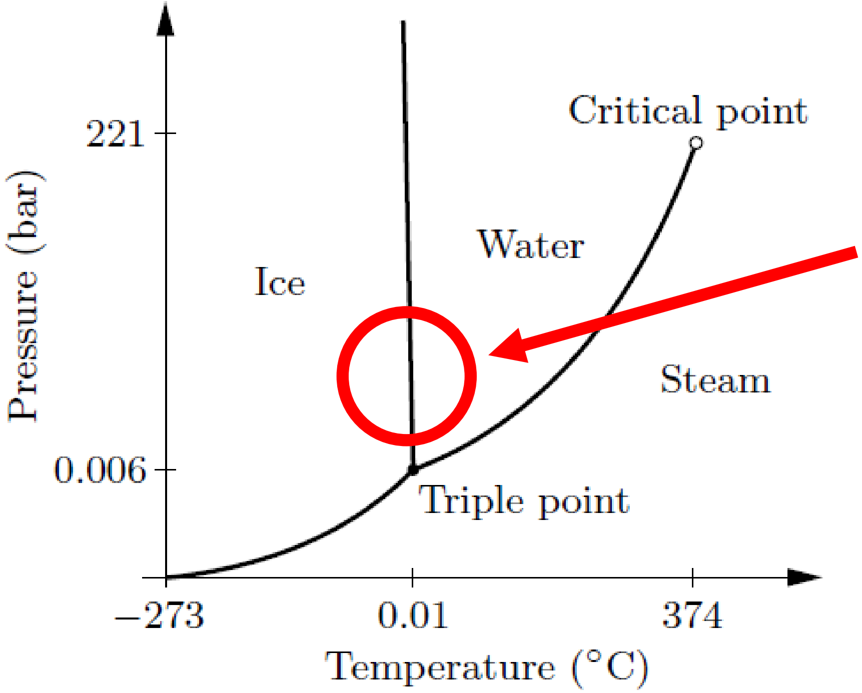
For 1 kg of water:
L=333000 J
$V_{solid}=1.091 \times 10^{-3}$ m^3 $V_{liquid}=1.0 \times 10^{-3}$ m^3

$$\frac{dP}{dT}=\frac{333000\text{ J}}{273K(1-1.091)\times 10^{-3}m^3}=-1.34\times 10^7\,Pa/K$$

Note that in this range, the coexistence line has negative slope meaning that as pressure increases, the melting temperature decreases.

Example of Clausius-Clapeyron equation -- for water ice and liquid at T=273 K and P= 1 atm=1.01325 x 10^5 Pa

For 1 kg of water:
L=333000 J
$V_{solid}=1.091 \times 10^{-3}\ m^3$ $V_{liquid}=1.0 \times 10^{-3}\ m^3$



$$\frac{dP}{dT} = -1.34 \times 10^7\ Pa/K$$

Unusual property of ice

What temperature does ice under P> 1 atm melt?

Example of Clausius-Clapeyron equation -- for water liquid and vapor at $T=T_{ref}$ =373 K and $P=P_{ref}$ = 1 atm=1.01325×10^5 Pa

For 1 mole of water:
L=407000 J
$V_{gas}=RT/P$ $V_{liquid} << V_{gas}$
R=8.315 J/K

$$\frac{dP}{dT} \approx \frac{L}{T(RT/P)}$$

$$\frac{dP}{P} = \frac{L}{R}\frac{dT}{T^2} \qquad \Rightarrow \ln P = -\frac{L}{RT} + (\text{constant})$$

$$\Rightarrow P(T) = P_{\text{Ref}} e^{-L/R\left(1/T - 1/T_{\text{Ref}}\right)}$$

Example of Clausius-Clapeyron equation -- for water liquid and vapor at $T=T_{ref}$ =373 K and $P=P_{ref}$ = 1 atm=1.01325×10^5 Pa

For 1 mole of water:
L=407000 J
$V_{gas}=RT/P$ $V_{liquid} << V_{gas}$
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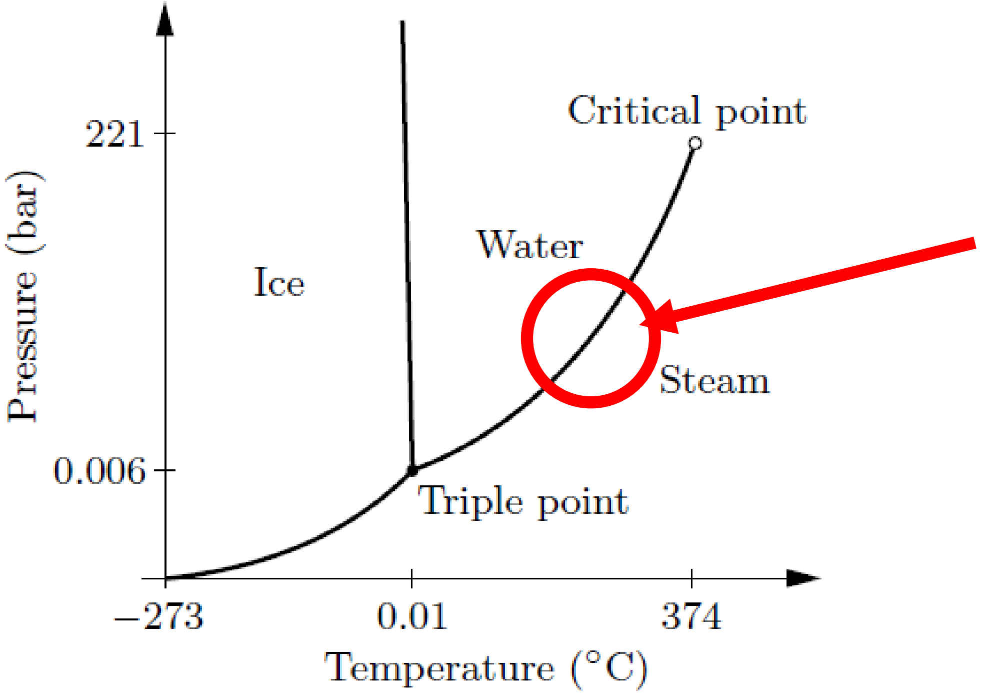

$$P(T) = P_{\text{Ref}}\, e^{-L/R\left(1/T - 1/T_{\text{Ref}}\right)}$$

$$= P_{\text{Ref}}\, e^{-131\left(373/T - 1\right)}$$

$$\text{for} \quad T \approx 373K$$

Example of Clausius-Clapeyron equation -- for water liquid and vapor at $T=T_{ref}$ =373 K and $P=P_{ref}$ = 1 atm=1.01325×10^5 Pa

For 1 mole of water:
L=407000 J
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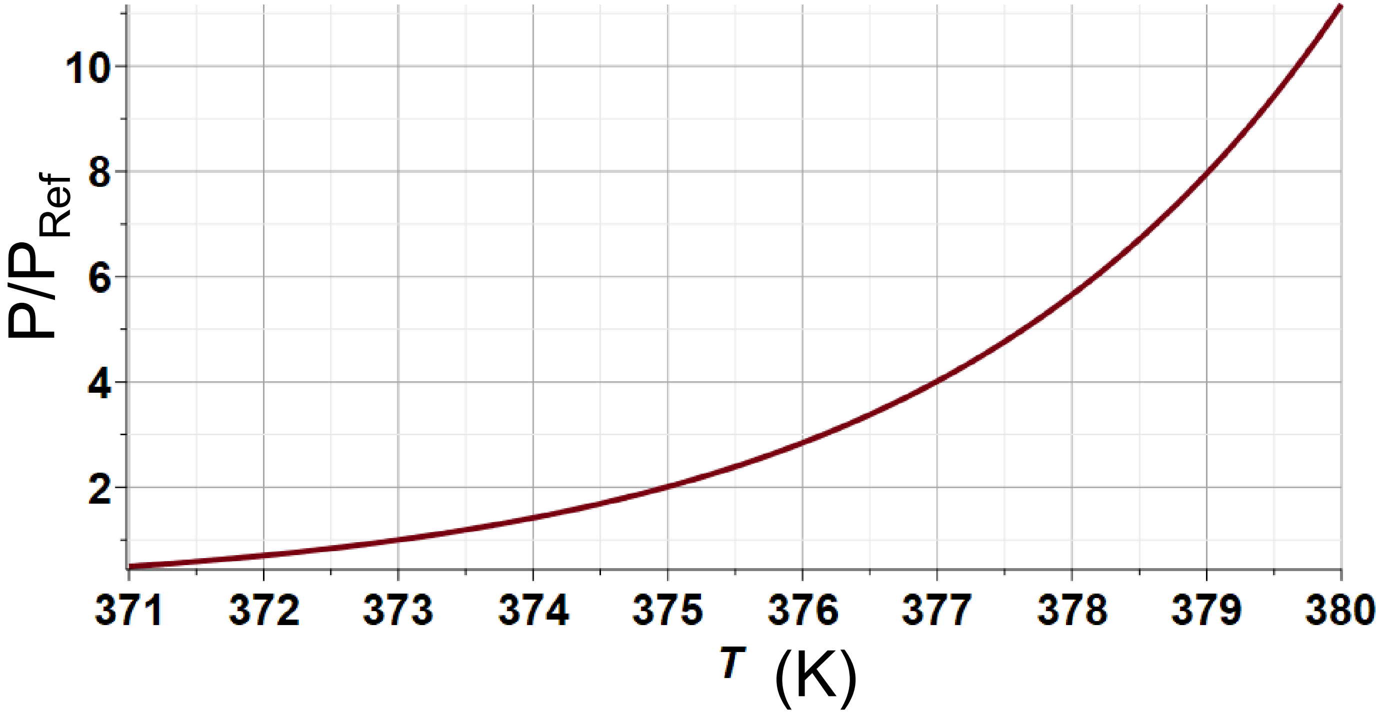
R=8.315 J/K

$$P(T) = P_{\text{Ref}} e^{-L/R\left(1/T - 1/T_{\text{Ref}}\right)}$$

$$= P_{\text{Ref}} e^{-131\left(373/T - 1\right)}$$

$$\text{for} \quad T \approx 373K$$



How can we understand phase transitions from the viewpoint of an equation of state? Obviously, the ideal gas law cannot help.

Ideal gas equation of state

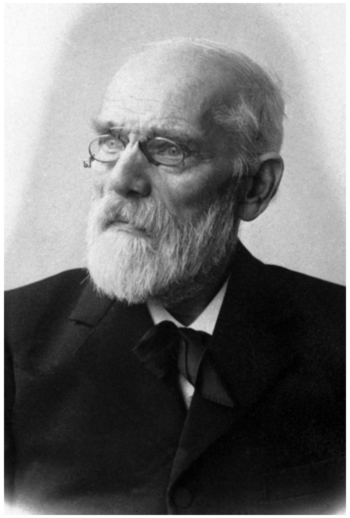
$$PV = Nk_BT$$

Van der Waals equation of state

$$\left(P+\frac{aN^2}{V^2}\right)(V-Nb)=Nk_BT$$

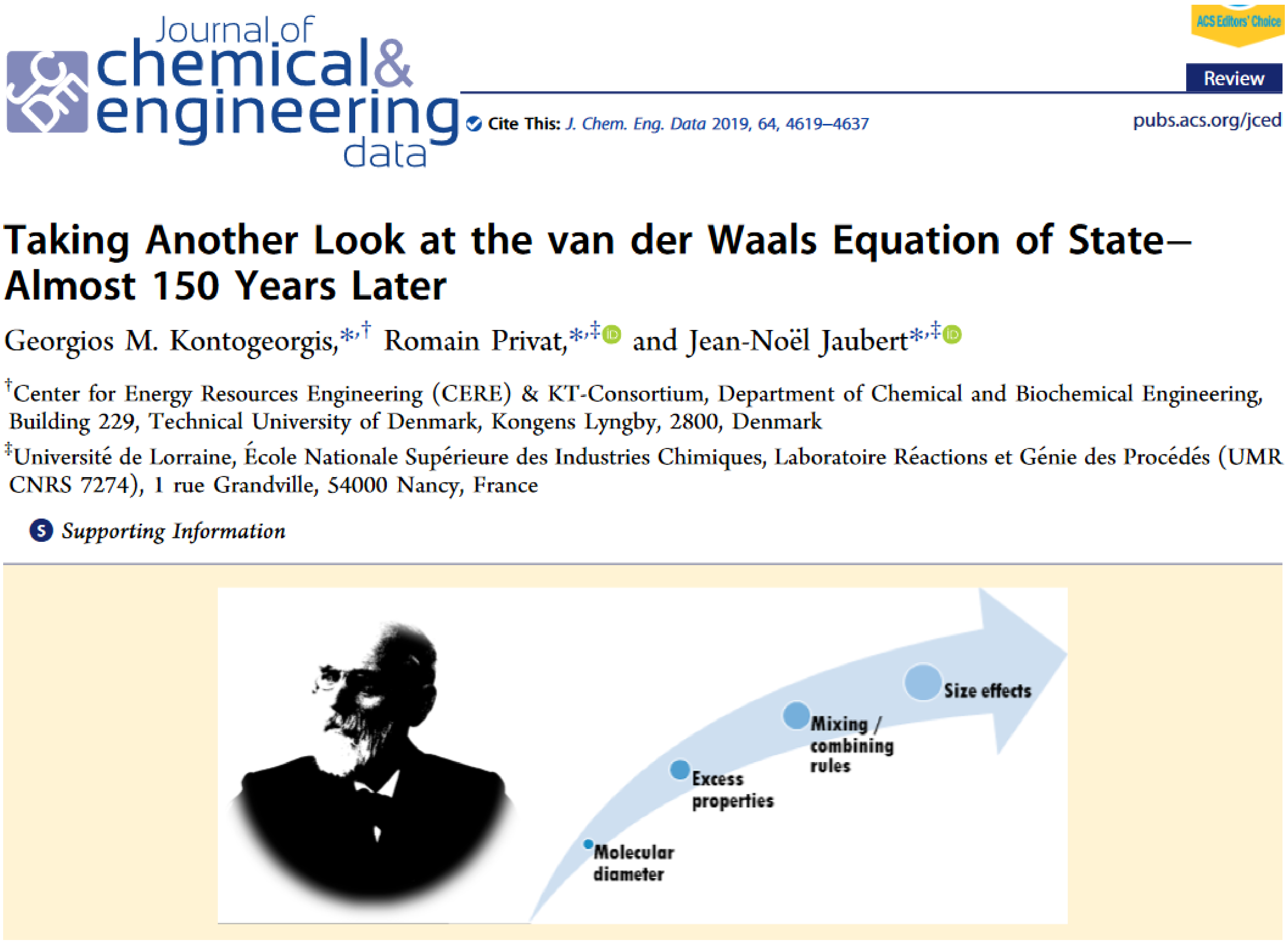
Representing attractive forces

Representing finite size effects



Johannes Diderik van der Waals 1837-1923
Developed equation in 1873
Awarded Nobel Prize in 1910

Interesting paper -- DOI:10.1021/acs.jced.9b00264



Journal of chemical & engineering data

ACS Editors' Choice

Review

Cite This: *J. Chem. Eng. Data* 2019, 64, 4619–4637

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Taking Another Look at the van der Waals Equation of State—Almost 150 Years Later

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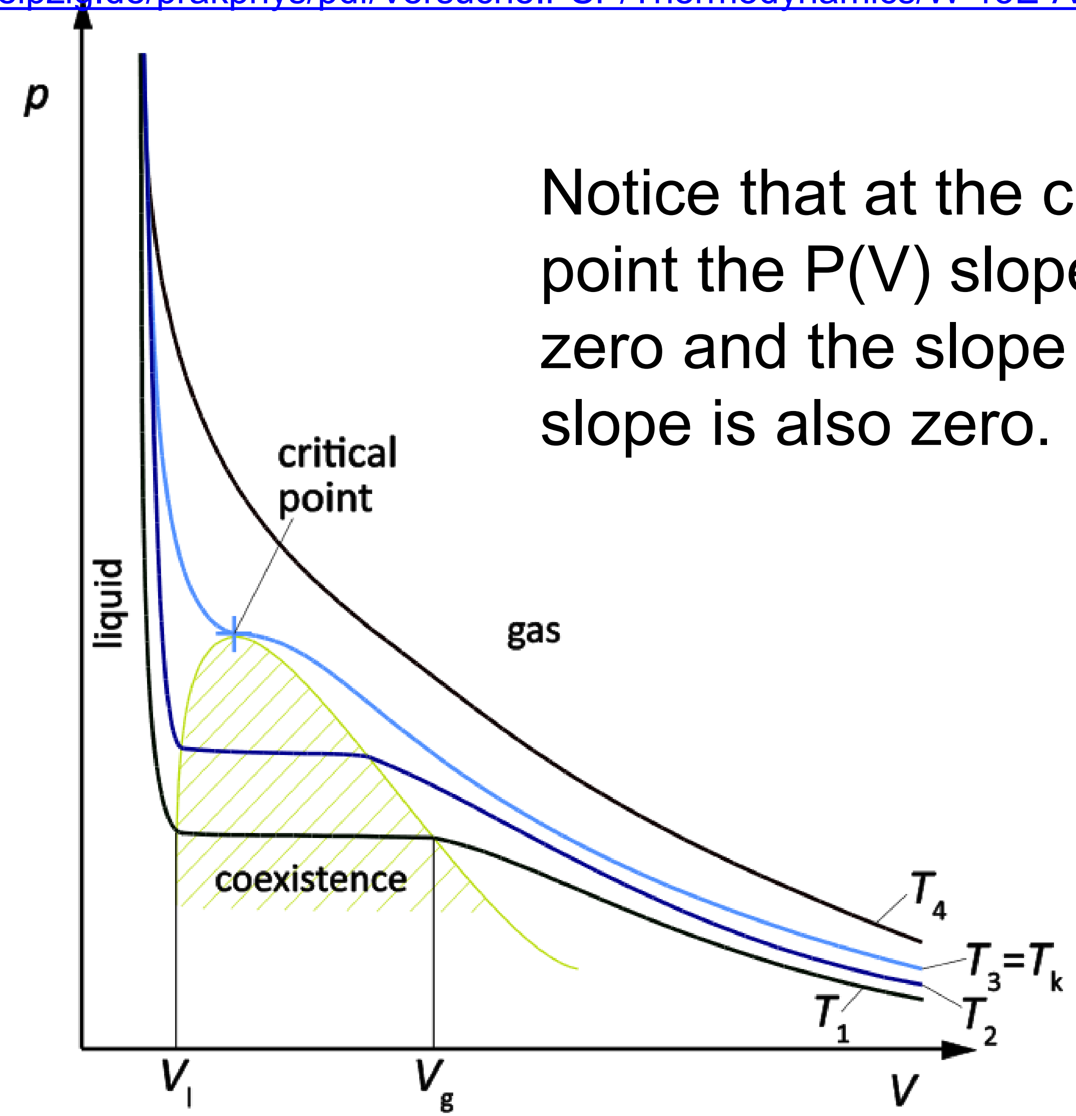
[†]Center for Energy Resources Engineering (CERE) & KT-Consortium, Department of Chemical and Biochemical Engineering, Building 229, Technical University of Denmark, Kongens Lyngby, 2800, Denmark

[‡]Université de Lorraine, École Nationale Supérieure des Industries Chimiques, Laboratoire Réactions et Génie des Procédés (UMR CNRS 7274), 1 rue Grandville, 54000 Nancy, France

Supporting Information

Pressure versus volume plots for a real system near its critical point: https://home.uni-leipzig.de/prakphys/pdf/VersucheIPSP/Thermodynamics/W-15E-AUF.pdf



Notice that at the critical point the P(V) slope is zero and the slope of the slope is also zero.

Can the Van der Waals equation of state represent this behavior?

Examine the equation near T_c, P_c, and V_c:

Van der Waals equation of state

$$\left(P+\frac{aN^2}{V^2}\right)\left(V-Nb\right)=Nk_BT \qquad P=\frac{Nk_BT}{\left(V-Nb\right)}-\frac{aN^2}{V^2}$$

Evaluating near critical point at $T=T_c$

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c}=\frac{-Nk_BT_c}{\left(V-Nb\right)^2}+\frac{2aN^2}{V^3}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c}=\frac{2Nk_BT_c}{\left(V-Nb\right)^3}-\frac{6aN^2}{V^4}$$

➔ Want to adjust parameters a and b so that these values are 0.

Evaluating near critical point at $T = T_c$

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = \frac{-Nk_BT_c}{(V_c - Nb)^2} + \frac{2aN^2}{V_c^3} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = \frac{2Nk_BT_c}{(V_c - Nb)^3} - \frac{6aN^2}{V_c^4} = 0$$

Solution --

$$\frac{V_c}{N} = 3b \qquad k_BT_c = \frac{8}{27}\frac{a}{b} \qquad P_c = \frac{1}{27}\frac{a}{b^2}$$

Some values from Thermal Physics by Ralph Baierlein

	a (eV ang^3)	b (ang^3)
Water	9.55	50.7
Sulfur dioxide	11.9	94.7
Carbon dioxide	6.3	71.3
Oxygen	2.38	52.9
Argon	2.36	53.8
Nitrogen	2.36	64.3
Hydrogen	0.428	44.3
Helium-4	0.0597	39.4

Some fudging --

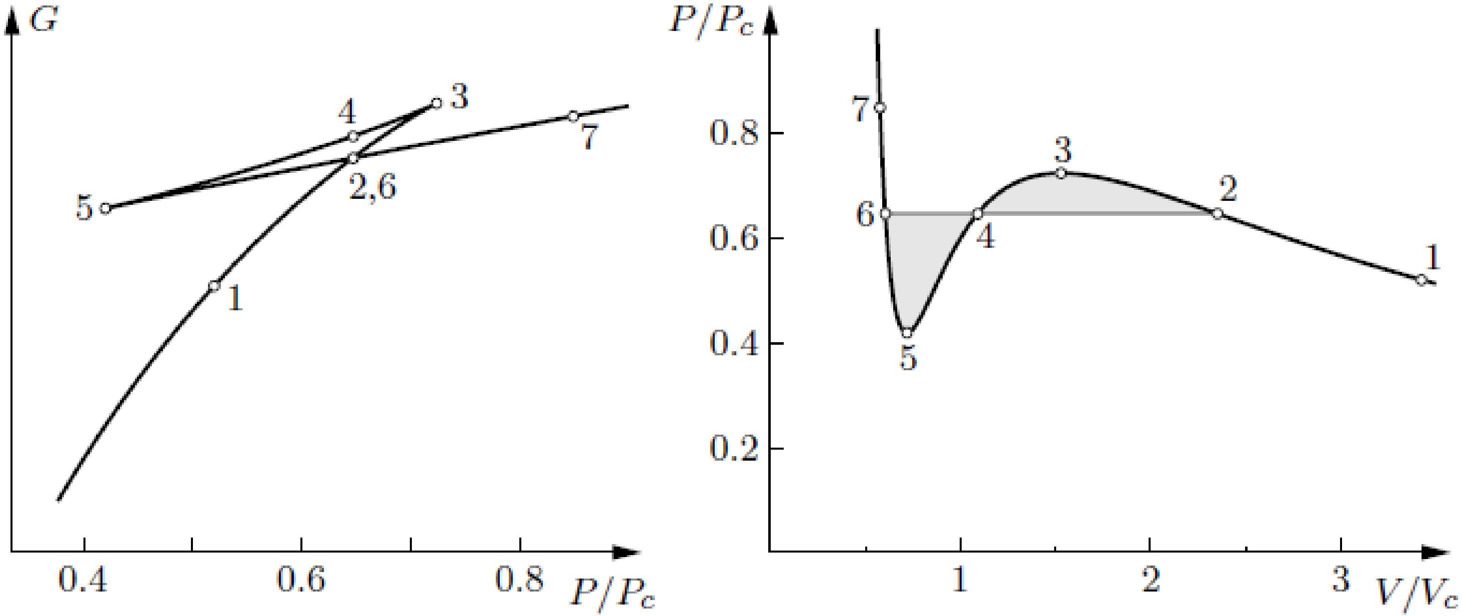
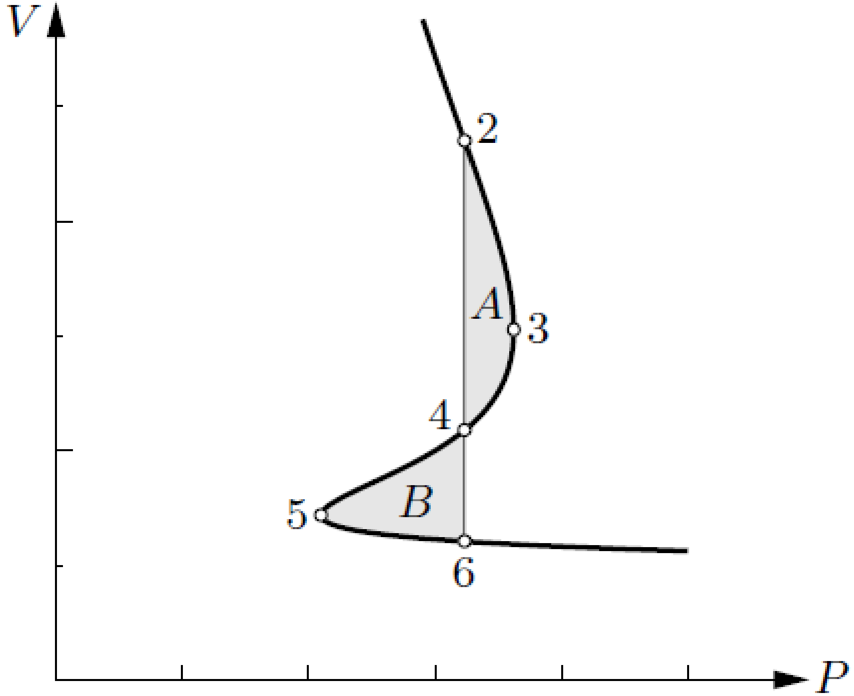


Figure 5.21. Gibbs free energy as a function of pressure for a van der Waals fluid at $T = 0.9T_c$. The corresponding isotherm is shown at right. States in the range 2-3-4-5-6 are unstable. Copyright ©2000, Addison-Wesley.

Comment on unphysical behavior of van der Waals equation of state below the critical point. V(P) is multivalued.

Figure 5.22. The same isotherm as in Figure 5.21, plotted sideways. Regions *A* and *B* have equal areas. Copyright ©2000, Addison-Wesley.



Van der Waals equation of state with Maxwell's modification

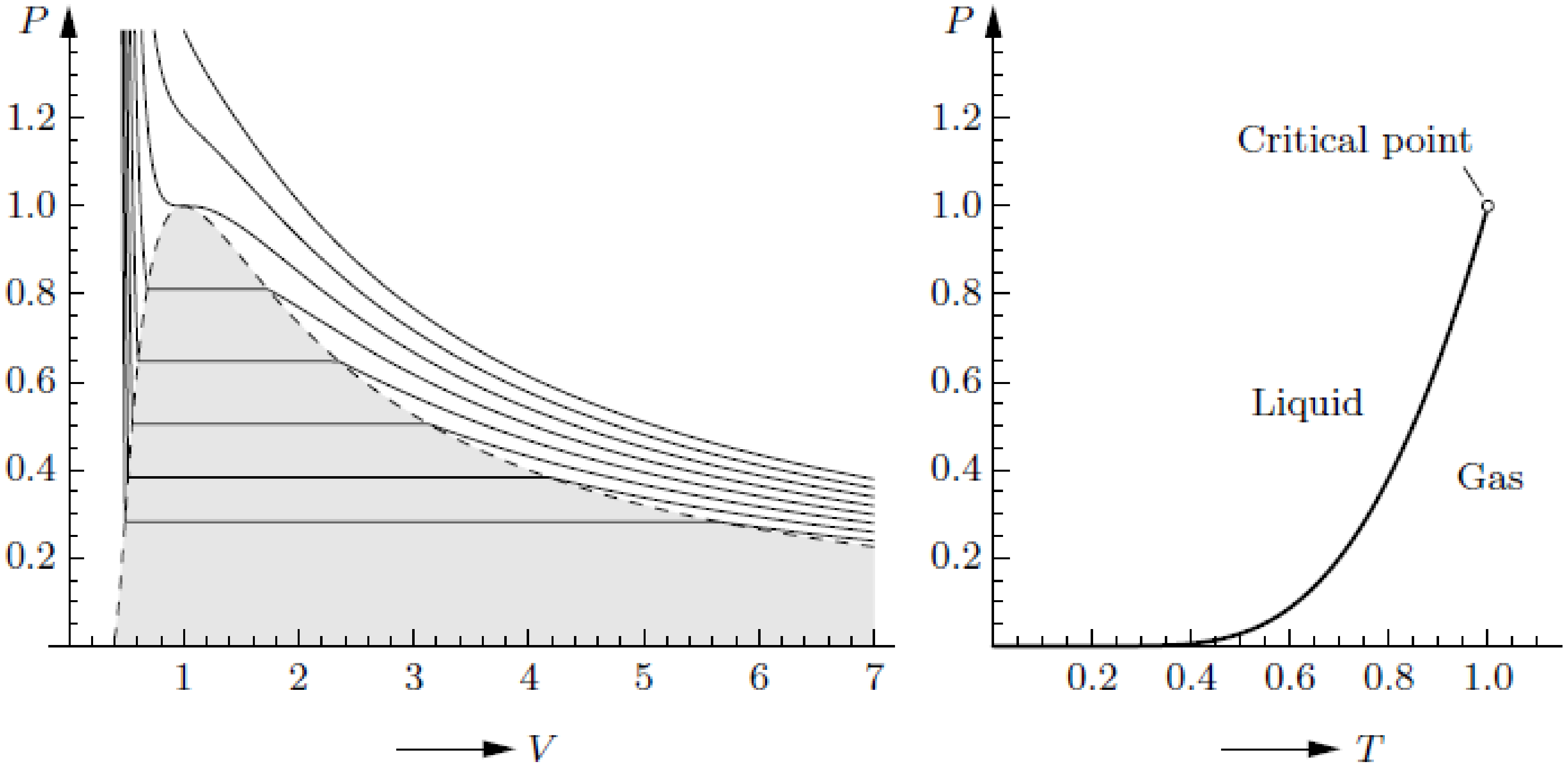


Figure 5.23. Complete phase diagrams predicted by the van der Waals model. The isotherms shown at left are for T/T_c ranging from 0.75 to 1.1 in increments of 0.05. In the shaded region the stable state is a combination of gas and liquid. The full vapor pressure curve is shown at right. All axes are labeled in units of the critical values. Copyright ©2000, Addison-Wesley.